THE UNIVERSITY OF MANITOBA

MECHANISM AND APPLICATIONS OF ION-PAIR EXTRACTION BY POLYURETHANE FOAM

BY

ANJUM SAEED KHAN

A thesis submitted to the Faculty of Graduate Studies
in partial fullfillment of the requirements for the
degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1981

Winnipeg, Manitoba

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Dedicated
To
My Parents

ACKNOWLEDGMENTS

It is a pleasure to express my deepest gratitude to Professor A. Chow for his guidance and encouragement throughout the course of this work.

I am also indebted to Dr. R. F. Hamon for giving so freely of his time, sharing his wide experience and for his invaluable help with the manuscript.

Thanks are also due to Dr. W. G. Baldwin and to my labmate Mr. S. J. Al-Bazi for informative discussions.

The financial support of the University of Manitoba and of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Finally, I would like to express thanks to my parents and wife for their encouragement and sacrifices.

Anjum Khan

TABLE OF CONTENTS

ACKNOWLEDGMENTS.. v

LIST OF TABLES... xi

LIST OF FIGURES.. xii

ABSTRACT... xvii

CHAPTER I. GENERAL INTRODUCTION

1. Polyurethane Foams and Their Analytical Applications......... 1

CHAPTER II. THE EXTRACTION OF ALKALI METAL SALTS BY POLYURETHANE FOAMS USING CROWN ETHERS 9

A. INTRODUCTION 9

1. Cyclic Polyethers and Their Complexes........................ 9

B. EXPERIMENTAL 20

1. Apparatus.. 20
2. Reagents... 20
3. Foams.. 22
4. Preparation of Standard and Sample Solutions................. 22
5. General Procedure.. 23
6. The Distribution of Crown Ether and Picric Acid Between Foam and Water... 25

C. RESULTS AND DISCUSSION 27

I. Extraction of Alkali Metal Cations by Polyether-Based Polyurethane Foam.. 27

1. Preliminary Experiments...................................... 27
2. Effect of Crown Ether Concentration on the Extraction of Alkali Metal Cations... 29

3. Variation of Distribution Ratio with Anion Type and Concentration.. 31
4. Effect of pH on the Extraction of Potassium................ 35
5. Effect of Metal Concentration on the Distribution Ratio..... 38
6. Extraction Equilibria.. 41
II Extraction of Alkali Metal Cations by Polyester-Based Polyurethane Foam............. 59
1. Effect of Metal Concentration on the Extraction of Alkali Metals by Polyester Foam........................... 60
2. Effect of Crown Ether Concentration on the Extraction of Alkali Metals by Polyester Foam........................... 62
3. Variation of Distribution Ratio with Anion Type and Concentration.. 66
4. Studies Under Varied Initial Concentrations of Crown Ether and Picric Acid.. 71
5. Extraction of Monovalent Cations Other than Alkali Metals... 73
6. Effect of Foam Type and Comparison with Solvent Extraction.. 75
D. CONCLUSION 88
CHAPTER III. EXTRACTION OF MONO AND DIVALENT CATIONS BY POLYETHER-BASED POLYURETHANE FOAM 90
A. INTRODUCTION 90
1. Complexing Ability of Ethers................................ 90
B. EXPERIMENTAL 107
1. Apparatus and Reagents...................................... 107
2. Foams... 110
3. General Procedure... 111

4. Preparation of Polyurethane Film.......................... 114

C. RESULTS AND DISCUSSION 115

I. Extraction of Monovalent Cations by Polyether-Based Polyurethane Foam.............................. 115

1. Preliminary Studies.................................... 115

2. Effect of Metal Concentration on the Distribution Coefficient.. 116

3. Effect of Aqueous/Foam Phase Ratio on the Extraction of Metal Picrates.. 121

4. Effect of Various Types and Concentrations of Anions on the Distribution Ratio.................................... 123

5. Extraction of Thallium Picrate into Various Organic Solvents.. 130

6. Extraction Equilibria.................................. 135

7. Effect of Temperature on the Extraction of Silver Picrate... 141

II. Extraction of Divalent Cations by Polyether-Based Polyurethane Foam.............................. 146

1. Preliminary Studies.................................... 146

2. Effect of Anion Type and Concentration on the Extraction of Metal Cations... 149

3. Effect of Alkali Metal Salts on the Extraction of Lead Picrate... 156

4. Extraction of Lead Picrate by Other Organic Phases.......... 158

5. Effect of Foam Weight on the Extraction of Lead Picrate..... 162

6. Extraction Equilibria.................................. 166

III. Extraction of Alkali Metal Cations by Polyether-Based Polyurethane Foam.. 172

D. INTERPRETATION

1. Possible Mechanism of Foam-Extraction.................... 175

2. Complexing Ability of Poly(ethylene oxide) and its Derivatives.. 177

3. Experimental Tests of Cation Chelation Mechanism.......... 184

    a. Cation Selectivity Measurements.................. 184

    b. Anion Selectivity................................ 197

    c. Polymer Sorption Abilities....................... 199

    d. Additional Evidence in Support of CCM............ 203

E. CONCLUSION 209

CHAPTER IV. EXTRACTION OF HETEROPOLY ANIONS BY POLYETHER-BASED POLYURETHANE FOAM 211

A. INTRODUCTION 211

B. EXPERIMENTAL 216

1. Apparatus and Reagents.................................. 216

2. Foam.. 217

3. General Procedure....................................... 218

4. X-Ray Analysis.. 219

C. RESULTS AND DISCUSSION 221

1. Preliminary Studies..................................... 221

2. Effect of Acid Concentration on the Extraction of Phosphomolybdate... 222

3. Effect of Molybdate Concentration on the Extraction of Phosphomolybdate... 226

4. Effect of Phosphate Concentration on the Extraction of Phosphomolybdate.. 231
5. Effect of Alkali Metal Chlorides on the Extraction of Phosphomolybdate.. 235
6. The X-Ray Fluorescence Determination of Phosphorus on Polyurethane Foam.. 242
D. CONCLUSION 248
CHAPTER V. SUMMARY AND POTENTIAL APPLICATIONS 250
REFERENCES 253

LIST OF TABLES

1. Code numbers and trivial names of cyclic polyethers......... 11

2. Ionic radii of metals and cavity radii of crown ethers...... 15

3. The equilibrium constants, K, for alkali metal ion-crown ether-picrate ion-pair extraction into polyurethane foam.... 57

4. The equilibrium constants, K, for alkali metal ion-crown ether-picrate ion-pair extraction into polyether-based polyurethane foam.. 83

5. The equilibrium constants, K, for alkali metal ion-crown ether-picrate ion-pair extraction with polyester-based polyurethane foam.. 87

6. Extraction of thallium-picrate into various organic phases.. 131

7. The equilibrium constants, K, for silver, thallium-picrate ion-pair extraction into polyether-based polyurethane foam.. 140

8. Extraction of lead-picrate into various organic phases...... 159

9. Extraction of lead-picrate as a function of foam weight..... 164

10. Effect of picrate concentration on the extraction of divalent cations by polyether foam................................. 169

11. Equilibrium constants, K, for lead, barium-picrate ion-pair extraction into polyether-based polyurethane foam.......... 171

12. Effect of common salts on the sorption of picrate by polyether-based polyurethane foam.......................... 185

13. Effect of specific cations on the sorption of picrate by polyether-based polyurethane foam.......................... 194

14. Effect of common salts on the sorption of complex metal anions by polyether-based polyurethane foam................ 204

15. Effect of lithium chloride on the extraction of phosphomolybdate.. 237

LIST OF FIGURES

1. Structural formulae of cyclic polyethers.................. 10

2. Extraction cell.. 21

3. Effect of crown ether on the sorption of alkali metal cations from aqueous picrate solution by polyether-based polyurethane foam.. 30

4. Effect of varying the initial concentration of picric acid on the sorption of alkali metal cations from the aqueous solution of crown ether by polyether foam................. 32

5. Extraction of potassium as a function of initial concentration of anions from aqueous crown ether solution by polyether foam.. 34

6. Effect of pH on the extraction of potassium picrate from the aqueous crown ether solution by polyether foam............ 36

7. The amount of picrate ion present in a 4×10^{-3} M picric acid solution at various pHs............................ 37

8. Effect of equilibrium solution potassium concentration on the distribution ratio.................................. 39

9. Effect of varying the initial concentration of picric acid on the distribution of alkali metal cation between polyether foam and aqueous solutions............................. 45

10. Effect of varying the initial concentration of crown ether on the distribution ratio of alkali metal picrates........ 46

11. Plots of log D vs log [crown ether] for the distribution of alkali metal picrates between polyether foam and aqueous solutions.. 47

12. Plots of $D[1 + K_4C_T/(1 + K_{1ex} w/v)]$ vs initial concentration of picric acid for the distribution of alkali metal cations between polyether foam and aqueous solutions...... 55

13. Plots of $D[1 + K_4C_T/(1 + K_{1ex} w/v)]$ vs initial concentration of crown ether for the extraction of alkali metal picrates.. 56

14. Distribution ratio as a function of initial concentration of DCHC-6 at different concentrations of potassium........ 61

15. Distribution of alkali metal picrates between polyester foam and aqueous solutions as a function of initial concentration of DCHC-6... 63

16. Plots of log D vs. log [crown ether] for the distribution of alkali metal picrates between polyester foam and aqueous solutions.. 65

17. Effect of varying initial concentration of picric acid on the distribution of potassium between polyester foam and aqueous solutions.. 67

18. Plot of log D vs log picric acid concentration for the distribution of potassium between polyester foam and aqueous solution.. 68

19. Plots of log D vs log of initial concentration of anion for the extraction of potassium by polyester foam from aqueous solutions.. 70

20. Extraction of potassium as a function of initial concentration of crown ether at different initial concentrations of picric acid.. 72

21. Plots of log D vs log of initial crown ether concentration for the distribution of Ag^+ and Tl^+ between polyester foam and aqueous solutions.. 74

22. Comparison of potassium-picrate sorption as a function of DCHC-6 from aqueous solutions by polyether and polyester-based polyurethane foam.................................. 76

23. Comparison of silver-picrate sorption as a function of DCHC-6 from aqueous solutions by polyether and polyester-based polyurethane foam.................................. 77

24. Effect of varying the initial concentration of crown ether on the distribution ratio for the sorption of alkali metal-picrates from aqueous solutions by polyether foam.... 82

25. Effect of varying the initial concentration of crown ether on the distribution ratio for the extraction of alkali metal picrates from aqueous solution by polyester foam..... 85

26. Plots of log $[D\ (1 + K_3A_T + K_4Cr)]$ vs log [crown ether] for the extraction of alkali metal picrates from aqueous solutions by polyester foam.................................. 86

27. Extraction cell for equilibrating polyurethane foam with solution.. 108

28. Thermostated automatic squeezing apparatus................. 109

29. Effect of equilibrium solution silver concentration on the extraction of silver from aqueous picrate solution......... 117

30. Effect of equilibrium solution thallium concentration on the sorption of thallium from aqueous picrate solution... 119

31. Distribution ratio as a function of initial concentration of picric acid at different concentrations of thallium......... 120

32. Distribution ratio as a function of foam weight............ 122

33. Effect of varying the initial concentration of picric acid on the extraction of silver............................... 124

34. Effect of varying the initial concentration of picric acid on the sorption of thallium................................ 125

35. Extraction of thallium as a function of initial concentration of anions.. 127

36. Effect of anions on the extraction of silver............... 128

37. Comparison of thallium extraction from aqueous picrate solution by polyether and polyester-based polyurethane foam. 133

38. Plot of log D $(1 + K_1[A])$ vs log [A] for silver/picrate system.. 138

39. Plot of log D $(1 + K_1[A])$ vs log [A] for thallium/picrate system.. 139

40. Water-jacketed distribution cell for equilibrating foam with solution at selected temperature...................... 142

41. Variation of log of distribution ratio as a function of 1/T. 144

42. Distribution ratio as a function of initial concentration of picric acid at different concentrations of Pb^{2+}............ 147

43. Effect of varying the initial concentration of picric acid on the extraction of Pb^{2+} from aqueous solution by polyether foam... 150

44. Effect of varying the initial concentration of picric acid on the sorption of barium from aqueous solution............... 151

45. Distribution ratio as a function of initial concentration of anions.. 153

46. Effect of varying the initial concentration of anions on the extraction of Ba^{2+}.................................. 155

47. Effect of alkali metal chlorides on the distribution of lead between polyether foam and aqueous picrate solution.... 157

48. Comparison of Pb^{2+} extraction from aqueous picrate solution by polyether and polyester foams.......................... 161

49. Distribution of lead between polyether foam and aqueous picrate solution as a function of foam weight.............. 163

50. Plots of log $D(1 + K_1[A] + K_1K_2[A]^2)$ vs log [picric acid] for divalent metal picrate systems......................... 170

51. Effect of varying the initial concentration of tetraphenyl borate on the distribution of alkali metal cations between polyether foam and aqueous solutions...................... 174

52. Sorption of picrate from aqueous solutions containing alkali metal cations a) by polyether foam, b) by dicyclohexyl-18-crown-6 in methylene chloride......................... 190

53. Extraction of picrate from aqueous solutions containing various divalent cations by polyether foam................. 191

54. Sorption of ANS from solutions containing various mono- and divalent cations by polyether foam..................... 192

55. Comparison of picrate extraction from solutions containing various alkali metal cations by polyether- and polyester-based polyurethane foams................................ 200

56. Comparison of ANS sorption from aqueous solutions containing various alkali metal cations by polyether- and polyester-based polyurethane foam................................. 201

57. Changes in the infrared spectrum of polyether-based polyurethane film accompanying sorption of $Na_2Co(SCN)_4$ from aqueous solution.................................... 206

58. Electronic spectra of $Co(SCN)_4^{2-}$ sorbed on polyether-based polyurethane film... 207

59. Influence of acidity on the formation of phosphomolbydate... 223

60. Effect of pH on the extraction of phosphomolybdate by polyether foam.. 224

61. Effect of molybdate on the formation and sorption of phosphomolybdate.. 227

62. Effect of varying the initial concentration of sodium molybdate on the extraction of phosphomolybdate............ 229

63. Effect of varying the initial concentration of phosphate on the extraction of phosphomolybdate...................... 232

64. Effect of varying the lithium chloride concentration on the sorption of phosphomolybdate.................................. 236

65. Effect of varying the initial concentration of alkali metal chlorides on the extraction of phosphomolybdate............ 241

66. X-ray fluorescence spectrum of phosphomolybdate sorbed on polyurethane foam.. 244

67. Relation between the intensity of MoK_α and the phosphate concentration in solutions.................................. 245

68. Plot of initial phosphate concentrations vs intensity of MoK_α lines.. 246

ABSTRACT

Polyurethane foam was employed for the extraction and separation of a number of metal ions. Analyses were performed by radiometric methods, flame photometry, atomic absorption and UV-visible spectrophotometry.

Both polyester-and polyether-based polyurethane foams were tested for the extraction of dicyclohexyl 18-crown-6 complex of monovalent cations (Na^+, K^+, Rb^+, Cs^+, Ag^+, Tl^+) from the aqueous solutions of bulky anions [picrate and 8-anilino-1-naphthalene sulphonate (ANS)]. Both types of polymer exhibit performance similar to that of organic solvents, with the polyester-based foam being slightly superior. The order of extraction for alkali metal ions is $K^+ > Rb^+ > Cs^+ > Na^+$ and is mainly dependent on the stabilities of the alkali metal-crown ether complexes.

It was noted that polyether-based polyurethane foam possesses some ability to extract metal picrates even in the absence of crown ether. This observation led us to study the mechanism whereby metal picrates are sorbed by polyurethane foams. Extraction of both anions and cations was studied and at least two types of mechanism were identified. The ion-pair extraction behaviour of polyester foam is consistent with treating the polymer as an analogue of organic solvents. Polyether foam is found to have additional abilities and the Cation Chelation Mechanism (C.C.M.) has been proposed to account for the observed phenomenon. According to this hypothesis, the polyether portion of the polymer is capable of chelating (solvating) a large number of cations in a wrap-around fashion. The extraction of ion-pairs including these cations is thus greatly facilitated and is very efficient in the case of large and hydrophobic anions. The observed order of selectivity of the polyether foam is $Li^+ < Na^+ < Cs^+ < Rb^+ < K^+ \sim NH_4^+ < Ag^+ \sim Tl^+$ for monovalent and $Ca^{2+} < Sr^{2+} < Ba^{2+} < Hg^{2+} < Pb^{2+}$ for divalent cations. The extraction of a particular cation increases with increasing size and hydrophobicity of the counter anion (NO_3^- < 2,4-dinitrophenolate$^-$ ≈ 2,6-dinitrophenolate$^-$ < ClO_4^- < picrate$^-$ < ANS$^-$ < $(C_6H_5)_4B^-$). Based on the selectivity results, polyether foam behaves similar to 18-crown-6 and thus can be regarded as a pseudo-crown ether.

Polyurethane foam was applied to the sorption and determination of phosphate as 12-phosphomolybdate. *In situ* X-ray fluorescence analysis of molybdenum proved to be a convenient method for the indirect determination of phosphate.

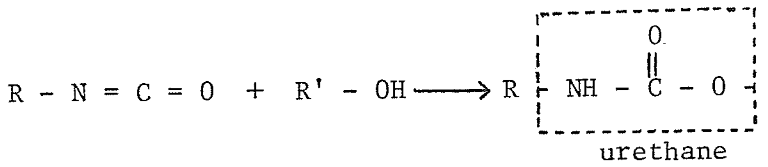
CHAPTER I. GENERAL INTRODUCTION

POLYURETHANE FOAMS AND THEIR ANALYTICAL APPLICATION

The technology of polyurethane foams (frequently called just urethane foams) was developed in the late 1930's in Germany. Professor Otto Bayer was the first to prepare rigid urethane foams(1) and the industries of the United States started production during 1945-47. Flexible urethane foam was first reported in 1952 by Hochtlen(2).

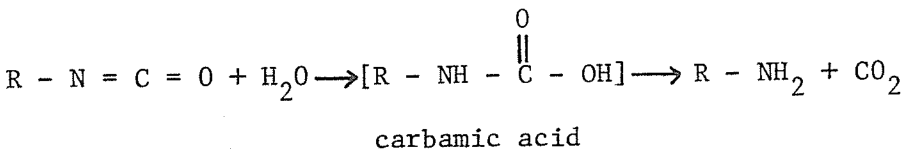
The chemistry of urethane foam formation is now well known(3). The reactive ingredients of a foam formation are an isocyanate, a hydroxyl terminated polymer (i.e. polyether or polyester polyol) and often water. The most important reactions in the production of flexible urethane foams are summarized below:

i. The reaction of isocyanate with a hydroxyl compound produces a urethane.



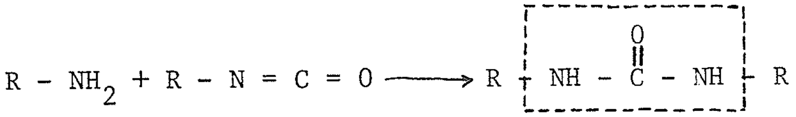
$$R - N = C = O + R' - OH \longrightarrow R\underset{\text{urethane}}{\boxed{- NH - \overset{\overset{O}{\|}}{C} - O -}}R' \qquad (1)$$

ii. The reaction of isocyanate with water is responsible for the formation of foam by liberation of carbon dioxide. The first step in this reaction is the formation of the unstable carbamic acid which decomposes to form amine and carbon dioxide.



$$R - N = C = O + H_2O \longrightarrow \underset{\text{carbamic acid}}{[R - NH - \overset{\overset{O}{\|}}{C} - OH]} \longrightarrow R - NH_2 + CO_2 \qquad (2)$$

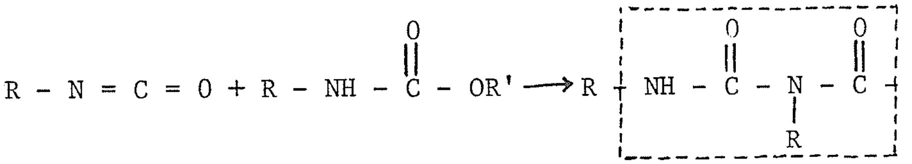
The amine from equation (2) then reacts with additional isocyanate to produce a substituted urea linkage as follows:



$$R - NH_2 + R - N = C = O \longrightarrow R \boxed{NH - \overset{O}{\overset{\|}{C}} - NH} R \qquad (3)$$

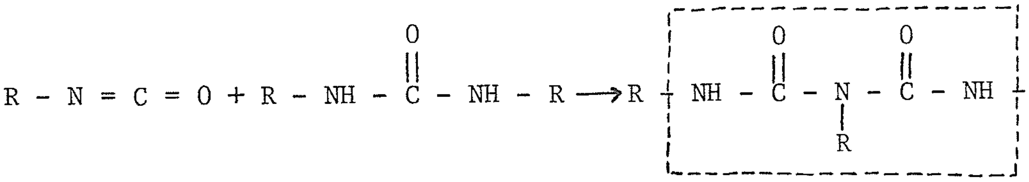
Urea

Reactions which lead to branching and cross-linking are the isocyanate-urethane reaction yielding an allophanate, equation (4), and that between isocyanate and urea producing biuret according to equation (5).



$$R - N = C = O + R - NH - \overset{O}{\overset{\|}{C}} - OR' \longrightarrow R \boxed{NH - \overset{O}{\overset{\|}{C}} - \underset{R}{\underset{|}{N}} - \overset{O}{\overset{\|}{C}}} O - R' \qquad (4)$$

allophanate



$$R - N = C = O + R - NH - \overset{O}{\overset{\|}{C}} - NH - R \longrightarrow R \boxed{NH - \overset{O}{\overset{\|}{C}} - \underset{R}{\underset{|}{N}} - \overset{O}{\overset{\|}{C}} - NH} R \qquad (5)$$

biuret

Most of the above reactions are too slow for the commercial production of polyurethane foams. Several catalysts are employed, therefore, to enhance the reaction rate and to control the balance between the chain extension and foam reactions.

Commercial production of polyurethane is usually achieved by either two different processes:

a. The "one-shot process" in which the diisocyanate, hydroxyl terminated polymer (polyether or polyester) and water are all mixed together.

b. The "pre-polymer process" in which the polyol is first reacted with isocyanate to produce a pre-polymer which may later be foamed by reaction with water. A small amount of catalyst may also be used to enhance the rate of foam formation.

Polyols ranging in molecular weight from 400-6000 are generally used in the synthesis of polyurethane foam. The most widely used isocyanate is toluene diisocyanate (TDI). Flexible foams are produced from polyols of moderately high molecular weight and low degree of branching, while rigid foams are produced from polyols of low molecular weight having highly branched chains.

The physical as well as chemical properties of urethane foams are a function of the preparation method(2). Bowen(4) examined the chemical resistance of some batches of commercial urethane foams and apart from reversibly swelling, the foams remain unaffected by water, hydrochloric acid up to 6 M, sulphuric acid up to 4 M, nitric acid up to 2 M, glacial acetic acid, 2 M ammonia, 2 M sodium hydroxide, and also organic solvents such as light petroleum, benzene, carbon tetrachloride, chloroform, diethyl ether, diisopropyl ether, acetone, isobutyl methyl ketone, ethyl acetate, isopentyl acetate, and various alcohols. Polyurethane foams, however, are dissolved by concentrated sulphuric acid and hot arsenic(III) chloride and are destroyed by concentrated nitric acid. Bowen also reported that foam is degraded when heated between 180-200°C, and slowly turns brown in ultraviolet light.

During the last few years, the high distribution coefficients obtained, non-toxicity, and the ease of handling of the system have aroused considerable interest in using polyurethane foams for the extraction and separation of inorganic and organic substances, and both polyether and polyester type foams have been employed for this purpose. Several reviews describing such studies have appeared in the literature(5,6). Although the general applications of the polyurethane foams have been increased either by physically loading the polymer with complexing agents(7,8,9), or by chemically modifying the polymer(10), the applications of particular interest to us are those in which plain polyurethane foam has been used.

Bowen(4) in 1971 reported the use of polyurethane foam for the extraction of several substances from aqeuous solutions. Mercury(II), gold(III), iron(III), antimony(V), thallium(III), molybdenum(VI), and rhenium(IV) have been extracted from acidic chloride media whereas the extraction of uranium(VI) has been accomplished from aluminum nitrate solution. The extraction of iodine, benzene, chloroform, and phenol was also reported. In addition, he observed high capacities of foam (0.5 - 1.5 mol /kg) for a few elements and thus concluded that the process is absorption rather than adsorption. Bowen also observed that most of the substances extracted by foam are those which are able to be extracted by diethyl ether. Furthermore, the possibility of foam acting as a weak anion exchanger on the basis of urethane or urea linkage has been suggested. The same author has also pointed out that the foam probably acts as an anion exchanger by the protonation of ether oxygens. Subsequently, he has reported the use of urethane foam for the recovery of gold(III) from liquid mineral wastes(4a). Schiller and Cook(11) following a recommendation by Bowen, applied polyurethane foam for the preconcentration of gold(III) from natural waters. The extraction of gold(III) has also been reported by Sukiman(12). Braun and Farag(13) have studied the extraction of gold thiourea complexes from perchloric acid solution by both polyether- and polyester-based polyurethane foams. Polyether foams were found to have higher capacities for the extractable complexes than did those of polyester type.

Gesser and coworkers(14) have reported the extraction of gallium from acid chloride media by polyether based polyurethane foam. The capacity of the foam (10% by weight of gallium) has been found to be too large to be due to adsorption. Further, the diffusion of gallium through a polyurethane membrane also confirms the absorption of the gallium complex into the bulk of the polymer. Later on, Gesser and coworkers(15) in a detailed study of the iron(III)/HCl system, have reported the extraction of $FeCl_3$ and $HFeCl_4$ by polyether-based polyurethane foam. On the basis of the results obtained, they equated the polyether foam to a liquid extractant of moderate dielectric constant in which the dissociation of $HFeCl_4$ has also been suggested.

Extraction of Sn(II) from acidic chloride using both polyether and polyester foam has been investigated by Lo(16). The results indicate a higher distribution coefficient for the polyether foam. The effect of some alkali metal halides on the extraction has also been studied. Lo(17) has also reported the extraction of Sb(III) and Sb(V) from acidic chloride solution by polyether foam. On the basis of these studies, he concluded that foam can be treated as a "solid solvent extractor."

Gesser and coworkers(18) further supported their earlier assumption of foam being equal to a liquid extractant of moderate dielectric constant on the basis of study of uranium(VI) extraction from nitrate solution.

Moore et al(19) have extended the use of polyurethane foams to the extraction of metal ions from organic solvents. Extraction of iridium(IV) and platinum(IV) from acetone and ethyl acetate has been studied by these authors and it has been concluded that the results obtained cannot be explained entirely on the basis of an ether-like solvent extraction mechanism (as had been suggested previously). As an alternative they have suggested the possibility of specific ion exchange sites.

Several metals have been extracted from thiocyanate media. Moody et al(20) have reported the extraction of cobalt(II), iron(III), cadmium(II), zinc(II), and lead(II) from the thiocyanate system by polyurethane foam. Braun and Farag(21) have also reported the extraction of cobalt and iron from thiocyanate media. The latter authors have drawn the conclusion that the process can be described as "ether-like solvent extraction."

Recently Hamon(22) has thoroughly investigated the extraction of $Co(SCN)_4^{2-}$ from thiocyanate solutions as a model system for the study of the extraction mechanism by polyurethane foam. Results of this extensive study suggest that ether-like solvent extraction cannot be the sole mechanism for the system and possibilities of several other mechanisms have been discussed, therefore. Most recently platinum metals have been included in the list of metals which can be extracted from thiocyanate media. Extraction of ruthenium, osmium, iridium, rhodium, platinum and palladium have been studied extensively by Al-Bazi(23,24).

Gesser and coworkers(25) have extended the application of polyurethane foams to the extraction of organic pollutants. Polychlorinated biphenyls (PCB) at various concentrations have been retained by passing aqueous solutions through plugs of foam. It is also reported that 93 - 100% of the sorbed PCBs can be eluted with acetone and hexane. Musty and coworkers(26) have investigated the various factors affecting the extraction and recovery of several organochlorine insecticides and polychlorinated biphenyls. The extraction and recovery of phthalate esters from water by polyurethane foam have also been carried out by

Gesser and coworkers(27).

The use of polyurethane foams for monitoring the organic compounds in drinking water has also been reported(28). Polyurethane foam has been used successfully as a trapping medium for pesticide vapours in air(29). The use of polyurethane foam to clean up oil spills in both fresh and sea water has been described in a report(30). It has been reported that polyurethane can effectively remove 99% of Bunker C oil, 70% of marine diesel oil and 60% of crude oil at a flow rate of approximately 400 L/min/m^2.

The use of polyurethane foam as a support in chromatography was first reported by Ross and Jefferson(31) in 1970. Open pore polyurethane column was prepared _in situ_ by filling the column with liquid urethane formulation. After the trapped air bubbles had been removed, the column was clamped shut at both ends and rotated at about five revolutions per minute on a vertical turntable in order to prevent setting and to eliminate channelling. The column was then flushed with solvent to remove the unreacted monomer and finally with nitrogen to remove excess solvent. The urethane columns were used to effect the separation of various compounds such as alcohols and both aromatic and aliphatic hydrocarbons.

An important application of polyurethane foam as a gas chromatographic column material is the separation of various metal chelates(32), such as the cis and trans isomers of $Cr(tfa)_3$ (tfa - 1,1,1 trifluoro pentane-2,4-dione) which are completely resolved in six minutes on a 25 cm polyurethane column.

The advantages claimed for polyurethane foam in gas chromatography include its open cellular structure and pore size (in the range of 0.05

- 0.20 cm) causing a very low pressure drop through the column(16). In addition to these, the presence of polar and nonpolar sites facilitates the efficient separation of polar, nonpolar, or polar and nonpolar mixtures(33). It is also reported that nonpolar substances separate in the order of their boiling points while polar compounds behave differently, i.e. they do not elute in the order of their boiling points. Lynn and coworkers(34) have reported the preparation and uses of polyurethane columns with different isocyanate to polyol ratios and good separation of dichloroanilines has been achieved by using a 2:1 excess of polyol to isocyanate. Hileman _et al_(32) have described the preparation of polyurethane columns of varying permeabilities by changing the monomer concentrations and reaction conditions. These columns have subsequently been used for the separation of alcohols, aromatic hydrocarbons and metal chelates. Schnecko and Bieber(35), who also studied some other foams, preferred preground material for packing columns rather than that produced _in situ_.

It is clear from the above-mentioned studies that polyurethane foams have been used successfully for the extraction and separation of a number of inorganic and organic substances. On the other hand, the mechanism of extraction, particularly of metal ions, by polyurethane foam is not well understood. The present study was initiated firstly to extend the analytical uses of the polyurethane foams to the extraction of a few more metals other than those studied earlier and, secondly, to understand the mechanism of polyurethane foam extractions.

CHAPTER II. THE EXTRACTION OF ALKALI METAL SALTS BY POLYURETHANE FOAMS USING CROWN ETHERS

A. INTRODUCTION

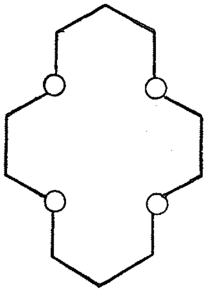
Cyclic Polyethers and Their Complexes

Due to their reluctance to form stable complexes with most of the complexing agents, the separation of alkali metals has usually been accomplished by ion exchange. The alternative precipitation procedures are not very selective and are generally not suitable for small quantities of alkali metals. The extractions of alkali metals reported before 1968 are almost all based upon the ion association principle and bulky anions (e.g. polyiodide(36), tetraphenyl borate(37), and phenols(38)) have been used for this purpose. The extraction of alkali metals into nitrobenzene using hexyl(39) (2,4,6,2',4',6'-hexanitro diphenylamine) is also related to ion association and the separation of only extreme members (i.e. lithium and cesium) has been achieved by this method under optimum conditions.

The macrocyclic polyethers, first prepared by Pedersen(40), have been used for the extraction of alkali metals during the last few years owing to their ability to form stable complexes with a number of metal ions (particularly those of the alkali metals). Synthesis, complexing ability and uses of crown ethers have been the topics of several recent reviews(41,42).

Figure 1

Structural formulae of Cyclic Polyethers.



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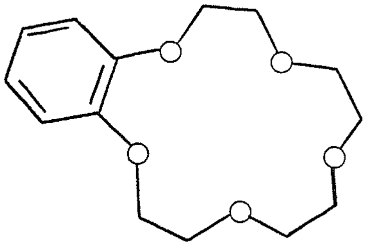

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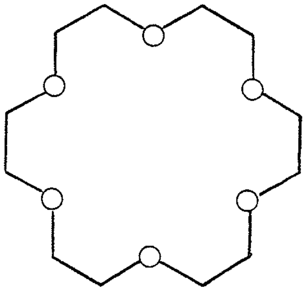

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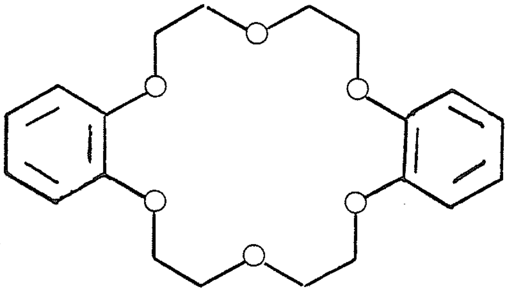

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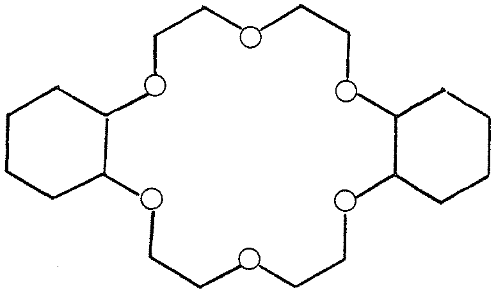

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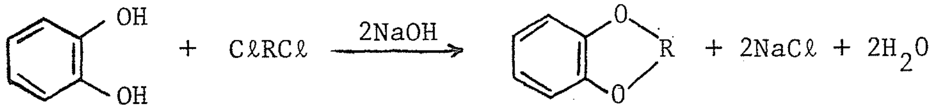
TABLE 1 CODE NUMBERS AND TRIVIAL NAMES OF CYCLIC POLYETHERS

Code Number	Trivial Name
1	14-crown-4
2	Benzo 15-crown-5
3	18-crown-6
4	Dibenzo 18-crown-6
5	Dicyclohexyl 18-crown-6

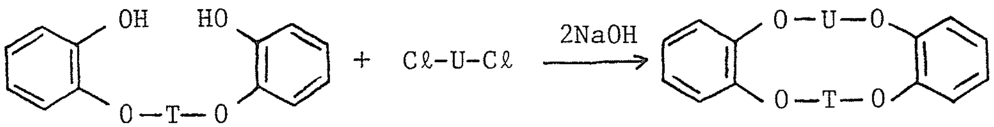
Macrocyclic polyethers form a large group of synthetic compounds, containing from nine to sixty membered rings and from three to twenty ether oxygens. The syntheses of various representatives of this group have been carried out at different times by several teams of investigators(40,43,44), but the most extensive work in both synthesis and study has been done by Pedersen(40). The structural formulae of some macrocylic ethers are represented in Figure 1.

Since the full names of these cyclic ethers according to I.U.P.A.C. rules are too cumbersome for everyday use, Pedersen(40) introduced an abbreviated nomenclature, giving these compounds the generic name of "crown" because of the peculiar shape of their molecular models (resembling a crown). For instance, compound 4 in Figure 1 has the abbreviated name of dibenzo-18-crown-6 whereas its full name is 2,3,11,12,-dibenzo-1,4,7,10,13,16,hexaoxyacyclo-octadeca-2,11,diene. Generally, the groups attached to the crown are mentioned first, then the number of atoms in the ring, followed after "-crown-" by the number of oxygen atoms in the crown. Some examples of this nomenclature are given in Table 1.

The aromatic crown ethers are prepared by straight-forward condensation methods. Four of the most commonly used methods are exemplified by the equations (6) to (9) in which R,T,U and V are divalent groups generally of the type $-(CH_2-CH_2-O)CH_2-CH_2$. The condensations are typically run in 2-butanol under reflux for 12 to 24 hours.



(6)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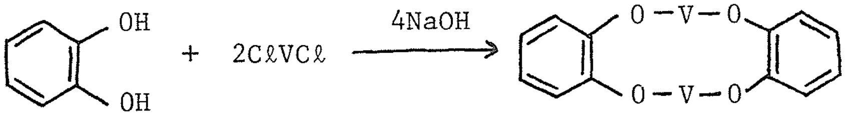
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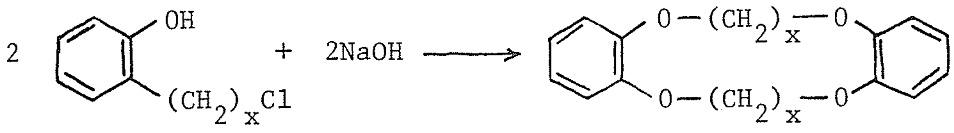
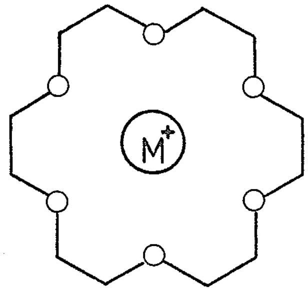

(9)

The second of the above methods is the most reliable for preparing cyclic polyethers with two or more aromatic rings. The third, though less reliable, is also frequently employed due to the greater availability of the starting materials. Saturated polyethers (obtained by hydrogenation of the corresponding aromatic compounds) have several asymmetric centres and therefore may be mixture of several diasterioisomers. Dicyclohexyl 18-crown-6 (DCHC-6), for example, is obtained as a mixture of two isomers, called "isomer A" and "isomer B", which can be separated by column chromatography$^{(49)}$.

Cyclic polyethers with aromatic side rings are colourless crystalline compounds nearly insoluble in water and sparingly soluble in alcohols as well as many other common solvents. On the other hand, the saturated polyethers are colourless viscous liquids or solids and are more soluble in all solvents than are their aromatic precursors. Most of them dissolve in petroleum ether and yet display appreciable water solubility as well.

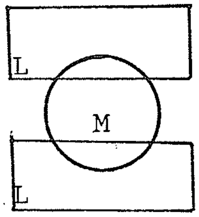
The most remarkable property of the cyclic ethers is their ability to form complexes with several cations. This unique property of polyethers has been qualitatively demonstrated on a large number of uni-, di-, and tri-valent metal ions including members of group IA(Li^+, Na^+, K^+, Rb^+, Cs^+) group IB(Ag^+), group II A(Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+}), group IIB(Zn^{2+}, Cd^{2+}, Hg^{2+} and Hg^+) group IIIA(Tl^+) group IIIB(La^{3+}), group IVA(Ti^{3+}), group IVB(Pb^{2+}) and group VA(V^{3+}). The complexes were found mostly to be of 1:1 stoichiometric ratio. In a typical 1:1 cation polyether complex, the cation is encircled by the oxygen atoms of the polyether ring and is being held there by the electrostatic attraction between negatively charged oxygen atoms of C-O dipoles and the cation.

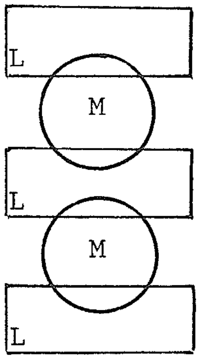


In presence of a large excess of polyether, 2:1 and 3:2 polyether to salt complexes are also reported(41,42). The former ones are known as sandwich and the latter ones as club sandwich complexes (shown below).

TABLE 2 IONIC RADII OF METALS AND CAVITY RADII OF CROWN ETHERS (Å)

CATION	IONIC RADIUS (201)	CROWN ETHER	CAVITY RADIUS (42)
Li^+	0.6	14-crown-4	0.6 - 0.75
Na^+	0.95	15-crown-5	0.85 - 0.11
K^+	1.33	18-crown-6	1.3 - 1.6
Rb^+	1.48		
Cs^+	1.69		
Ag^+	1.26		
Tl^+	1.40		
Ba^{2+}	1.35		
Hg^{2+}	1.1		
Sr^{2+}	1.13		
Pb^{2+}	1.20		





The stability constants of various crown ether-cation complexes have been measured both in aqueous and in organic media by calorimetric titration techniques(45), by potentiometric measurements(46), and also by spectrophotometric methods(47). On the basis of these studies it has been concluded that the stability of the metal-crown ether complex is basically determined by the fit of M^+ in the cavity of the ligand, i.e. the most stable complexes are formed when the ionic radius of the cation is nearly equal to the size of the cavity (Table 2). Other factors which can also influence the stability of the metal-crown ether complexes, as reported by these authors(45-47), are the nature of the accompanied anion (e.g. iodide, thiocyanate, and picrate are reported to yield more stable complexes), the charge of the cation, and the nature of the solvent. In addition to these factors, it has also been reported by Pedersen(42) that crown ethers containing five to ten oxygen atoms each separated from the next by two carbon atoms are the most effective complexing agents. Truter and coworkers(61) have also reported that acetal oxygens are less effective than are those of the ethylene dioxy group.

As has been mentioned earlier, pre-1967 literature has very few reports on the solvent extraction of the alkali metals. However, several studies on the solvent extraction of alkali metals by crown ethers have been reported in the last two decades after the discovery of the complexing ability of crown ethers.

Frensdorff and Pedersen(42) reported the extraction of potassium picrate from aqueous solution into methylene chloride and hexane with various derivatives of 18-crown-6 and concluded that the extraction is efficient only when the anion is large and highly polarizable. Jawid et al(48) have also reported a higher extraction of M-crown$^+$ complex with large and highly polarizable anions. In another study, Frensdorff(49) reported the extraction of sodium and potassium picrates from water into methylene chloride and into hexane using both isomer A and isomer B of dicyclohexyl 18-crown-6 (DCHC-6). He reported a higher value of K_{ex} for the potassium/picrate system containing isomer A than that containing isomer B and also found that K_{ex} is one hundred times smaller in n-hexane than it is in methylene chloride. Jaber et al(50) also have reported the extraction of alkali and alkaline earth metal picrates into methylene chloride with dicyclohexyl 18-crown-6.

Extraction of several mono- and divalent metal picrates into benzene using 15-crown-5 and 18-crown-6 polyethers has been reported by Japanese workers. Sadakane et al(51) have studied the extraction of alkali metal picrates into benzene using dibenzo 18-crown-6 and have found that the K_{ex} value increases, passes through a maximum at potassium and then falls off as the size of the alkali metal cation increases further. They also noticed higher extraction of the cation in more polar organic solvents. Takeda et al(52) have reported the extraction of several monovalent metal picrates with two different sizes of crown ethers

(15-crown-5 and 18-crown-6) into benzene. They have found the following order for K_{ex}: $Ag^+ > Na^+ > T\ell^+ >> K^+ > Rb^+ > Cs^+ > Li$ and $T\ell^+ > K^+ > Rb^+ > Ag^+ > Cs^+ > Na^+ >> Li^+$ for 15-crown-5 and 18-crown-6 respectively. In another study the same authors have determined the K_{ex} sequence of bivalent(53) metal picrates for 15-crown-5, 18-crown-6 and dibenzo 18-crown-6.

Although the enhancement of extraction with increase in polarity of organic phase has been observed by most of the workers, Danesi *et al*(54) have reported some interesting results from a study of the extraction of alkali metal picrates into different mixtures of nitrobenzene and toluene with dibenzo 18-crown-6. In 50:50 and 30:70 mixtures of nitrobenzene and toluene (dielectric constant "D" = 15.6 and 10.6) K_{ex} was decreased with respect to pure nitrobenzene (D = 35). On the other hand, they observed an increase in the extraction for 5:95 mixture of nitrobenzene and toluene (D = 3.4).

In contrast to most of the studies, Marcus and Asher(55) have studied the extraction of potassium and sodium halides with 18-crown-6 and have concluded that the extraction coefficient is related to the solvation of the anion in the organic phase.

Separation of alkali metals has also been reported using crown ethers either anchored to a resin or loaded on a solid support. Blasius *et al*(56) have reported the synthesis of several exchangers with crown ethers as anchor groups, and have demonstrated the ability of these exchangers to separate various cations with a common anion as well as different anions with a common cation. Smulek and Lada(57) have reported the separation of alkali metals using dibenzo 18-crown-6 loaded on Kieselguhr. From all that has been said above, it is very evident that crown ethers, which possess a unique ability to complex alkali metals, have been successfully used for the separation and extraction of alkali metals.

In the present work, polyurethane foams of both polyether and polyester type have been explored as supports for the extraction of alkali metals using crown ethers. Attempts have also been made to compare the extraction behaviour of polyurethane foams towards these cations with the previous results employing various solvents.

B. EXPERIMENTAL

Apparatus

Varian Model 634 S UV-Visible Spectrophotometer

Evans Electroselenium Ltd. Flame Photometer

Perkin-Elmer Model 306 Atomic Absorption Spectrophotometer

Varian Techtron Hollow Cathode Lamps

Fisher Accumet Model 520 pH Meter

Glass and Saturated Calomel Electrodes

Extraction Cells (Figure 2) (Custom Made)

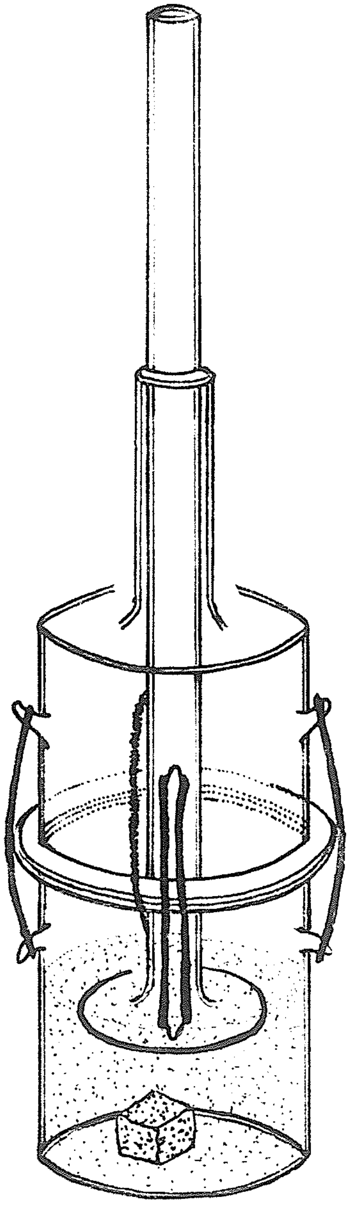
Reagents

The following chemicals of reagent grade were obtained from the sources indicated:

Chemical	Supplier
Lithium Chloride	Fisher Scientific Co.
Sodium Chloride	Fisher Scientific Co.
Potassium Chloride	Fisher Scientific Co.
Rubidium Chloride	Fisher Scientific Co.
Cesium Chloride	Fisher Scientific Co.
Silver Nitrate	Fisher Scientific Co.
Thallium Chloride	Fisher Scientific Co.
Picric Acid	B.D.H. England
8-Anilino-napthalene Sulphonic Acid as Magnesium salt	Eastman Kodak Co.

Figure 2.

Extraction cell.



The following crown ethers were obtained in the best available purity from the Aldrich Chemical Co.:

Dibenzo 18-Crown-6
Dicyclohexyl 18-Crown-6
18-Crown-6

Although dicyclohexyl 18-crown-6 is reported to exist in two isomeric forms, the separation of the supplied product on an alumina column using n-hexane and ethyl ether mixture (80:20) as the eluent indicates that the commercial product contains mainly (approximately 90%) one isomer identified as isomer B by its melting point (70°C). No further attempts were made to separate the isomers and the compound supplied by the manufacturer was considered as isomer B of dicyclohexyl 18-crown-6.

Foams

Polyether-based polyurethane foam used in these experiments was obtained from G. N. Jackson Ltd. (Winnipeg, Manitoba) and is designated as #1338 by the supplier.

Polyester type foam (Dispo) employed in this study was the product of Scientific Products (McGraw Park, Illinois) and distributed by Canlab (Winnipeg, Manitoba).

Preparation of Standard and Sample Solutions

Solutions of 0.01 M in each cation were prepared by dissolving the appropriate weight of each salt in water. The salts were dried for three hours at 110°C prior to weighing.

The solution of dicyclohexyl 18-crown-6 was prepared by dissolving the appropriate amount of crown ether (assuming a molecular weight of 372.5 g/mol and no molecule of solvation) in doubly distilled deionized water to give a final concentration of 0.01 M.

A 0.01 M stock solution of 8-anilino-naphthalene sulphonate (ANS) was obtained by dissolving 3.1050 g of the magnesium salt in water to give one liter of solution.

Standard picric acid solution was prepared by filtering approximately 900 mL saturated solution of picric acid in a one liter volumetric flask, diluting to the mark, and finally standardizing potentiometrically against standard sodium hydroxide solution.

A series of ten solutions was prepared in separate 50 mL volumetric flasks for each experiment by diluting the necessary volume of the above solutions to give the required concentrations.

The water used in preparing all solutions was doubly distilled and deionized.

General Procedure

Small cubes of approximately 0.2 g each were cut from a single sheet of polyurethane foam 5.1 cm (2 inches) in thickness. Prior to use, the foam cubes were soaked in 0.5 M HNO_3 for ten hours to remove any possible inorganic contaminants followed by washing with distilled water until free from acid. They were then extracted with acetone in a soxhlet apparatus for six hours to remove the non-polymeric organic materials. Finally, the residual solvent was removed by air drying in a 60°C oven or under vacuum at room temperature.

Each experiment was carried out by placing the sample solution and foam cube in one of the extraction cells (Figure 2). The foam cube was squeezed in solution in order to flush out the solution and to allow fresh solution to equilibrate with it. The process of squeezing was carried out at thirty minute intervals (20 strokes each time) for six hours. Aliquots of the solution were then removed and analyzed for the species of interest.

Both flame photometry and atomic absorption spectrophotometry were used for the analysis of metal solutions. The flame photometer was employed in the case of lithium, sodium and potassium, while solutions of rubidium, cesium, silver and thallium were analyzed by atomic absorption spectrophotometry.

The percentage of extraction of metal was determined by measuring the concentration of the metal in the sample solution before and after exposure to the foam (assuming that all of the metal disappearing from the solution was extracted by the foam).

The percentage of extraction is then given by the equation:

$$\% \text{ Extraction} = \left(1 - \frac{C'}{Co}\right) \times 100 \qquad (10)$$

Co = Concentration before extraction

C' = Concentration after extraction

The distribution coefficient for metal is given by the ratio of the metal concentration in the foam to the concetration of the metal left in the solution at equilibrium

$$D = \frac{\text{concentration of metal on the foam}}{\text{concentration of metal left in solution}} \qquad (11)$$

Since the volume of the foam cannot be determined accurately, the concentration of the metal on the foam is expressed as moles per kg. Furthermore, since the percentage of extraction (%E) and the percentage left in solution (100 - %E) are proportional to the number of moles of metal on the foam and number of moles of metal in solution at equilibrium, the distribution ratio is represented as:

$$D = \frac{\text{\% of metal on the foam}}{\text{weight of foam (kg)}} \quad \text{x} \quad \frac{\text{Volume of solution (L)}}{\text{\% of metal left in solution}} \qquad (12)$$

Defined in this way, "D" has the units of volume per weight, i.e. L kg^{-1}.

The Distribution of Crown ether and Picric Acid between Foam and Water

The distribution ratio between foam and water for dicyclohexyl 18-crown-6 (DCHC-6) was determined as follows. To a 25 mL aliquot of crown ether solution, a large excess of potassium hydroxide and picric acid were added and the resulting solution was extracted with an equal volume of methylene chloride. Another 50 mL aliquot of crown ether solution was first equilibrated with polyurethane foam as in the metal extraction procedure. After six hours, 25 mL of this solution was transferred to a separatory funnel and a large excess of potassium hydroxide and picric acid was added. The resulting solution was then extracted with an equal volume of methylene chloride. Under these conditions, the crown ether is extracted together with an equivalent quantity of picrate ion. Thus, the spectrophotometric analysis of picrate in the two methylene chloride extracts allowed us to calculate the concentration of crown ether before and after foam extraction. The amount of crown ether extracted by foam was thus easily determined. The distribution ratio of crown ether was determined in this way for a number of concentrations between 0.001 and 0.01 M. The average value of the distribution ratio (K_{1ex}) was found to be 15 ± 3 L kg^{-1}.

The distribution ratio for picric acid between water and polyureane foam was determined by studying the extraction of picric acid in the absence of both alkali metal ions and of crown ether. Picric acid extraction was studied over a wide pH range (1.0 to 8.0) using solutions with an initial picric acid concentration of 4 x 10^{-3} mol L^{-1} in the aqueous phase. The picrate ion concentration was determined spectrophotometrically at 420 nm. The distribution ratios thus obtained were found to be constant over the pH range 2.5 to 8.0 and these values were averaged for use in subsequent calculations. The average value, together with the standard deviation was found to be 35 ± 5 L kg^{-1}.

C. RESULTS AND DISCUSSION

I. Extraction of Alkali Metal Cations by Polyether-Based Polyurethane Foam

1. Preliminary Experiments

These studies were carried out to select a suitable crown ether for the extraction of alkali metals by polyurethane foams. Since 18-crown-6 and its derivatives form the most stable complexes with these cations and many studies regarding the use of these crown ethers for the extraction of alkali metals have already appeared in the literature, the experiments were designed to establish the effectiveness of 18-crown-6 and its derivatives for the extraction of potassium by foam. Due to the very low solubility of dibenzo 18-crown-6 in water, attempts were made to prepare foams loaded with this and other crown ethers.

A known amount of crown ether was transferred to a 100 mL beaker and dissolved in approximately 50 mL of methylene chloride. Small cubes of foam each weighing approximately 0.1 g were soaked in the solution and squeezed several times while remaining in the solution about half an hour. The pieces of foam were then taken out of the solution, vacuum dried and weighed.

In the case of dibenzo 18-crown-6, most of the crown ether was precipitated after the removal of solvent (i.e. CH_2Cl_2) showing its insolubility in polyurethane foam. Although, by contrast, both 18-crown-6 and dicyclohexyl 18-crown-6(DCHC-6) showed appreciable solubility in the foam, sufficient extraction of potassium was nevertheless achieved only by foams loaded with DCHC-6. However, this method was discontinued entirely due to difficulties in reproducing the amount of crown ether loaded onto individual foam pieces.

Since both 18-crown-6 and dicyclohexyl 18-crown-6 (DCHC-6) are appreciably soluble in water, experiments were carried out in which potassium was extracted by untreated foams from aqueous solutions containing K^+, picrate and crown ether. Similar to the results obtained for loaded foams, no appreciable amount of potassium was extracted by foams using 18-crown-6 and thus only DCHC-6 was used for further study. Pedersen(40) also reported that DCHC-6 is a better complexing agent than any of the other 18-crown-6 polyethers.

Blank experiments showed little or no extraction of potassium if either the crown ether or picric acid was absent from alkali metal solutions. In order to determine the time required to establish equilibrium, experiments were performed by squeezing the foam in a solution (50 mL) containing 5×10^{-5} M K^+, 4×10^{-3} M picric acid and 4×10^{-3} M DCHC-6 for different time periods. The results indicated that the percentage of extraction becomes constant after one hour; however, foam was squeezed for six hours in all later studies in order to ensure the achievement of equilibrium.

To establish the optimum conditions for the extraction of alkali metal picrates by polyether type polyurethane foam using DCHC-6, the effects of a number of variables were investigated.

2. Effect of Crown Ether Concentration on the Extraction of Alkali Metal Cations

Solutions (40 mL) of varying DCHC-6 concentrations containing 4×10^{-3} M picric acid and 1×10^{-4} M alkali metal cations were equilibrated for six hours with foam cubes (0.20 ± 0.01 g). Samples were then analyzed by flame photometry or by atomic absoprtion spectrophotometry. Figure 3 shows the effect of DCHC-6 concentration on the extraction of alkali metal picrates by polyether type polyurethane foam. As can be seen, extraction generally increases with an increase in crown ether concentration. However, the extraction of potassium, and to some extent that of rubidium, increases sharply then starts to level off. Potassium extraction may reach a plateau at some higher concentration of DCHC-6 in aqueous phase, however, it was not possible to study the extraction of potassium under those conditions due to the limited solubility of DCHC-6. Cesium and sodium extract poorly even at a very high concentration of crown ether, while lithium does not extract at all under these conditions. It is clear from these results that the order of extractability of alkali metal picrates by polyether type polyurethane foam using DCHC-6 is $K^+ > Rb^+ > Cs^+ > Na^+ >> Li^+$. A parallel trend in the stability constants of alkali metal complexes with DCHC-6 has also been found, tending to suggest that extraction of these alkali metal cations is mainly dependent upon the ability of the crown ether to complex them. This in turn, depends primarily on the ratio of the ionic size of the cation to the cavity size of the crown ether. Similar trends for the extraction of alkali metal picrates by various organic solvents using 18-crown-6 and its derivatives have been reported previously and have always been attributed to the stability of the cation-crown ether complex.

Figure 3

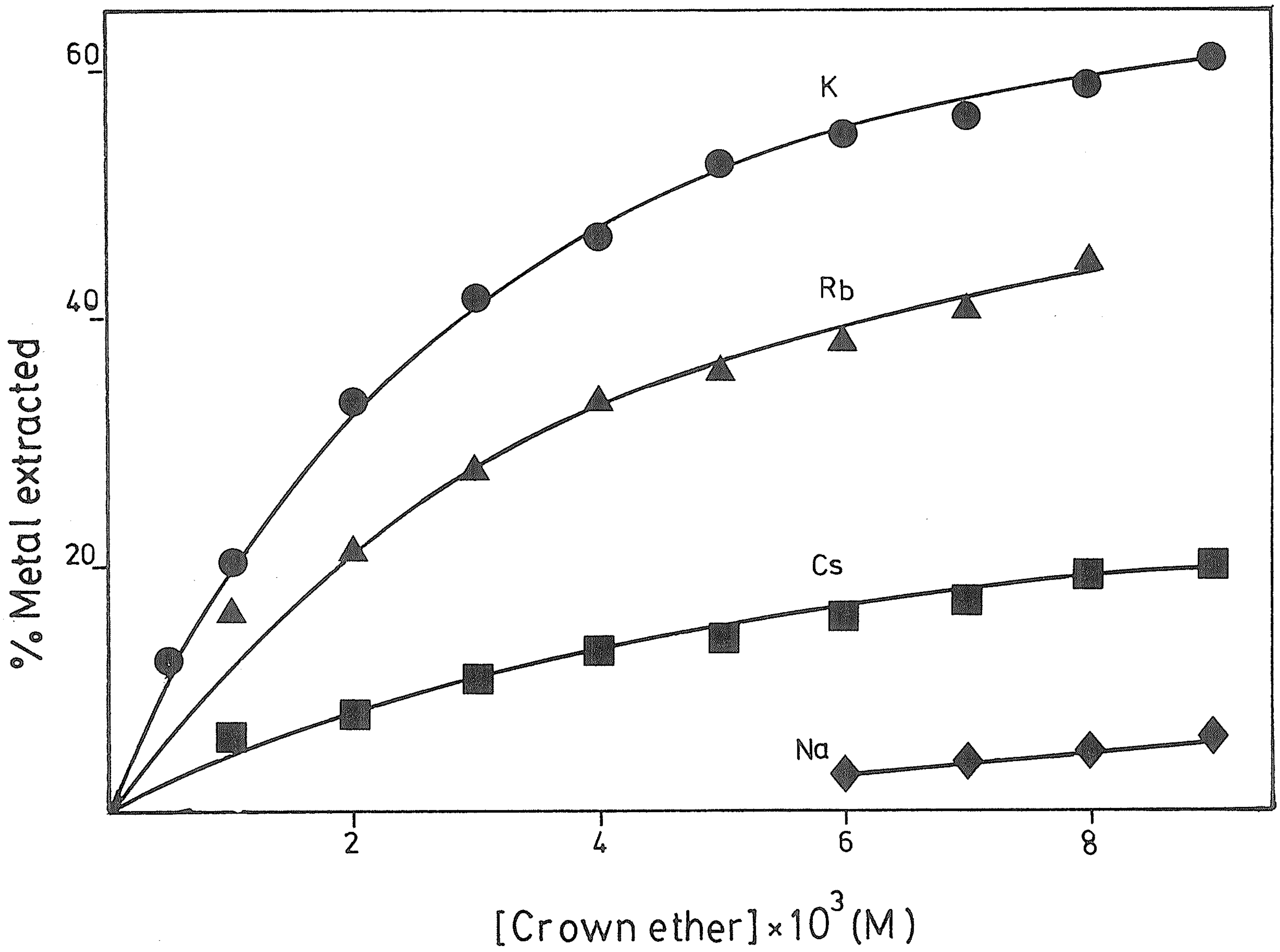
Effect of crown ether (DCHC-6) on the sorption of alkali metal cations from aqueous picrate solution by polyether-based polyurethane foam.

Initial Solution Conditions:

[Metal cation]	1×10^{-4} M
[Picrate]	4×10^{-3} M
Solution Volume	40 mL
Foam Weight	0.20 ± 0.01 g
Temperature	25.00 ± 0.05°C

Notes:

Na^+	(◆)
K^+	(●)
Rb^+	(▲)
Cs^+	(■)


% Metal extracted
60
40
20
2
4
6
8
[Crown ether] × 10^3 (M)
K
Rb
Cs
Na

3. Variation of Distribution Ratio with Anion Type and Concentration

The effect of picrate concentration on the extraction of metal cations was studied by measuring the percentage of extraction of $M^+(Li^+$, Na^+, K^+, Rb^+ and $Cs^+)$ from solutions of different concentrations of picric acid but having the same amount of alkali metal (1×10^{-4} M) and of crown ether (4×10^{-3} M). These solutions had already been equilibrated with foams of equal weights (0.20 ± 0.01 g) at constant temperature. The results of such studies for Na^+, K^+, Rb^+ and Cs^+ are shown in Figure 4. In these experiments, the concentration of picrate was varied from 0.5×10^{-3} to 1.5×10^{-2} M for each cation. Although all cations show a general trend toward higher extraction with increasing picrate concentration, a small change in picrate concentration resulted in quite a large increase in the degree of extraction for K^+ and Rb^+. On the other hand, a similar change in picrate concentration does not result in a prominent increase in the extraction of Na^+ and Cs^+. Thus, it is reasonable to assume that although the extraction of these cations can be enhanced by the concentration of anion, the stability of the cation-crown ether complex remains the most important factor in the extraction of these alkali metal cations by polyether type polyurethane foam.

Since it is generally accepted that ion-pair extraction can be greatly influenced by the nature of the counter ion (i.e. more hydrophobic counter ions yield higher extraction), the effect of different anions on the extraction of potassium from DCHC-6 crown ether solution was investigated in the hope of enhancing the extraction of potassium.

Foam cubes weighing 0.20 ± 0.01 g were squeezed for six hours in a

Figure 4

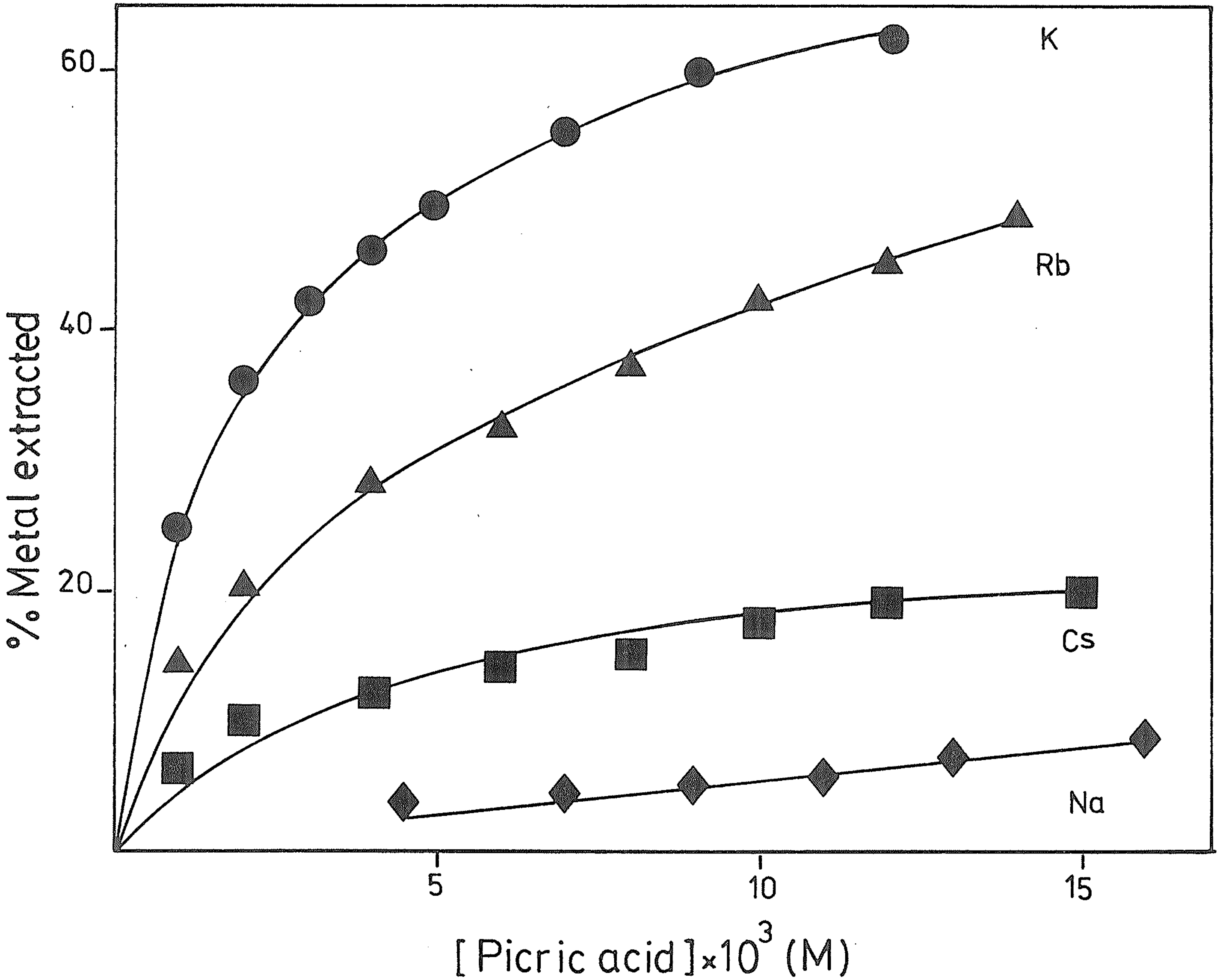
Effect of varying the initial concentration of picric acid on the sorption of alkali metal cations from the aqueous solution of crown ether (DCHC-6) by polyether foam.

Initial solution conditions:

[Metal cation]	1×10^{-4} M
[DCHC-6]	4×10^{-3} M
Solution volume	40 mL
Foam weight	0.20 ± 0.01 g
Temperature	25.00 ± 0.05°C

Notes:

Na^+	(◆)
K^+	(●)
Rb^+	(▲)
Cs^+	(■)


K
Rb
Cs
Na
60
40
20
% Metal extracted
5
10
15
[Picric acid] × 10^3 (M)

series of solutions (40 mL) each containing 1 x 10^{-4} M potassium and 4 x 10^{-3} M of crown ether with varying concentrations of anion. Samples were then analyzed by flame photometry. In Figure 5, curve a and b show the dependence of distribution ratio "D" on the initial concentrations of 8-anilino-napthalene sulphonate (ANS) and picrate respectively at constant initial concentrations of potassium and DCHC-6. Under similar conditions, no extraction of potassium was observed with bromide, iodide, 2,4 dinitrophenolate and 2,6 dinitrophenolate anions. It is obvious from Figure 5 that the extraction is improved by a bulkier anion (ANS), whereas no detectable amount of potassium is extracted in the presence of less hydrophobic anions. This is in complete accordance with the results of Pedersen(42) and others(48) who have also reported that efficient extraction can be achieved only in the presence of large and easily polarizable anions. On the basis of these findings, one can conclude that the extraction of these cations can be further improved in the presence of more hydrophobic anions. However, the possibility of increasing extraction by the use of highly hydrophobic counter anions is limited by the fact that the available concentration of the counter ion in aqueous phase also decreases with increasing hydrophobic character due to decreasing solubility.

Figure 5

Extraction of potassium as a function of initial concentration of anions from aqueous crown ether solution by polyether foam.

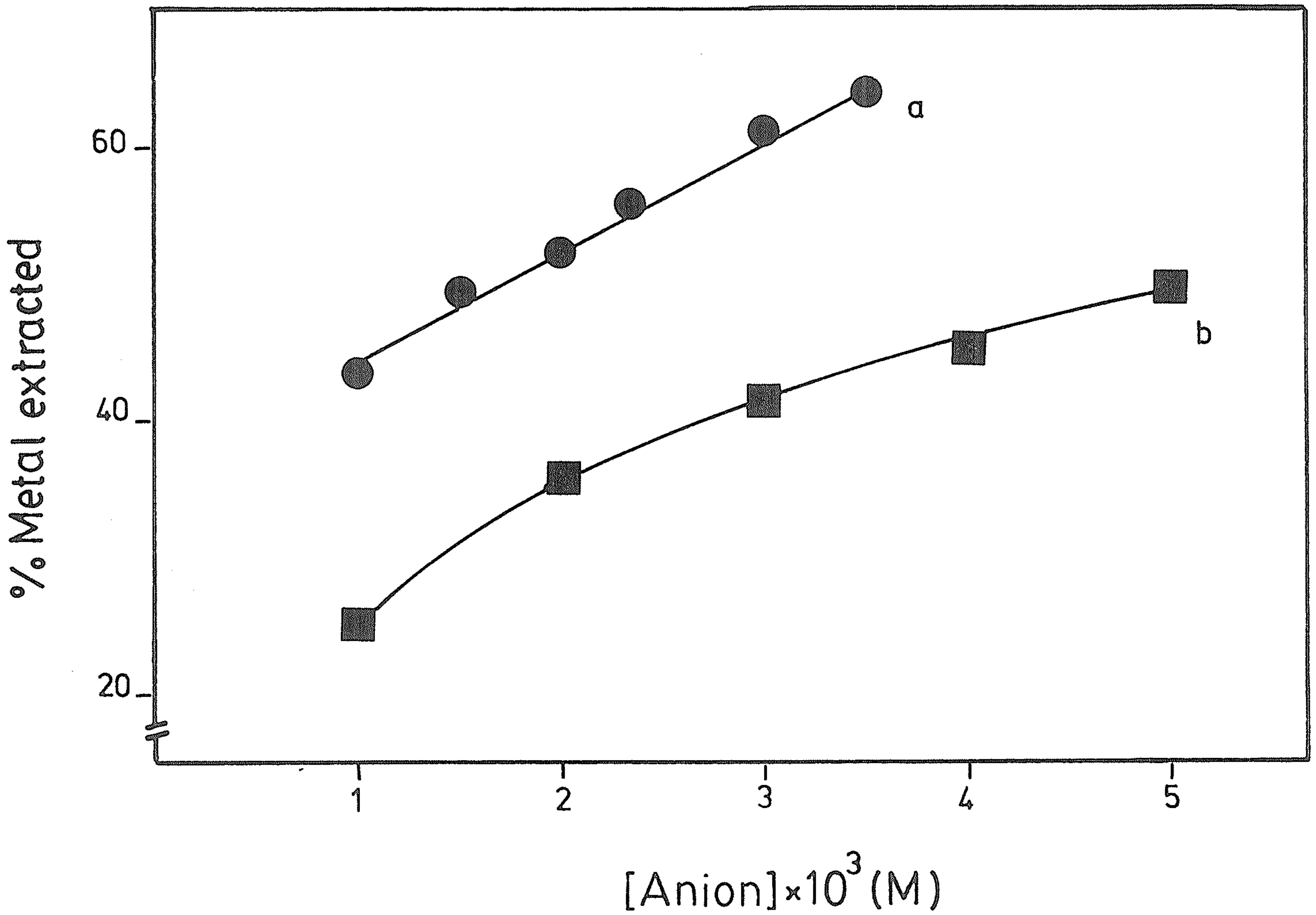
Initial solution conditions:

[Potassium]	1×10^{-4} M
[DCHC-6]	4×10^{-3} M
Solution volume	40 mL
Foam weight	0.20 ± 0.01 g
Temperature	25.00 ± 0.05°C

Notes:

ANS (●)

picrate (■)


% Metal extracted
60
40
20
1
2
3
4
5
[Anion]×10³ (M)
a
b

4. Effect of pH on the Extraction of Potassium

To study the effect of pH, foams were squeezed for six hours in solutions of varying pH values containing constant amount of potassium (1×10^{-4}M), picric acid (4×10^{-3} M) and crown ether (4×10^{-3} M). The pH values were adjusted by the addition of HCl or tetraethyl ammonium hydroxide. The concentration of potassium before and after extraction was determined by flame photometry.

Figure 6 shows the pH dependence of potassium picrate extraction by polyether type polyurethane foam using DCHC-6. Extraction initially increases sharply with increasing pH, reaching a maximum at pH 2.5 and remaining constant up to pH 8. It is interesting to compare Figure 6 with Figure 7 (where the amount of picrate ion present in a 4×10^{-3} M picric acid solution is calculated at various pHs by using the reported value of pKa(58)). From the figures, it is obvious that the sharp initial increase in potassium extraction with increasing pH followed by independence above pH 2.5 can be attributed to the concentration of picrate ion available at different pH values. Since in all other experiments in this study the extraction of alkali metal cations was carried out at pH > 2.5, it is reasonable to assume that the extraction of alkali metal cations by polyurethane under these conditions is independent of hydrogen ion concentration.

Figure 6

Effect of pH on the extraction of potassium picrate from the aqueous DCHC-6 solution by polyether foam.

Initial solution conditions:

[Potassium]	1×10^{-4} M
[DCHC-6]	4×10^{-3} M
[Picrate]	4×10^{-3} M
Solution volume	40 mL
Foam weight	0.20 ± 0.01 g
Temperature	25.00 ± 0.005°C

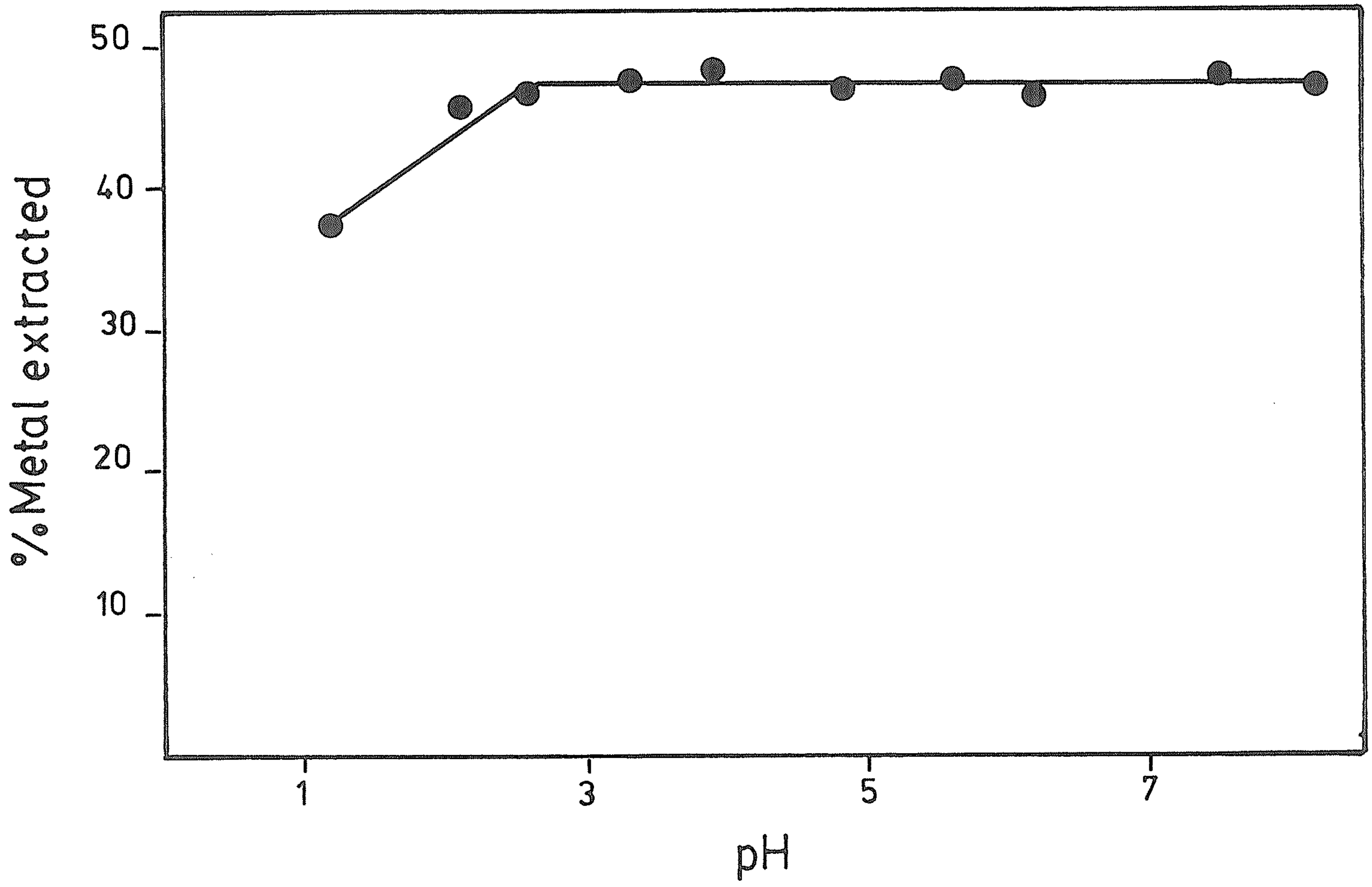
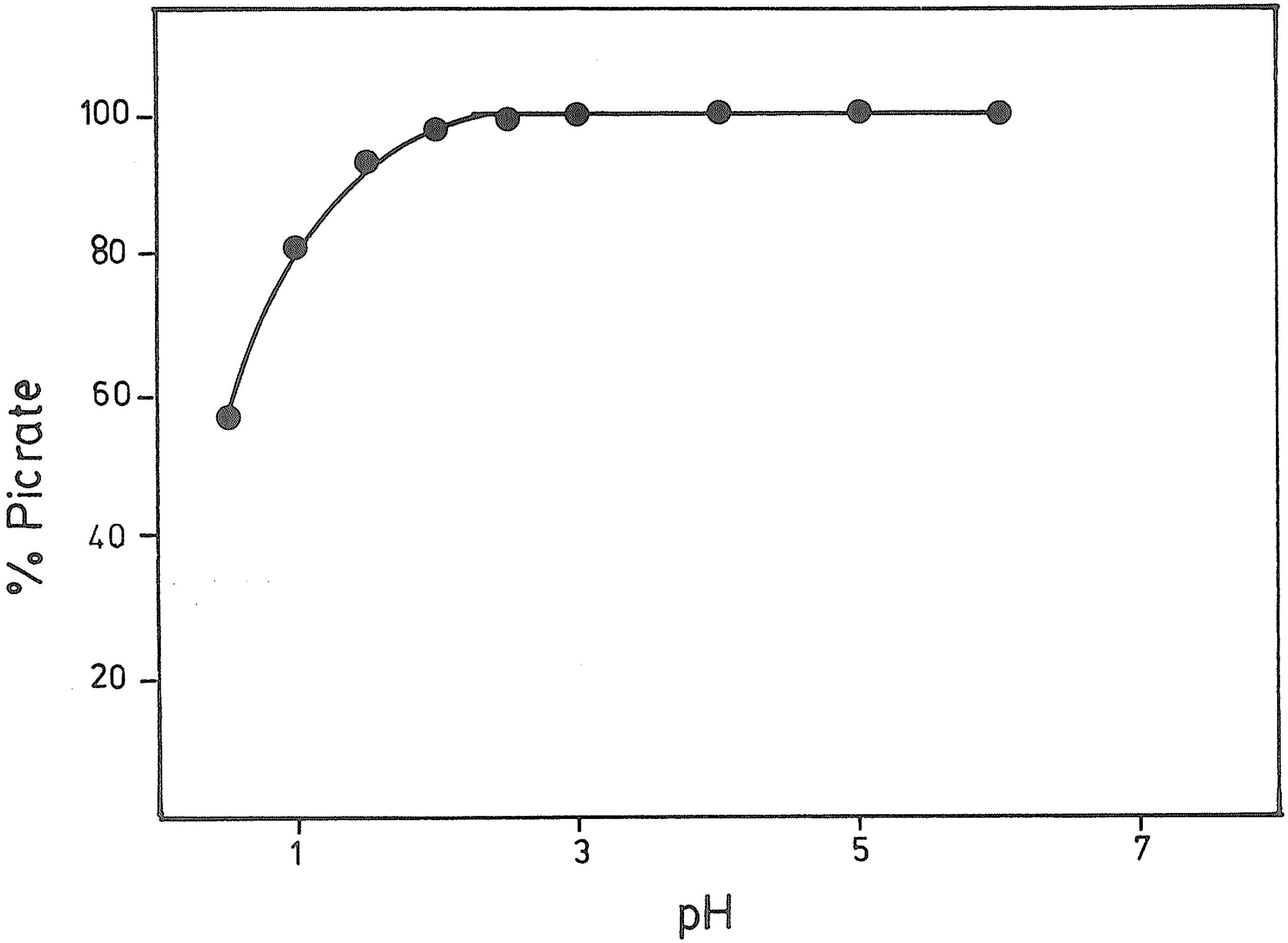

50
40
30
20
10
% Metal extracted
1
3
5
7
pH

Figure 7

The amount of picrate ion present in a 4×10^{-3} M picric acid solution at various pHs.



% Picrate
100
80
60
40
20
1
3
5
7
pH

5. Effect of Metal Concentration on the Distribution Ratio

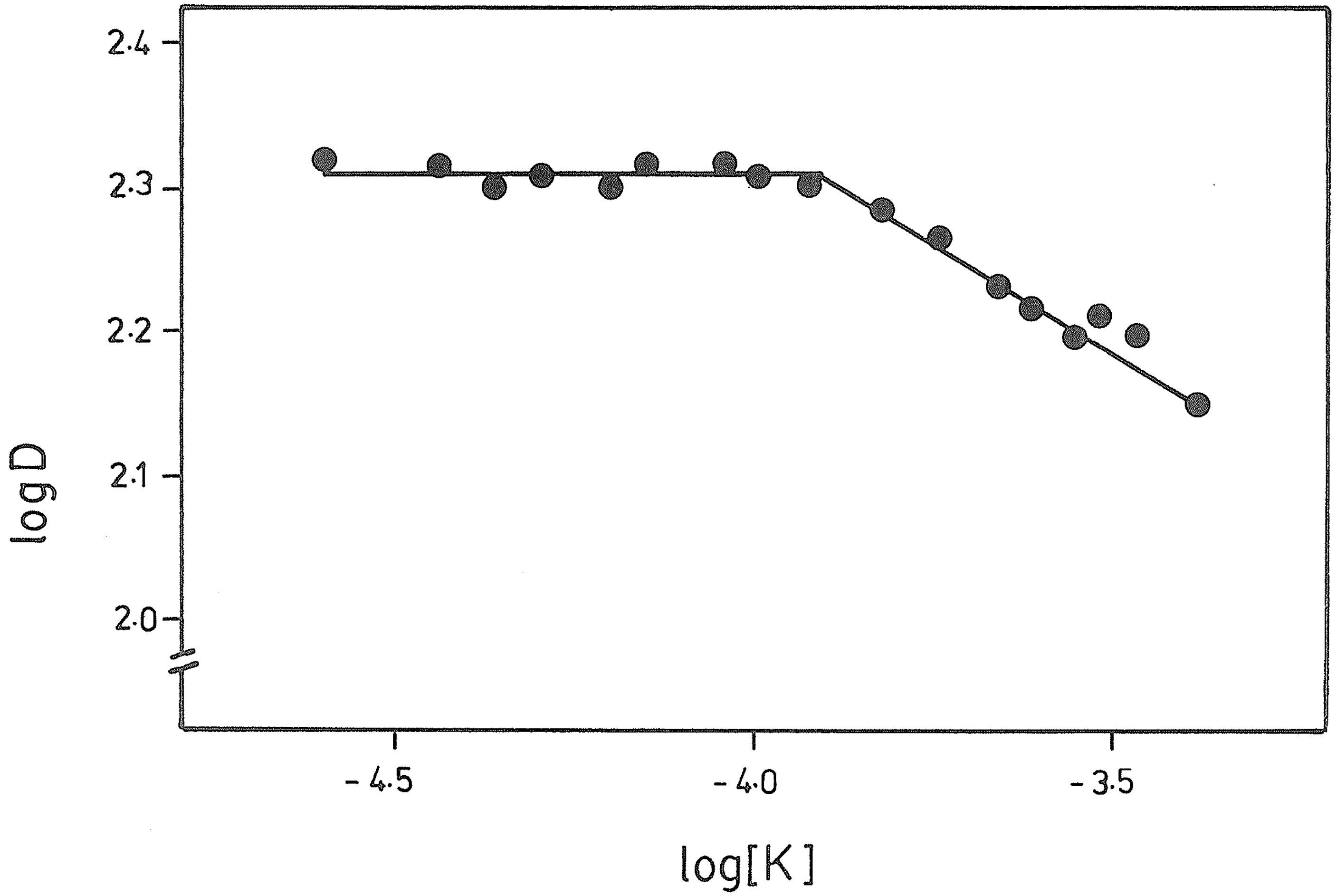
To determine the effect of metal concentration on the extraction of potassium picrate by polyurethane using DCHC-6, solutions containing various concentrations of potassium together with constant concentrations of picric acid (7×10^{-3} M) and crown ether (4×10^{-3} M) were equilibrated with foam for six hours. Samples were then analyzed for potassium by flame photometry. The results of one such study are shown in Figure 8 where log D is plotted as a function of log $[K^+]$. As can be seen, the "D" values remain virtually constant up to 3×10^{-4} M initial concentration of potassium and drop at higher concentrations with a resulting slope of 0.2. The constancy of the distribution ratio up to 3×10^{-4} M initial concentration of potassium suggests the extraction of mononuclear species under these conditions so the concentration of cation was always kept below this value for rest of the study. The drop in the distribution coefficient at higher potassium concentrations may be caused by a number of phenomena such as the formation of dimers in the aqueous phase, dissociation of the extractable complex in the foam, saturation of the polymer or a lack of sufficient crown ether and/or picrate in the aqueous phase. Because of a perfect match between the size of potassium ions and the cavity of the DCHC-6, the existence of a dimer is not possible and, in fact, no dimer has been reported in the literature for the K^+/DCHC-6 system. Considering the capacity of the foam as the probable cause for this drop in "D" values also raises some doubts since a value of about 1 mole/kg or higher has been reported by several workers as the capacity of foam for different systems(22). It seems most unlikely, therefore, that foam has such a low (0.035 mol/kg) capacity for potassium. Furthermore, a slope of -1 has been reported for the plots of log D vs log [M]

Figure 8

Effect of equilibrium solution potassium concentration on the distribution ratio.

Initial solution conditions:

[Picric acid]	7×10^{-3} M
[DCHC-6]	4×10^{-3} M
Solution volume	40 mL
Foam weight	0.20 ± 0.01 g
Temperature	25.00 ± 0.05°C


2.4
2.3
2.2
2.1
2.0
log D
-4.5
-4.0
-3.5
log[K]

when foam has reached the capacity. Obviously a slope of -0.2 resulting from log D vs log $[K^+]$ (Figure 8) also tends to rule out the idea of foam achieving capacity. In addition to that, such a small value of slope (-0.2) is also unlikely to result from the dissociation of the extractable complex in the foam (although such a dissociation in foam has been suggested by Gesser and coworkers for the Fe/Cl/H system where a plot of log D vs log [Fe] results in a slope of 0.5)(15). It seems likely, therefore, that the drop in distribution coefficient with increasing initial concentration of potassium shown in Figure 8 is due to a lack of sufficient picrate and/or crown ether at higher concentrations of potassium.

6. Extraction Equilibrium

An attempt is made to quantitatively explain the extraction behaviour of alkali metal picrates by polyether type polyurethane foam.

The overall extraction equilibrium between an aqueous phase containing a metal ion (M^+), picrate ion (A^-), crown ether (Cr) and polyurethane foam may be represented by the following equation:

$$M^+ + Cr + A^- \xrightleftharpoons{K_{ex}} MCrA_{(f)} \tag{13}$$

$$K_{ex} = [MCrA]_f/[M^+][Cr][A^-] \tag{14}$$

where MCrA represents the ion-pair between the metal-crown ether cation MCr^+ and picrate anion A^-. The subscript "f" denotes the foam phase and the absence of subscript refers to the aqueous phase. The overall equilibrium is thought to consist of the following equilibria:

i. The distribution of free crown ether between foam and aqueous phases

$$Cr \xrightleftharpoons{K_{1ex}} Cr_f \tag{15}$$

$$K_{1ex} = [Cr]_f/[Cr] \tag{16}$$

ii. Distribution of picric acid between the two phases

$$HA \underset{}{\overset{K_{2ex}}{\rightleftharpoons}} HA_f \qquad (17)$$

$$K_{2ex} = [HA]_f/[HA] \qquad (18)$$

iii. Dissociation of picric acid

$$HA \overset{K_{3d}}{\rightleftharpoons} H^+ + A^- \qquad (19)$$

$$K_{3d} = [H^+][A^-]/[HA] \qquad (20)$$

iv. Reaction of metal ion with the crown ether

$$M^+ + Cr \overset{K_4}{\rightleftharpoons} MCr^+ \qquad (21)$$

$$K_4 = [MCr^+]/[M^+][Cr] \qquad (22)$$

v. Association of complexed cation with picrate anion

$$MCr^+ + A^- \overset{K_5}{\rightleftharpoons} MCrA \qquad (23)$$

$$K_5 = [MCrA]/[MCr^+][A^-] \qquad (24)$$

vi. Distribution of the ion-pair between the two phases

$$MCrA \overset{K_{5ex}}{\rightleftharpoons} MCrA_f \qquad (25)$$

$$K_{5ex} = [MCrA]_f/[MCrA] \qquad (26)$$

The distribution ratio of the metal is defined as

$$D = [M_T]_f/[M_T] \tag{27}$$

$[M_T]_f$ and $[M_T]$ are the total metal concentrations in the foam and aqueous phases respectively. The distribution ratio can be calculated as

$$D = [MCrA]_f/[M^+] + [MCr^+] + [MCrA] \tag{28}$$

From equations 16, 20, 22, 24 and 25

$$D = K_4 . K_5 . K_{5ex}[M^+][Cr][A^-]/[M^+] + K_4[M^+][Cr] + K_4K_5[M^+][Cr][A^-] \tag{29}$$

$$D = \frac{K_4 . K_5 . K_{5ex}[Cr][A^-]}{1 + K_4[Cr] + K_4 . K_5[Cr][A^-]} \tag{30}$$

Since for all experiments the initial concentration of picrate $[A_T]$ is always large compared to metal concentration $[M_T]$, it is reasonable to assume that $[A^-] \simeq [A_T]$. The values of [Cr] can be estimated by making a few assumptions. First of all, since for all experiments $[M_T]$ is always $\leq$ 1/10th of $[Cr_T]$, $[MCr^+] + [MCrA]$ will also be $\leq$ 1/10th of $[Cr_T]$. Thus it is also reasonable to assume that

$$[Cr_T] = [Cr]_f + [Cr] \tag{31}$$

$$= K_{1ex} [Cr] + [Cr] \tag{32}$$

$$[Cr] = [Cr_T]/(1 + K_{1ex}) \tag{33}$$

Substituting the values of [Cr] and $[A_T]$ and other constants (the values of K_4 have been reported in the literature(46) and the values of K_5 have been estimated by FUOSS method(62)) it can be seen that the denominator in equation 30 is approximately unity

$$D \simeq K_4 . K_5 . K_{5ex}\ [Cr][A^-] \tag{34}$$

On the basis of this equation, one can predict the following:

i. The distribution coefficient is independent of metal ion concentration and depends only on the concentration of crown ether and anion;

ii. A plot of D vs [Cr] at constant $[A^-]$ or D vs $[A_T]$ at constant [Cr] will be a straight line passing through the origin;

iii. The plots of log D vslog [Cr] and log D vs log $[A_T]$ at constant $[A_T]$ and $[Cr_T]$ respectively will also yield straight lines of unit slopes.

It is obvious from Figure 8 that the extraction of alkali metal picrate by polyether-based polyurethane foam using DCHC-6 is independent of metal concentration. Figures 9 and 10 show the plots of D vs [Picric Acid] and D vs [Crown Ether] for K^+, Rb^+, Cs^+ and Na^+. As can be seen, a linear relationship as predicted by equation 34 does exist between "D" and either crown ether or anion concentration. Moreover, equation 34 predicts a zero intercept for these straight lines yet this is not true for the observed data. Furthermore, the "D" for potassium is no longer proportional to DCHC-6 at higher concentration. In addition to these discrepancies, the plots of log D vs log [Cr] (Figure 11) also do not yield a slope of unity even though such a slope has been reported by

Figure 9

Effect of varying the initial concentration of picric acid on the distribution of alkali metal cations between polyether foam and aqueous solutions.

Initial solution conditions:

[Cation]	1×10^{-4} M
[DCHC-6]	4×10^{-3} M
Solution volume	40 mL
Weight of foam	0.20 ± 0.01 g
Temperature	25.00 ± 0.05°C

Notes:

Na^+ (◆)
K^+ (●)
Rb^+ (▲)
Cs^+ (■)

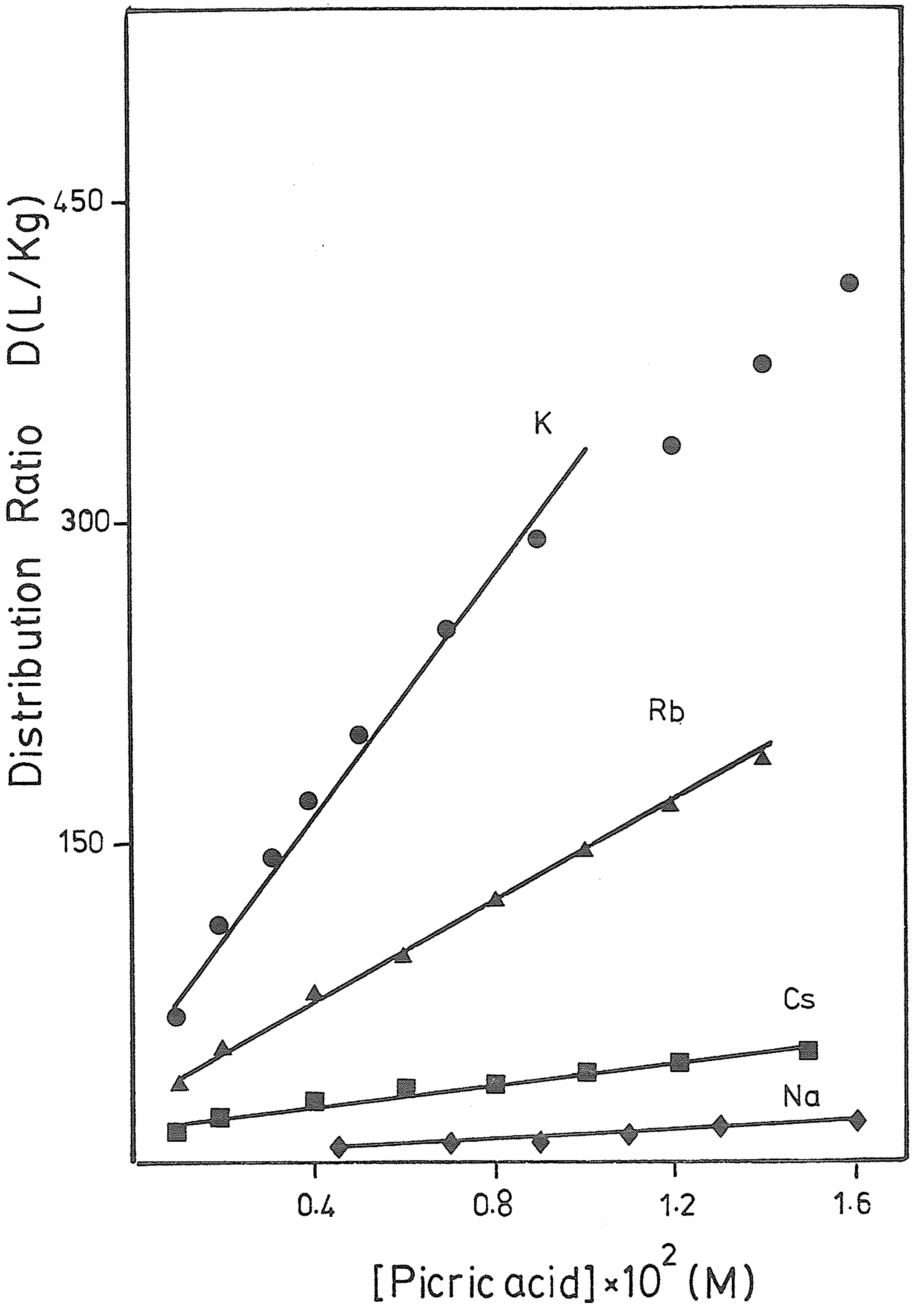

Distribution Ratio D(L/Kg)
450
300
150
0.4
0.8
1.2
1.6
[Picric acid]×10^2 (M)
K
Rb
Cs
Na

Figure 10

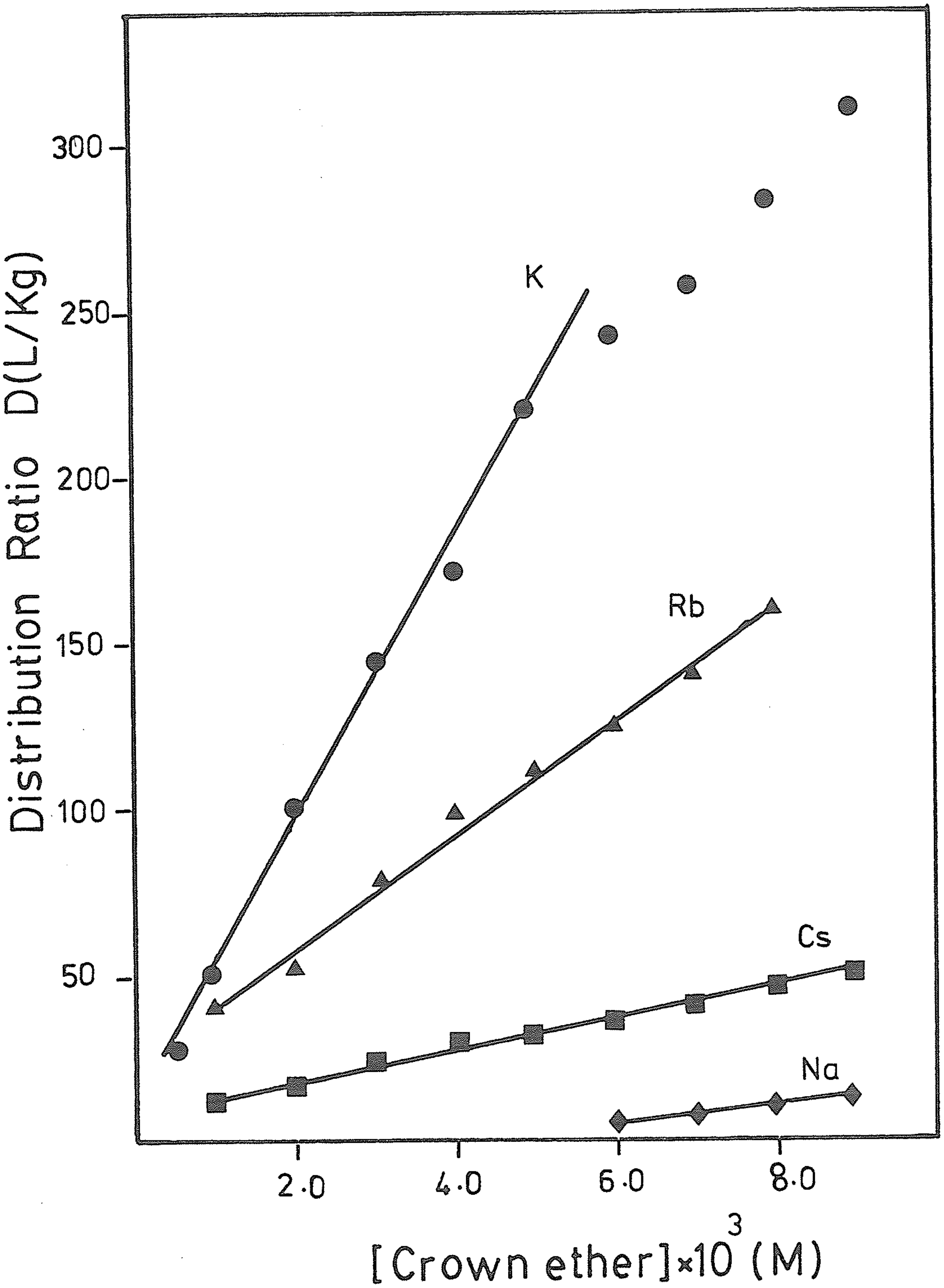
Effect of varying the initial concentration of crown ether on the distribution ratio of alkali metal picrates.

Initial solution conditions:

[Cation]	1×10^{-4} M
[Picric acid]	4×10^{-3} M
Solution volume	40 mL
Foam weight	0.20 ± 0.01 g
Temperature	$25.00 \pm 0.05°$ C

Notes:

Na^+	(◆)
K^+	(●)
Rb^+	(▲)
Cs^+	(■)



Distribution Ratio D(L/Kg)
300
250
200
150
100
50
K
Rb
Cs
Na
2.0
4.0
6.0
8.0
[Crown ether]×10^{3} (M)

Figure 11

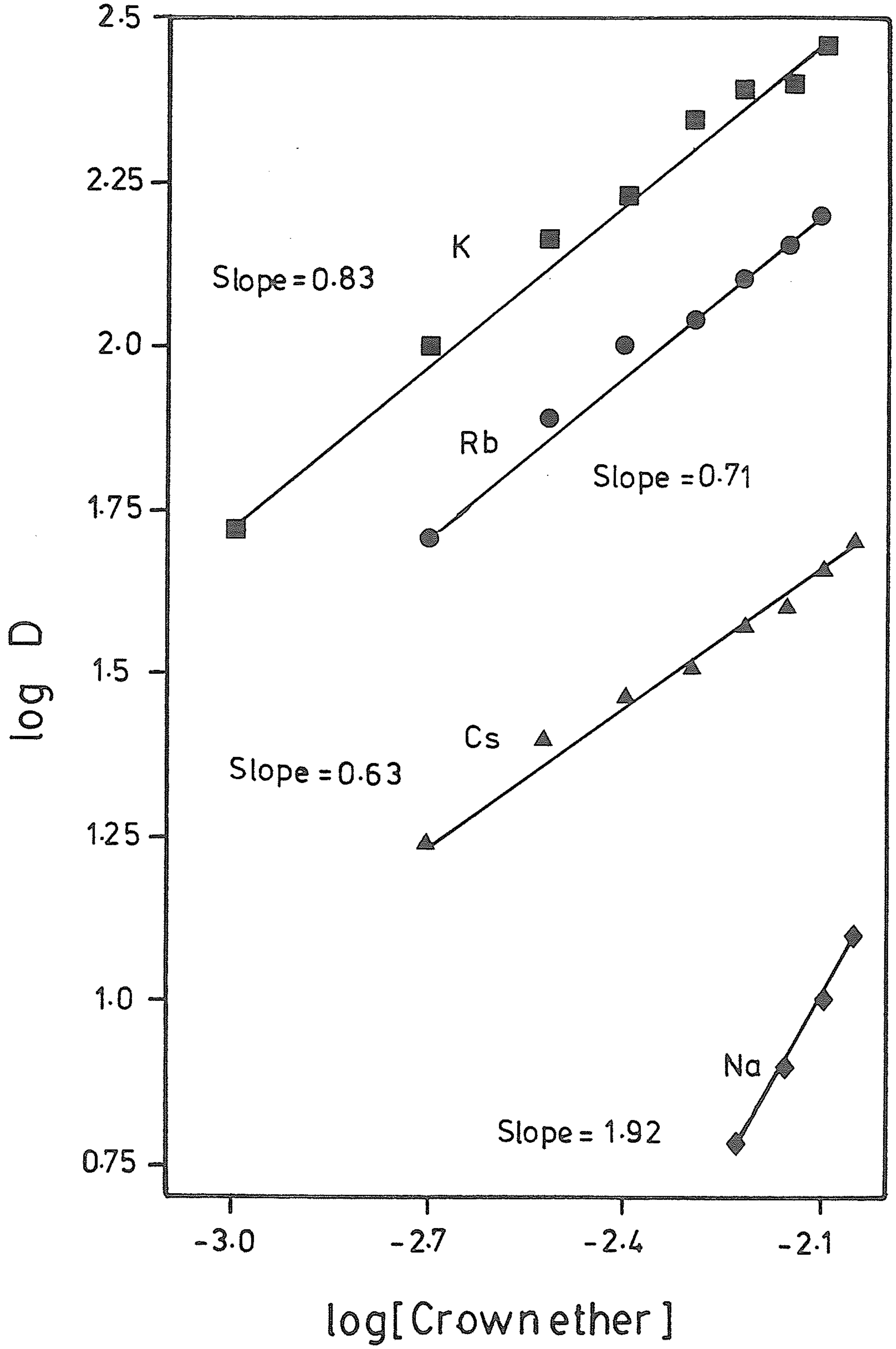
Plots of log D vs log [crown ether] for the distribution of alkali metal picrates between polyether foam and aqueous solution.

Initial solution conditions:

[Cation]	1×10^{-4} M
[Picric acid]	4×10^{-3} M
Solution volume	40 mL
Foam weight	0.20 ± 0.01 g
Temperature	25.00 ± 0.05°C

Notes:

Na^+ (◆)
K^+ (■)
Rb^+ (●)
Cs^+ (▲)


2.5
2.25
2.0
1.75
1.5
1.25
1.0
0.75
log D
-3.0
-2.7
-2.4
-2.1
log[Crown ether]
K
Slope = 0.83
Rb
Slope = 0.71
Cs
Slope = 0.63
Na
Slope = 1.92

several other workers(51,52,53) for the extraction of alkali metal picrates into various organic solvents (e.g. benzene, CH_2Cl_2) using 18-crown-6 and its derivatives as complexing agent. The deviation in slope from that predicted tends to suggest either that the nature of the extracting species in the polyurethane system is quite different from that involved in solvent extraction or that the present system (i.e. extraction of alkali metal picrates by polyurethane foam using DCHC-6) cannot be well represented by equation 34. Since the system in hand is fairly simple one, the formation and extraction of any polymeric species seems remote. Attempts have been made to modify the equation 34 so that the extraction behaviour of alkali metal picrates can be well represented by the resulting equation. Despite the fact that polyurethane foam has been equated with a "solvent of moderate dielectric constant" and the dissociation of the extracted species has also been discussed by Gesser et al in their recent publication (15), we have earlier ruled out the possibility of dissociation of the extracted species in the foam as a cause of drop in the distribution ratio with increasing potassium concentration (Figure 8) because the resulting slope has a lower value (-0.2) than that expected (-0.5). However, the intercepts in Figure 9, where the distribution coefficient is plotted against crown ether concentration, can be rationalized by assuming that foam is a "solvent of moderate dielectric constant" in which dissociation of the extracted species can take place.

Taking into consideration the dissociation of the extracted species into foam, the overall extraction equilibrium between polyurethane foam and the aqueous phase containing a metal ion (M^+), picrate ion (A^-) and crown ether (Cr) may be assumed to involve the following equilibria:

i. The distribution of crown ether between foam and the aqueous phase

$$\mathrm{Cr} \xrightleftharpoons{K_{1ex}} \mathrm{Cr}_f \tag{15}$$

$$K_{1ex} = [\mathrm{Cr}]_f/[\mathrm{Cr}] \tag{16}$$

ii. The distribution of picric acid between the two phases

$$\mathrm{HA} \xrightleftharpoons{K_{2ex}} \mathrm{HA}_f \tag{17}$$

$$K_{2ex} = [\mathrm{HA}]_f/[\mathrm{HA}] \tag{18}$$

iii. The dissociation of picric acid in both phases

$$\text{a.}\quad \mathrm{HA} \xrightleftharpoons{K_{3d}} \mathrm{H}^+ + \mathrm{A}^- \tag{19}$$

$$K_{3d} = [\mathrm{H}^+][\mathrm{A}^-]/[\mathrm{HA}] \tag{20}$$

$$\text{b.}\quad \mathrm{HA}_f \xrightleftharpoons{K_{3d}^*} [\mathrm{H}^+]_f + [\mathrm{A}^-]_f \tag{35}$$

$$K_{3d}^* = [\mathrm{H}^+]_f[\mathrm{A}^-]_f/[\mathrm{HA}]_f \tag{36}$$

vi. The reaction of the metal ion with the crown ether

$$\mathrm{M}^+ + \mathrm{Cr} \xrightleftharpoons{K_4} \mathrm{MCr}^+ \tag{21}$$

$$K_4 = [\mathrm{MCr}^+]/[\mathrm{M}^+][\mathrm{Cr}] \tag{22}$$

v. The association of complexed cation with the picrate anion

$$\mathrm{MCr}^+ + \mathrm{A}^- \xrightleftharpoons{K_5} \mathrm{MCrA} \tag{23}$$

$$K_5 = [MCrA]/[MCr^+][A^-] \tag{24}$$

vi. The distribution of the ion-pair between the two phases

$$MCrA \xrightleftharpoons{K_{5ex}} MCrA_f \tag{25}$$

$$K_{5ex} = [MCrA]_f/[MCrA] \tag{26}$$

vii. The dissociation of the ion-pair in the foam

$$MCrA_f \xrightleftharpoons{K_{5d}^*} MCr^+{}_f + A^-{}_f \tag{37}$$

$$K_{5d}^* = [MCr^+]_f[A^-]_f/[MCrA]_f \tag{38}$$

viii. The dissociation of the metal ion-crown ether complex in the foam

$$MCr^+{}_f \xrightleftharpoons{K_{4d}^*} M^+{}_f + Cr_f \tag{39}$$

$$K_{4d}^* = [M^+{}_f][Cr]_f/[MCr^+]_f \tag{40}$$

The distribution of picric acid in the absence of both metal ion and crown ether was studied at different pH values and was found to be constant over the pH range from 2.5 to 8.0. The distribution ratio D' of picrate in the absence of metal ion is equal to

$$D' = \frac{\text{Total picrate per unit weight of foam}}{\text{Total picrate per unit volume of solution}}$$

$$= \{[HA]_f + [A^-]_f\} \Big/ \{[HA] + [A^-]\} \tag{41}$$

Substituting for the values of $[HA]_f$ and [HA] using equations 20 and 36,

$$D = \left\{ \frac{[H^+]_f[A^-]_f}{K_{3d}^*} + [A^-]_f \right\} \Bigg/ \left\{ \frac{[H^+][A^-]}{K_{3d}} + [A^-] \right\} \tag{42}$$

$$= \frac{[A^-]_f}{[A^-]} \cdot \frac{K_{3d}([H^+]_f + K_{3d}^*)}{K_{3d}^*([H^+] + K_{3d})} \tag{43}$$

The value of K_{3d} has been determined$^{(58)}$ as 0.51 mol/L. Thus, at pH values higher than 2.5, $([H^+] + K_{3d})$ is approximately equal to K_{3d} and equation 43 reduces to

$$D' \approx \frac{[A^-]_f}{[A^-]} \times \frac{K_{3d}([H^+]_f + K_{3d}^*)}{K_{3d} \cdot K_{3d}^*} \tag{44}$$

Since the distribution ratio for picric acid was constant over the pH range from 2.5 to 8, it seems reasonable to assume that $([H^+]_f + K_{3d}^*)$ is approximately equal to K_{3d}^* over the pH range studied. Thus

$$D' \approx [A^-]_f/[A^-] \tag{45}$$

over the pH range 2.5 to 8.0.

The distribution of crown ether was also studied in the absence of both picrate and of metal ion. The distribution ratio

$$K_{1ex} = [Cr]_f/[Cr] \tag{16}$$

was determined for various initial concentrations of crown ether (1×10^{-3} to 1×10^{-2}M) and was found to have a constant value of 15 $\pm$ 3 L kg^{-1}.

The distribution ratio of the metal ion is defined as

$$D = \frac{\text{Total metal on foam per unit weight of foam}}{\text{Total metal in solution per unit volume of solution}} \tag{27}$$

Thus, using the equilibria in 15 through 40

$$D = \frac{[M^+]_f + [MCr^+]_f + [MCrA]_f}{[M^+] + [MCr^+] + [MCrA]} \qquad (46)$$

Substituting from equations 22, 24, 26, 28 and 40 gives

$$D = \frac{\dfrac{K_4 \cdot K_5 \cdot K_{5ex} \cdot K_{4d}{}^* K_{5d}{}^* mca}{c_f \cdot a_f} + \dfrac{K_4 K_5 K_{5ex} \cdot K_{5d}{}^* mca}{a_f} + K_4 K_5 \cdot K_{5ex} mca}{m + K_4 mc + K_4 \cdot K_5\ mca} \qquad (47)$$

where $m = [M^+]$, $c = [Cr]$, $a = [A^-]$, $c_f = [Cr]_f$, $a_f = [A^-]_f$.

Substituting for c_f and a_f using equation 16 and 45 respectively

$$D = \frac{\dfrac{K_4 \cdot K_5 \cdot K_{5ex} \cdot K_{4d}{}^* \cdot K_{5d}{}^*}{K_{1ex} D'} + \dfrac{K_4 \cdot K_5 \cdot K_{5ex} \cdot K_{5d}{}^* c}{D'} + K_4 \cdot K_5 \cdot K_{5ex} ca}{1 + K_4 c + K_4 \cdot K_5 ca} \qquad (48)$$

Since for all the experiments the total metal ion is always less than 1/10th of the total crown ether, it seems reasonable to approximate

$$vCr_T = vc + wc_f \qquad (49)$$

where Cr_T is the initial concentration of crown ether in the aqueous phase, v is the volume of solution and w is the weight of foam used. Thus,

$$vCr_T = v_c + wK_{1ex}c \qquad (50)$$

$$c = Cr_T/(1 + K_{1ex}w/v) \qquad (51)$$

Similarly,

$$a = A_T/(1 + D'\ w/v) \tag{52}$$

Substituting these values of c and a into equation 48 gives

$$D = \frac{\dfrac{K_{4d}{\ast}K_{5d}{\ast}K_{5ex}K_5K_4}{K_{1ex}D'} + \dfrac{K_{5d}{\ast}K_{5ex}K_5K_4Cr_T}{D'(1 + K_{1ex}w/v)} + \dfrac{K_{5ex}K_5K_4Cr_TA_T}{(1 + K_{1ex}w/v)(1 + D'w/v)}}{1 + \dfrac{K_4Cr_T}{(1 + K_{1ex}\ w/v)} + \dfrac{K_5K_4Cr_TA_T}{(1 + K_{1ex}w/v)(1 + D'w/v)}} \tag{53}$$

Both K_{1ex} and D' have been determined above. The stability constants of alkali metal ion-DCHC-6 complexes, K_4 in the above equation, have been reported in the literature$^{(46)}$ and are listed in Table 3. The ion pair association constants, K_5, may be estimated using the following equation derived by FUOSS$^{(62)}$ for ions in contact:

$$K = 2.524 \times 10^{-3}\ \mathring{a}^3\ e^b$$

$$b = Z^2/aDkT$$

Where Z is the electron charge,'a' is the center-to-center distance of the ions in a pair, D is the dielectric constant of the medium and k is Boltzmann's constant. Using the Pauling ionic radii given in Table 2 and value of 2.23 Å for the radius of picrate ion$^{(63)}$, values for the ion-pair association constants, K_5, were estimated. The values are given in Table 3. Substituting the appropriate values of K_4, K_5, Cr_T and A^{-}_{T} it can be seen that the denominator in equation (53) can be approximated by

$$1 + K_4\ Cr_T\ /\ (1 + K_{1ex}\ w/y)$$

Thus, after rearranging it can be seen that plots of $D[1 + K_4Cr_T/1 + K_{1ex}\ w/v]$ against both A_T and Cr_T will be straight lines, the slopes and intercepts of which allow us to estimate $K_{4d}*$, $K_{5d}*$ and $K_5.K_{5ex}$. The values of these constants were calculated for Na^+, K^+, Rb^+ and Cs^+ from the values of the slopes and intercepts obtained from Figures 12 and 13. The preferred values for the constants are given in Table 3.

Similar results have been reported for the solvent extraction of alkali metal complexes of 18-crown-6 and its derivatives with picrate and other anions(46, 48 and 51). Solvent extraction data are commonly reported as overall extraction constants, K_{ex}, defined analogously to equation (14). From equations 22, 24 and 26 it can be shown that

$$K_{ex} = K_4.K_5.K_{5ex} \tag{54}$$

Values of K_{ex} have been calculated and are given in Table 3. It can be seen from these K_{ex} values that the extraction of alkali metal picrates by polyurethane foam using DCHC-6 increases in the order $Na^+ < Cs^+ < Rb^+ < K^+$. This is consistent with the results obtained by previous workers(46,51) for solvent extraction studies and is due to the fact that the stability of the cation-crown ether complex depends mainly on the ratio of the ionic size of the cation to the cavity size of the crown ether(42). From Table 2, one might predict K^+ will fit snugly into the DCHC-6 ring. Cations both larger (Rb^+ and Cs^+) or smaller (Na^+ and Li^+) than the optimum size form less stable complexes since in the former case the cation is too large to fit into the cavity, while in the latter the ring is too large to allow the cation to be simultaneously close to all the

Figure 12

Plots of $D[1 + K_4C_T/(1 + K_{1ex}\ w/v)]$ vs initial concentration of picric acid for the distribution of alkali metal cations between polyether foam and aqueous solutions.

Initial solution conditons:

[Cation]	1×10^{-4} M
[DCHC-6]	4×10^{-3} M
Solution volume	40 mL
Foam weight	0.20 ± 0.01 g
Temperature	25.00 ± 0.05°C

Notes:

Na^+ (▲)
K^+ (■)
Rb^+ (●)
Cs^+ (◆)

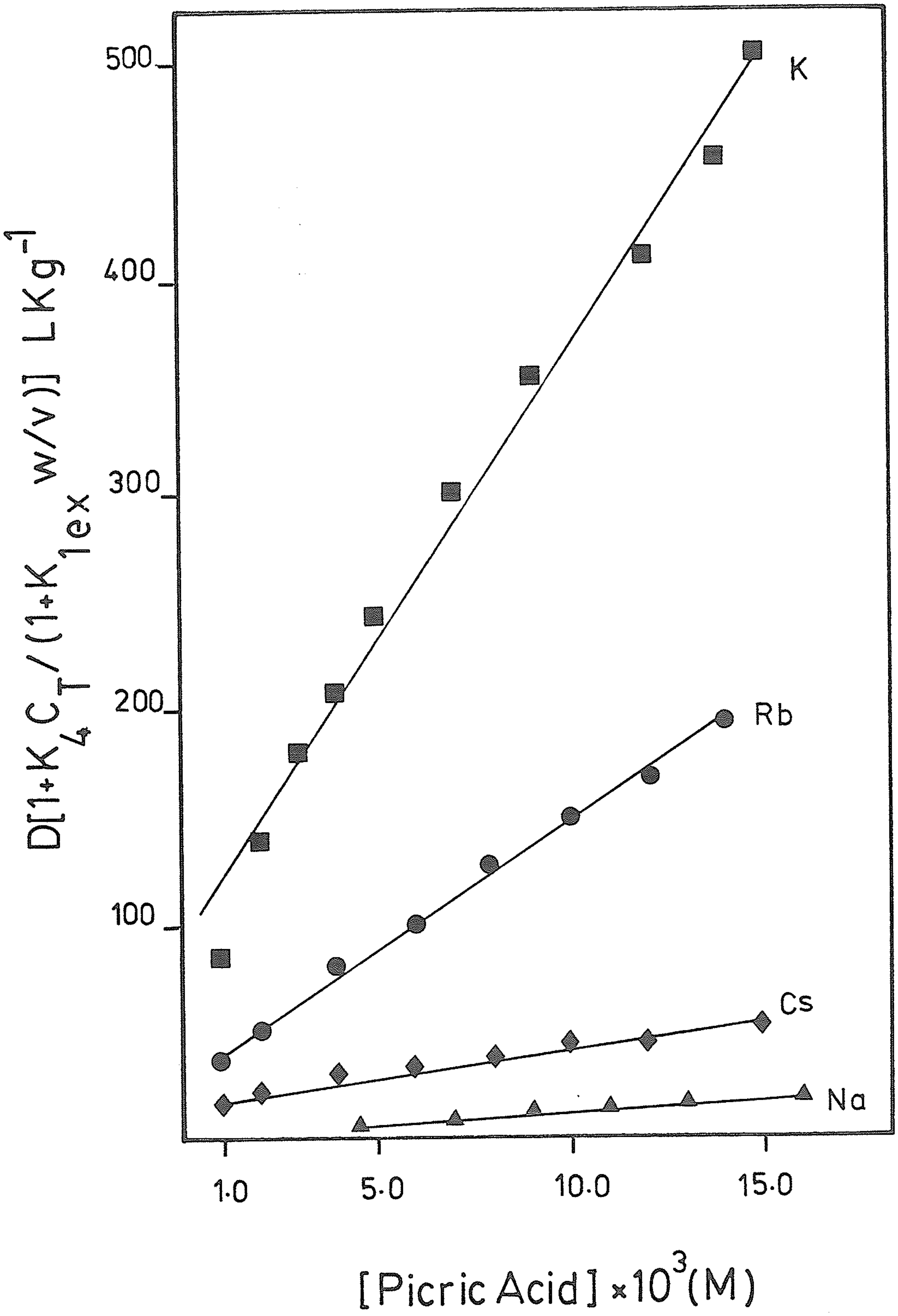

500
400
300
200
100
1.0
5.0
10.0
15.0
K
Rb
Cs
Na
$D[1+K_4C_T/(1+K_{1ex}w/v)]$ L Kg^{-1}
[Picric Acid] ×10^3(M)

Figure 13

Plots of $D[1 + K_4C_T/(1 + K_{1ex}\,w/v)]$ vs initial concentration of crown ether for the extraction of alkali metal picrates.

Initial solution conditions:

[Cation]	1×10^{-4} M
[Picric acid]	4×10^{-3} M
Solution volume	40 mL
Foam weight	0.20 ± 0.01 g
Temperature	25.00 ± 0.05°C

Notes:

Na^+	(▲)
K^+	(■)
Rb^+	(●)
Cs^+	(◆)

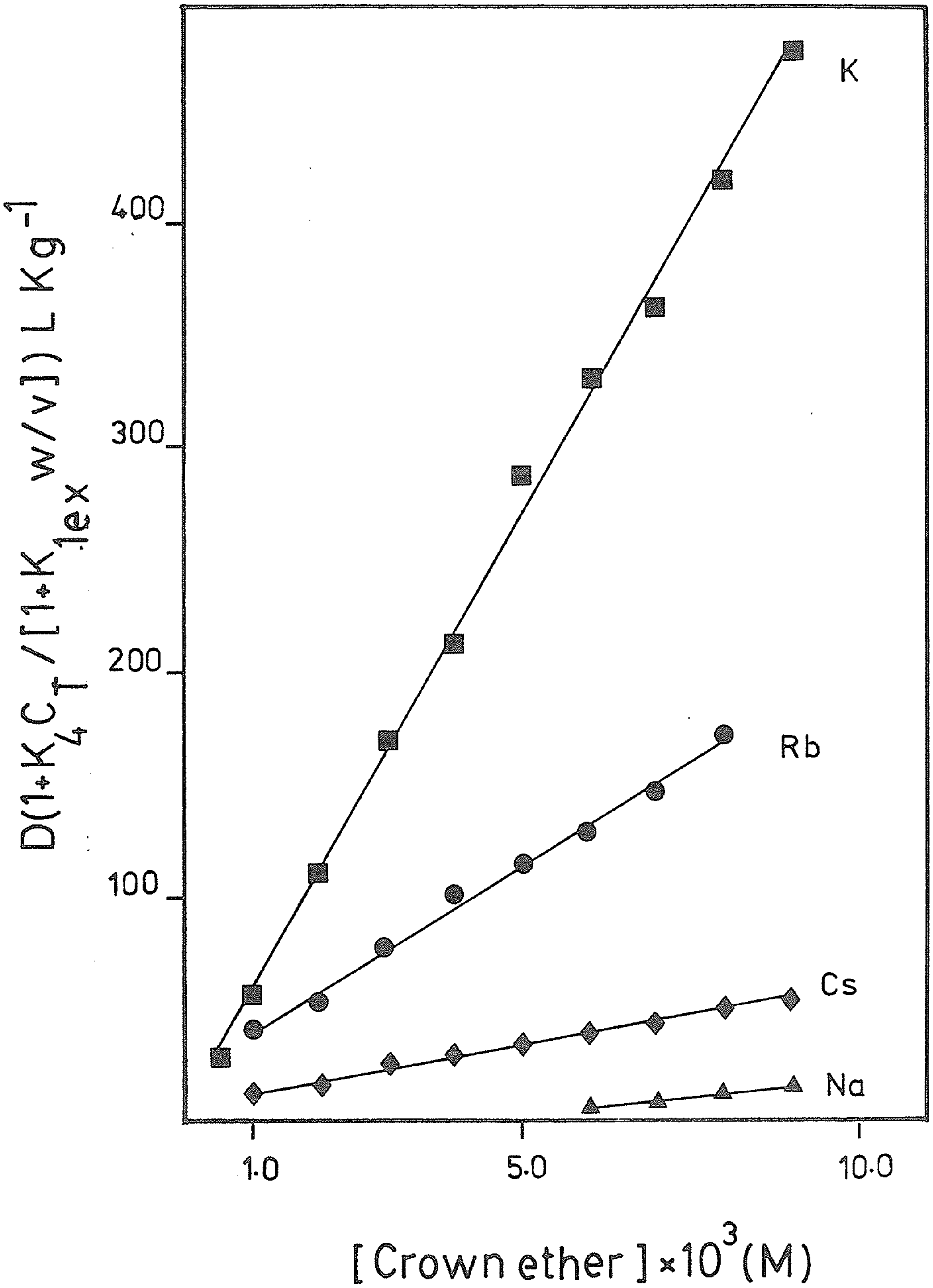

D(1+K4CT/[1+K1ex w/v]) L Kg-1
100
200
300
400
1.0
5.0
10.0
[Crown ether] ×10^3 (M)
K
Rb
Cs
Na

TABLE 3 THE EQUILIBRIUM CONSTANTS, K, FOR ALKALI METAL ION-CROWN ETHER-PICRATE ION-PAIR EXTRACTION INTO POLYURETHANE FOAM.

Cation	$\frac{K_4}{\mathrm{L\ mol^{-1}}}$[+]	$\frac{K_5}{\mathrm{L\ mol^{-1}}}$[‡]	$\frac{K_{5ex}}{\mathrm{L\ Kg^{-1}}}$	$\frac{K_{4d}}{\mathrm{mol\ Kg^{-1}}}$[*]	$\frac{K_{5d}}{\mathrm{mol\ Kg^{-1}}}$[*]	$\frac{K_{ex}}{\mathrm{L^3 mol^{-2}\ Kg^{-1}}}$
Na^+	25	0.77	1.6×10^4	3.6×10^{-2}	0.25	3.1×10^5
K^+	63	0.85	1.58×10^5	4.2×10^{-3}	0.11	8.5×10^6
Rb^+	8	0.88	5.37×10^5	4.7×10^{-2}	0.064	3.8×10^6
Cs^+	8	0.94	1.06×10^5	.05	0.11	8.0×10^5

[+] Reference 46

[‡] Estimated by Fuoss method.

oxygens. Thus, a weaker complexation of Li^+, Na^+, Rb^+ and Cs^+ with DCHC-6 results in poor extraction of these cations compared to that of K^+, which forms the most stable complex with DCHC-6 (Table 3).

II. Extraction of Alkali Metal Cations by Polyester-Based Polyurethane Foam

It has been reported by several authors that an increase in the polarity of the organic phase results usually in an increase in alkali metal picrate extraction using 18-crown-6(49,51). Experimental values for the dielectric constant of polyether and polyester type foams used in the present study are unfortunately not available. However, it is generally accepted that esters are more polar than ethers and so the use of polyester foam was initiated in the hope of improving the degree of extraction. Since initial experiments showed that in the presence of DCHC-6, polyester is a better extractor than polyether foam for alkali metal picrates, the effects of various variables were studied using the polyester system in order to optimize the extraction conditions.

1. Effect of Metal Concentration on the Extraction of Alkali Metals by Polyester Foam

The possible formation of polynuclear species was examined by studying the extraction of potassium by polyester foam as a function of crown ether for three different concentrations of potassium. The results of this study are shown in Figure 14. Plots of log D as a function of log of initial crown ether concentration for three different concentrations of potassium are coincident indicating that the extraction, similar to that of the polyether system, is independent of metal concentration. This observation rules out the possibility of extracting any polynuclear species.

Figure 14

Distribution ratio as a function of initial concentration of DCHC-6 at different concentrations of potassium.

Initial solution conditions:

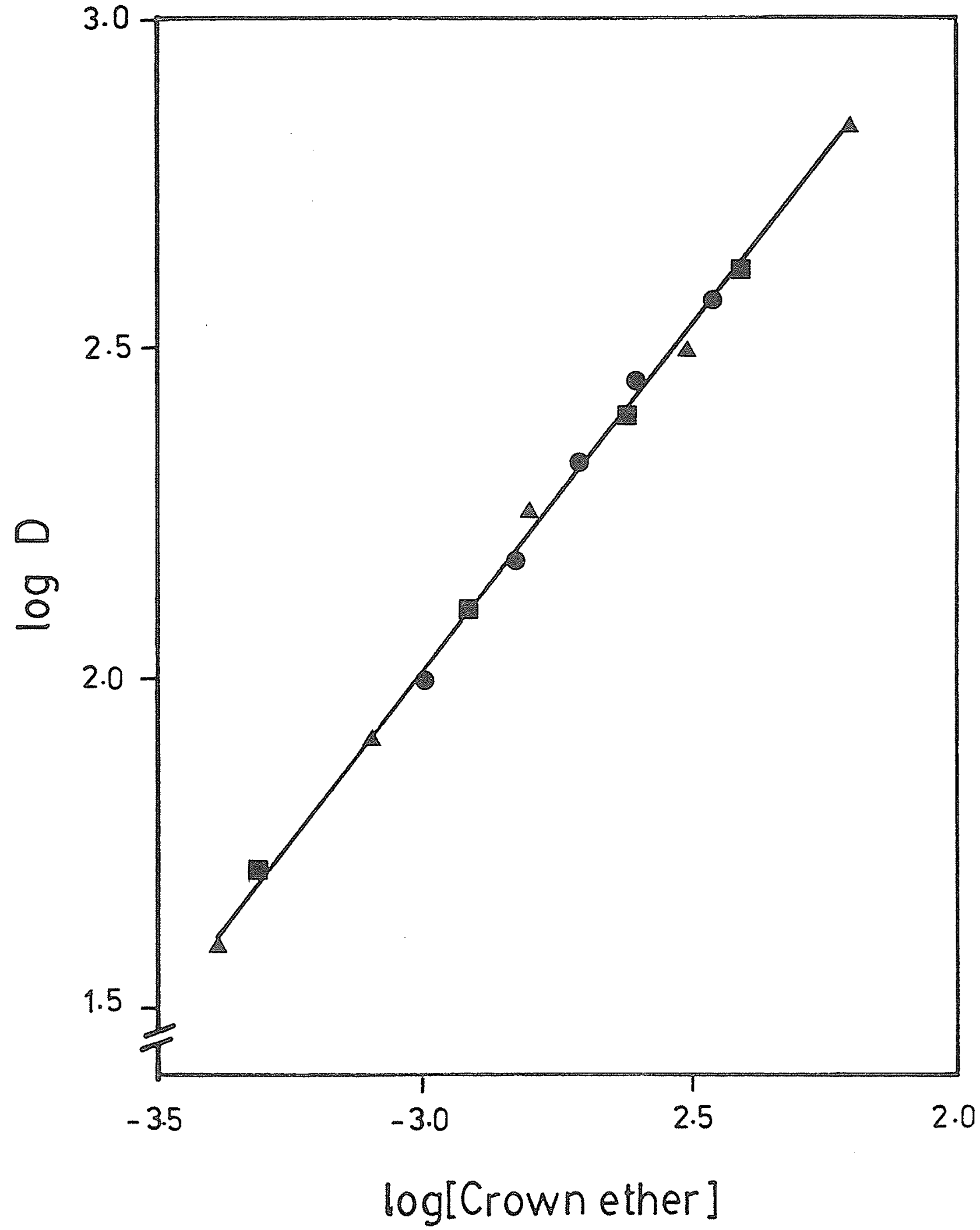
[Picric acid]	4×10^{-3} M
Solution volume	40 mL
Foam weight	0.20 ± 0.01 g
Temperature	25.00 ± 0.05°C

Notes:

(▲) 0.25×10^{-4} M K^+

(■) 1×10^{-4} M K^+

(●) 2×10^{-4} M K^+


3.0
2.5
2.0
1.5
log D
-3.5
-3.0
2.5
2.0
log[Crown ether]

2. Effect of Crown Ether Concentration on the Extraction of Alkali Metals by Polyester Foam

Foam cubes each weighing 0.20 ± 0.01 g were squeezed for six hours in solutions (40 mL) containing an initially constant amount of metal cations (1×10^{-4} M), picric acid (4×10^{-3} M) and various amounts of DCHC-6 ranging from 0.5×10^{-3} M to 9×10^{-3} M. Samples were taken after six hours and analyzed by flame photometry or by atomic absorption spectrophotometry. The results of such studies for Na^+, K^+, Rb^+ and Cs^+ are shown in Figure 15, where the distribution coefficient is plotted as a function of crown ether concentration. It is evident from these results that the extraction of all cations increases with increasing crown ether concentration. Comparing these results with those of the polyether system (Figure 10), it is clear that the sequence of extraction of alkali metal picrates using DCHC-6 is the same for both polyether and polyester type foams but there is a marked difference in the magnitude of the extraction. As mentioned earlier for the polyether system, the order of extraction can be attributed to the ability of DCHC-6 to complex these cations, whereas the higher magnitude of extraction is most likely due to the greater polarity of polyester foam, consistent with the work of others. A. Sadakane _et al_(51) have reported a higher extraction of potassium picrate using dibenzo 18-crown-6 in polar solvents (e.g. isobutyl methyl ketone and nitro benzene) than in benzene. Frensdorff(49) has also reported that methylene chloride ($K_{ex} = 10^{5.65}$) is a better solvent than is benzene ($K_{ex} = 10^{4.65}$) for the extraction of potassium picrate using dibenzo 18-crown-6. On the basis of these observations, it is reasonable to conclude that the extraction of alkali metal picrates using DCHC-6 is

Figure 15

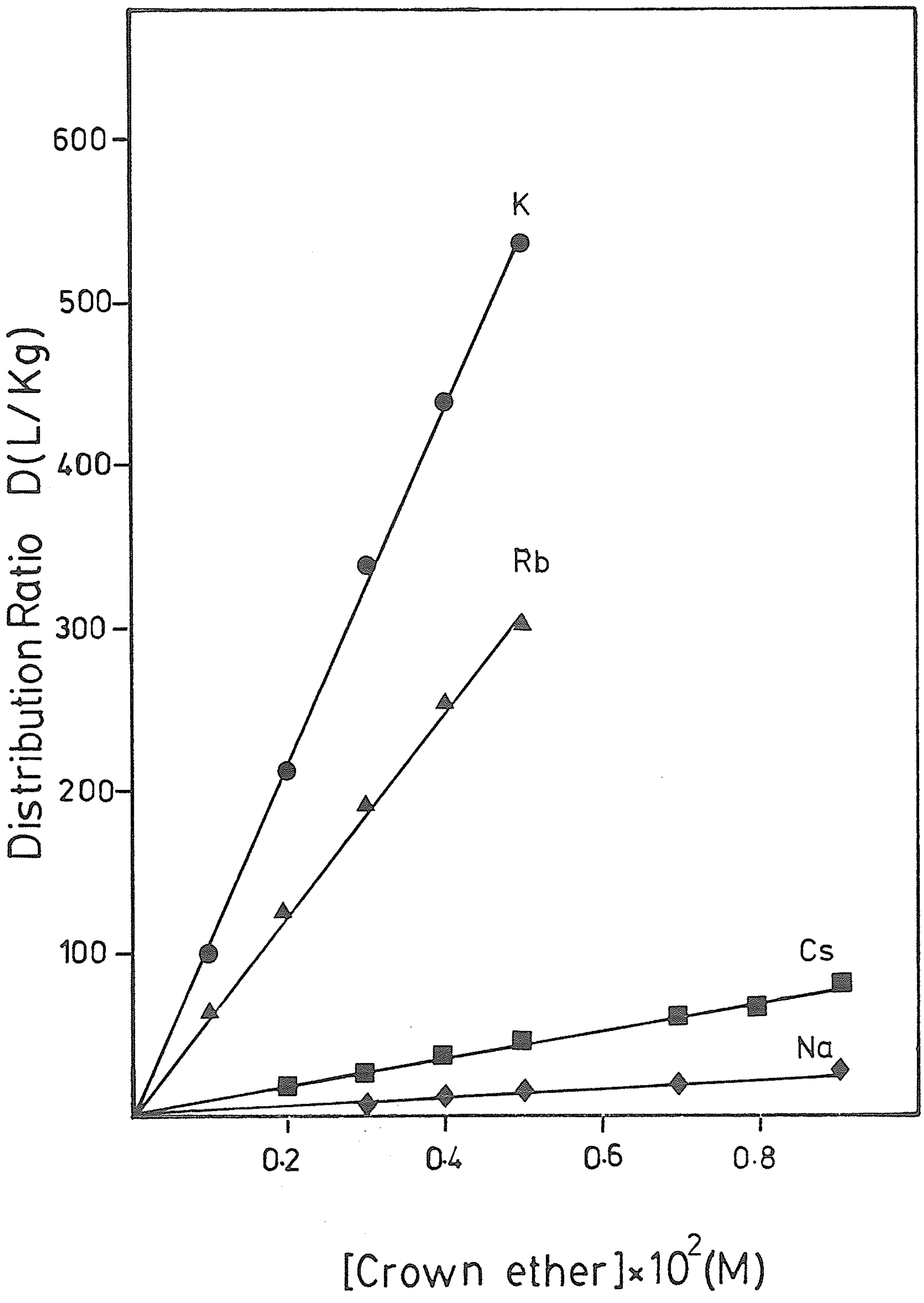
Distribution of alkali metal picrates between polyester foam and aqueous solutions as a function of initial concentration of DCHC-6

Initial solution conditions:

[Cation]	1×10^{-4} M
[Picric acid]	4×10^{-3} M
Solution volume	40 mL
Foam weight	0.20 ± 0.01 g
Temperature	25.00 ± 0.05°C

Notes:

Na^+ (◆)
K^+ (●)
Rb^+ (▲)
Cs^+ (■)


600
500
400
300
200
100
Distribution Ratio D(L/Kg)
K
Rb
Cs
Na
0·2
0·4
0·6
0·8
[Crown ether]×10²(M)

governed not only by the strength of complexation between metal ion and crown ether but also by the solubility of the resulting complex in the organic phase.

It is important to note that the extraction behaviour of alkali metal picrates by polyester foam (Figure 15) differs from that of polyether (Figure 10) not only in magnitude but also in the respect that potassium extraction increases linearly even at higher concentrations of crown ether in the former case. Furthermore, the plots of log D vs log [Cr] (Figure 16) for the extraction of all cations by polyester give straight lines with slope of nearly one suggesting a 1:1 stoichiometry of the extracting complex between crown ether and cation. On the other hand, the similar plots for the polyether system (Figure 11) yield a smaller slope. Unit slope has been reported by several authors for the extraction of monovalent cations into various organic solvents using 18-crown-6 and its derivatives(51,52,53,59) Takeda et al(52,53) have studied the extraction of several monovalent metal picrates by 15-crown-5 and 18-crown-6 into benzene, and on the basis of slope analysis have concluded that both crown ethers form 1:1 complexes with all metal cations studied.

Figure 16

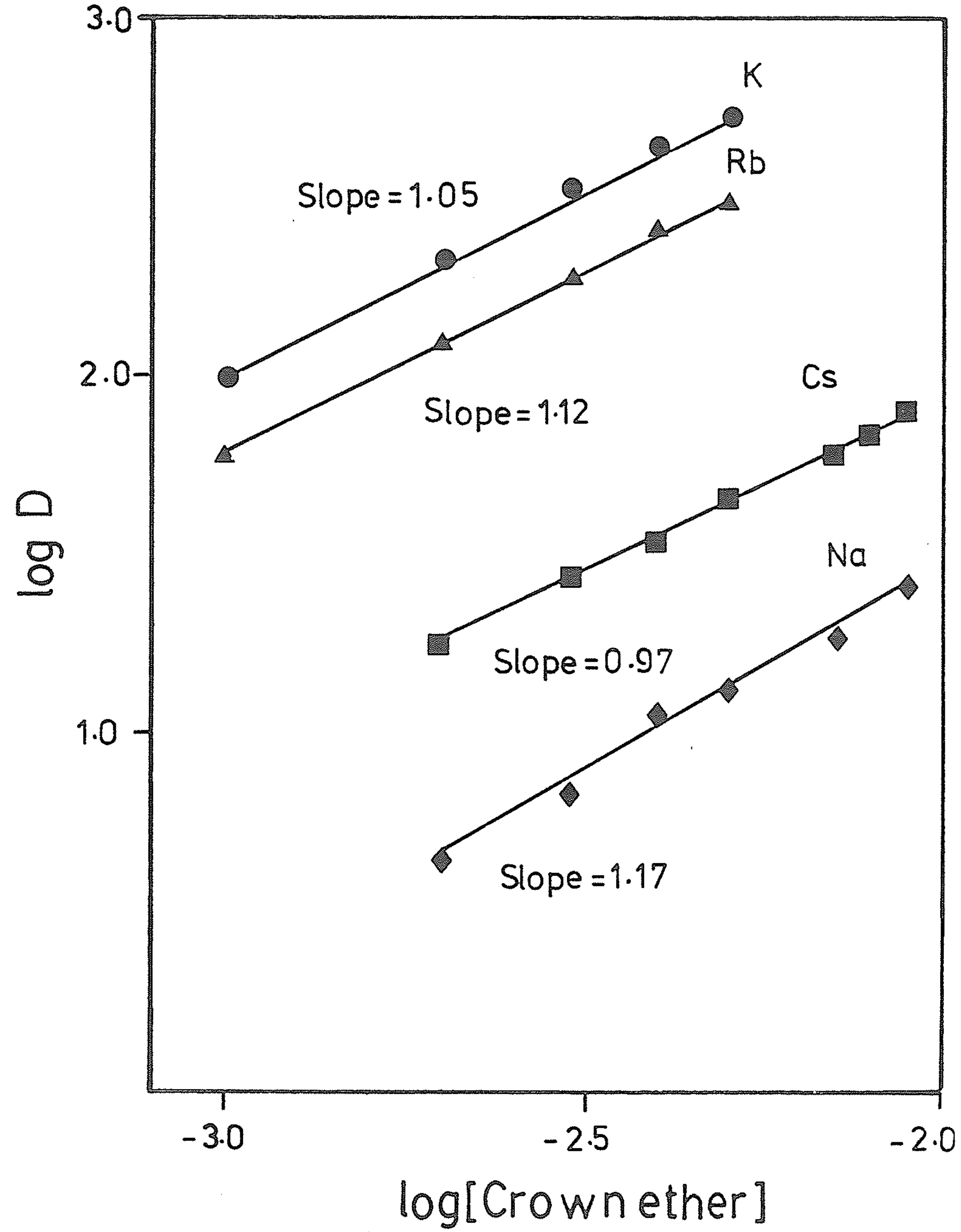
Plots of log D vs log [crown ether] for the distribution of alkali metal picrates between polyester-foam and aqueous solutions.

Initial solution conditions:

[Cations]	1 x 10^{-4} M
[Picric acid]	4 x 10^{-3} M
Solution volume	40 mL
Foam weight	0.20 ± 0.01 g
Temperature	25.00 ± 0.05°C

Notes:

- Na^+ (◆)
- K^+ (●)
- Rb^+ (▲)
- Cs^+ (■)


3.0
2.0
1.0
log D
-3.0
-2.5
-2.0
log[Crown ether]
K
Rb
Cs
Na
Slope = 1.05
Slope = 1.12
Slope = 0.97
Slope = 1.17

3. Variation of Distribution Ratio with Anion Type and Concentration

To establish the effect of anion concentration, small cubes of polyester foam weighing 0.20 ± 0.01 g were squeezed for six hours in a series of solutions (40 mL), 1×10^{-4} M in potassium and 4×10^{-3} M in DCHC-6, and containing various concentrations of picric acid. Samples were then removed and analyzed for potassium by flame photometry. The results are shown in Figure 17. As can be seen, except for the magnitude of extraction, the shape of the plot of percentage extraction vs initial concentration of picric acid for polyester foam is similar to that of polyether (i.e. the percentage of extraction increases sharply with increasing picric acid concentration and starts to level off at higher concentrations of picric acid). On the other hand, a plot of log D vs log A (Figure 18) results in a straight line with a slope of unity suggesting a stoichiometry of 1:1 between cation-crown ether complex and picrate.

It is well established that electrostatic interaction depends on the properties of the anion; its charge, its size, its polarizability and hydrophobicity in addition to several other factors. Thus, experiments were carried out to study the effect of anion size on the extraction of potassium. A series of solutions (40 mL) containing various concentrations of ANS, 4×10^{-3} M in DCHC-6 and 1×10^{-4} M in potassium were equilibrated for six hours with polyether foam cubes, each weighing 0.20 ± 0.01 g. The results are shown in Figure 19, along with those of a similar study with

Figure 17

Effect of varying initial concentration of picric acid on the distribution of potassium between polyester foam and aqueous solution.

Initial solution conditions:

[Potassium]	1×10^{-4} M
[DCHC-6]	4×10^{-3} M
Solution volume	40 mL
Foam weight	0.20 ± 0.01 g
Temperature	25.00 ± 0.05°C

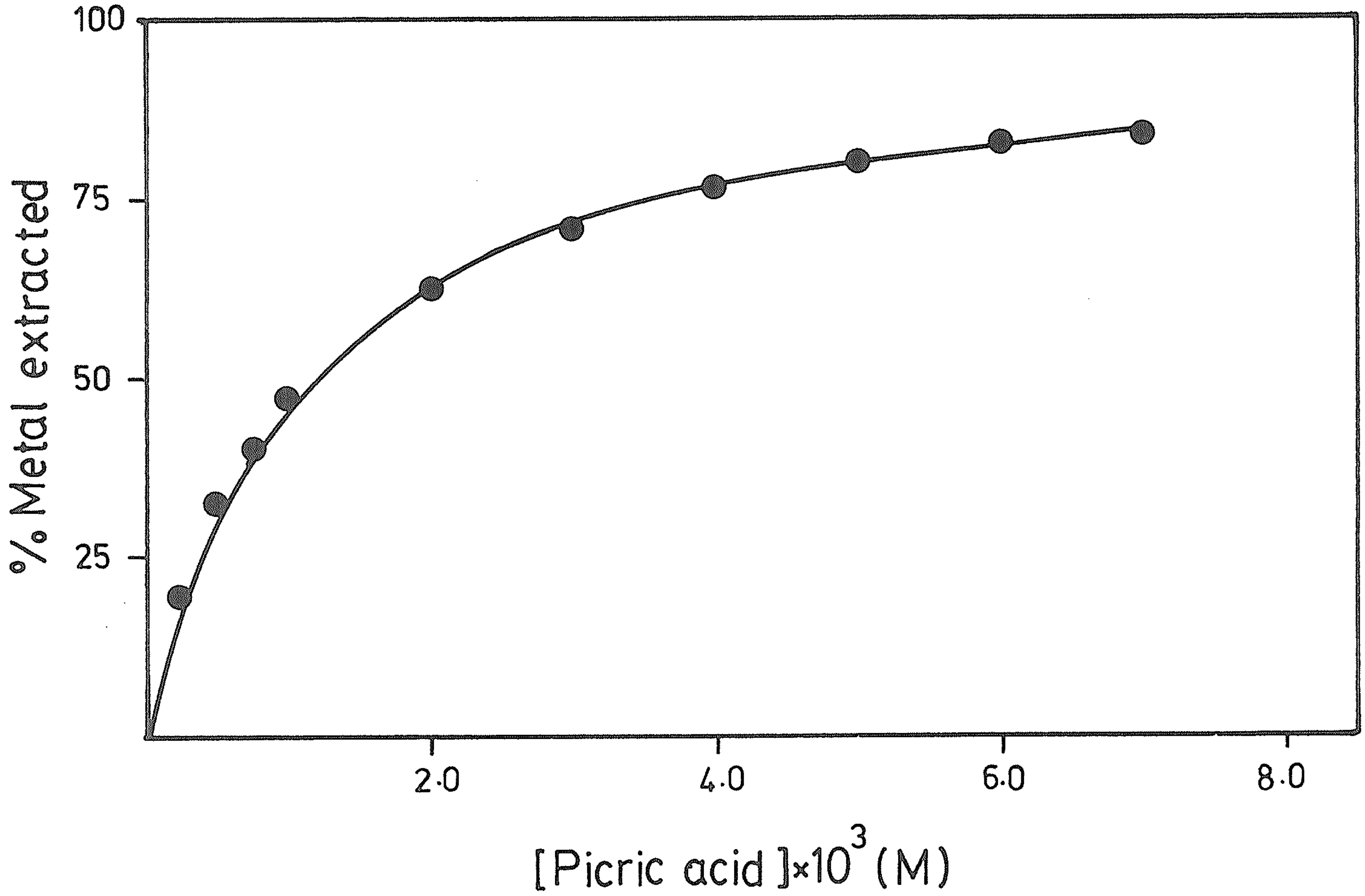
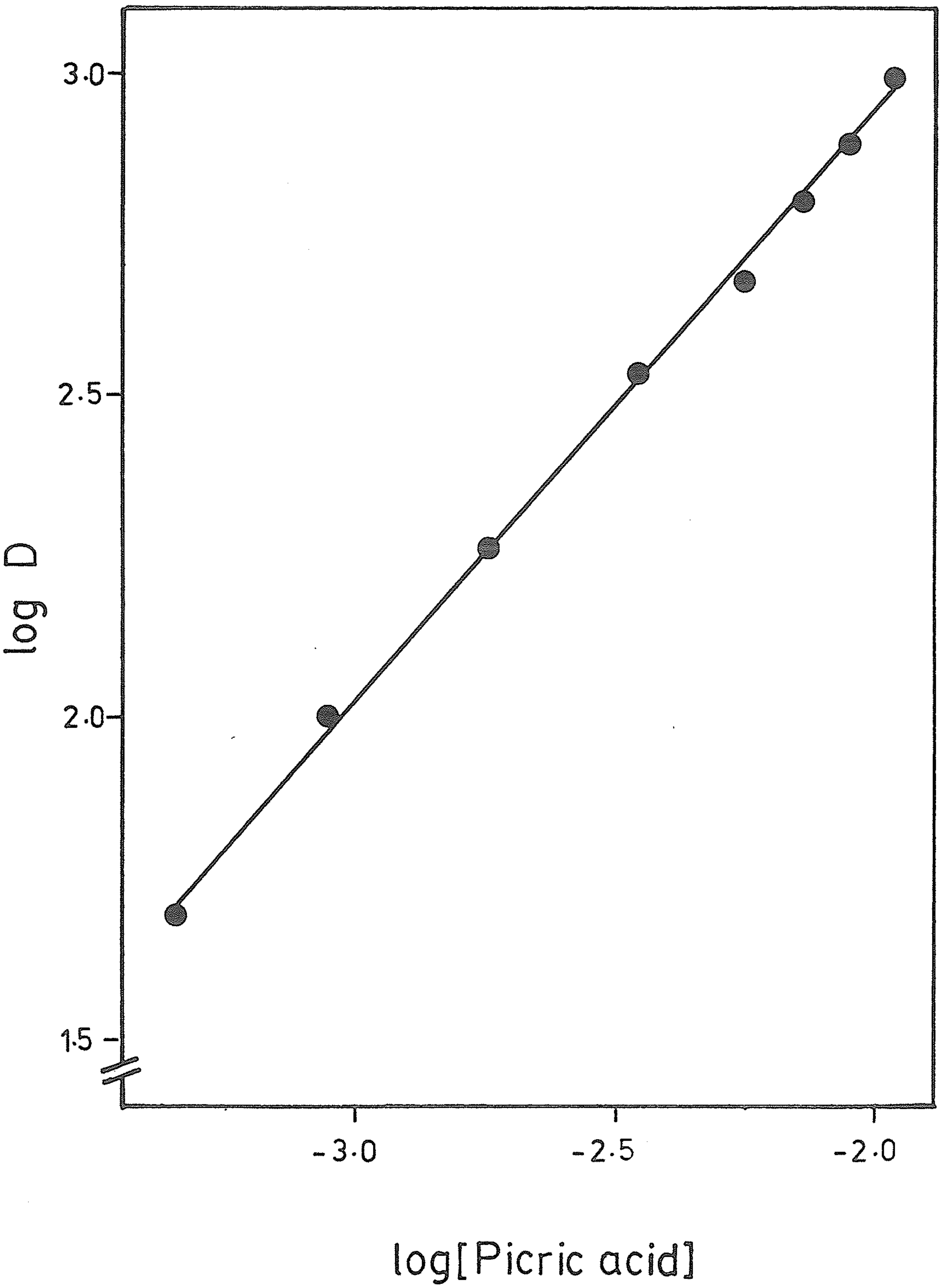

100
75
50
25
% Metal extracted
2·0
4·0
6·0
8·0
[Picric acid]×10^3 (M)

Figure 18

Plot of log D vs log picric acid concentration for the distribution of potassium between polyester foam and aqueous solution.

Initial solution condition:

[Potassium]	1×10^{-4} M
[DCHC-6]	4×10^{-3} M
Solution volume	40 mL
Foam weight	0.2 ± 0.01 g
Temperature	25.00 ± 0.05°C


3.0
2.5
2.0
1.5
log D
-3.0
-2.5
-2.0
log[Picric acid]

picrate anion included for comparison. It can be seen by this that extraction of potassium is greatly enhanced in the presence of a bulkier anion. It has been reported by others that the counter anion influences the strength of the metal-crown ether interaction in solution. For example, the stability of the 1:1 complex of Na^+ with benzo 15-crown-5 in methanol decreases as the counter anion is changed from picrate (log K = 5.49) to dinitrophenol (log K = 4.36) to orthonitrophenol (log K = 3.52)(60). However, it is most unlikely that replacement of picrate with ANS in water, a highly solvating media, can influence the formation of the metal-crown complex to such an extent. On the other hand, higher extraction of potassium in the presence of ANS, a bulky anion, can well be attributed to the fact that large anions having low charge density and, therefore, low free hydration energy, are better extracted in polyurethane foam (i.e. into a phase of low dielectric constant) thus favouring the greater solubilization of potassium into the foam as well. Whether or not the nature of anion has any significant influence on the formation of the metal-crown ether complex in an aqueous system is admittedly difficult to conclude from the data in hand. However, it is evident that the nature of the anion plays an important role in the extraction of the metal-crown ether complex. The importance of anions in the extraction of alkali metals by crown ethers into organic solvents has also been noticed by Pedersen(42) who stated that extraction is efficient only in the presence of soft anions such as iodide, thiocyanate, picrate etc.

Figure 19

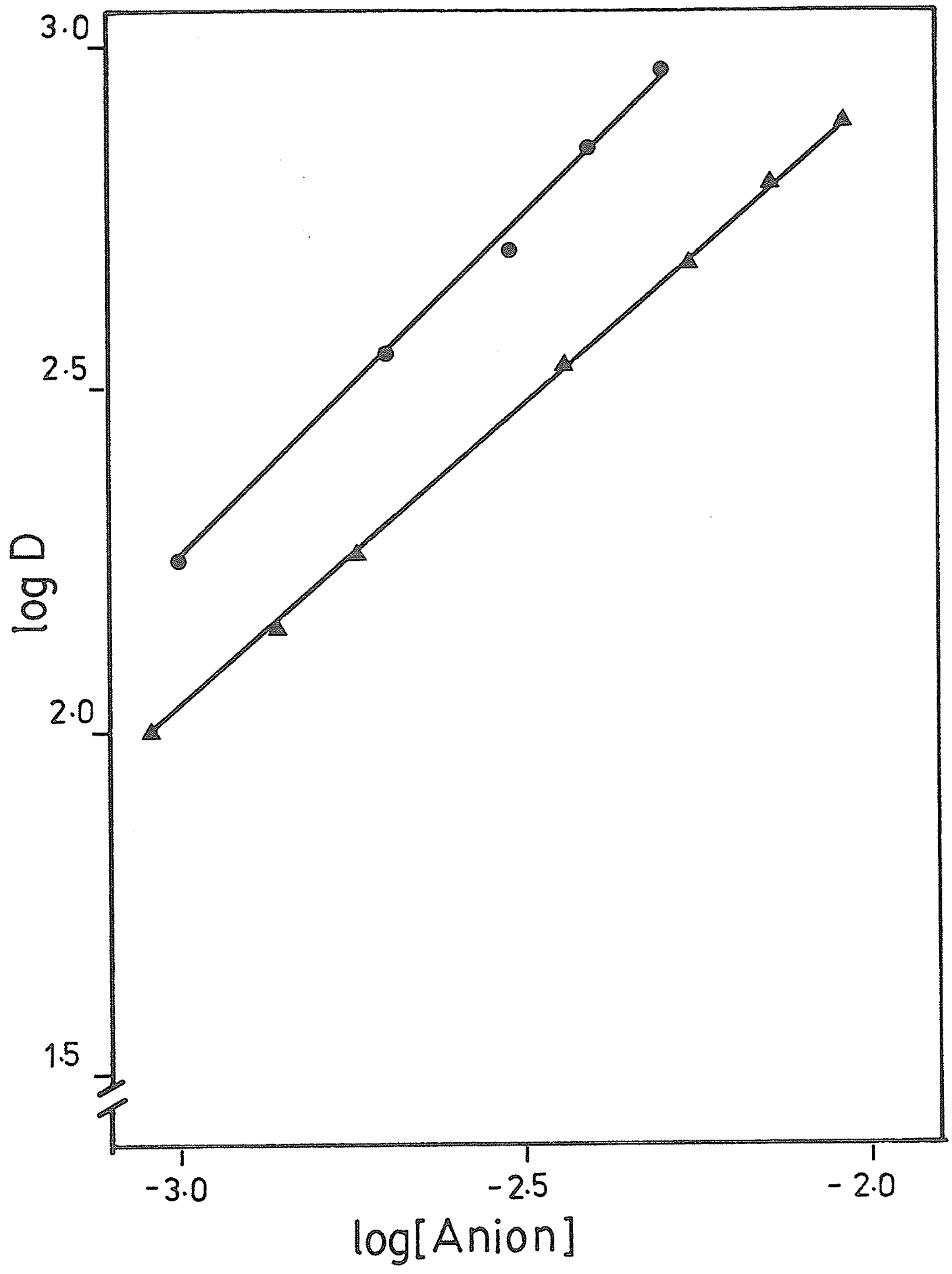
Plots of log D vs log of initial concentrations of anion for the extraction of potassium by polyester foam from aqueous solutions.

Initial solution conditions:

[Potassium]	1×10^{-4} M
[Picric acid]	4×10^{-3} M
Solution volume	40 mL
Foam weight	0.20 ± 0.01 g
Temperature	25.00 ± 0.05°C

Notes:

ANS (●)
Picric acid (▲)


3·0
2·5
2·0
1·5
log D
-3·0
-2·5
- 2·0
log[Anion]

4. Studies Under Varied Initial Concentrations of Crown Ether and Picric Acid

Experiments were carried out under varied crown ether and picrate concentrations in order to confirm the validity of 1:1 stoichiometry of complex formation between crown ether and metal cation over a wide range of picrate (anion) concentrations. The extraction of potassium by DCHC-6 into polyester-based polyurethane foam was studied under three sets of experimental conditions differing in the initial concentration of picric acid. The results are shown in Figure 20, where the log of the distribution coefficient is plotted against initial crown ether concentration. It is obvious from the figure that the extraction increases with an increase in crown ether as well as picrate concentrations. However, the feature of prime importance in Figure 20 is that all plots are straight lines with a slope of nearly unity further demonstrating that a 1:1 complex of crown ether and potassium is formed regardless of the initial concentrations of crown ether and of anion. Similar stoichiometry has been claimed previously for extracting species involved in the extraction of alkali metal picrates using 18-crown-6 and its derivatives into various organic solvents(52). Although the formation of L_2M and L_3M_2 has been reported in the excess of crown ether(41,42), the data of these experiments verify that the stoichiometry of the extracting species is indeed 1:1 in crown ether and cation here.

Figure 20

Extraction of potassium as a function of initial concentration of crown ether at different initial concentrations of picric acid.

Initial solution conditions:

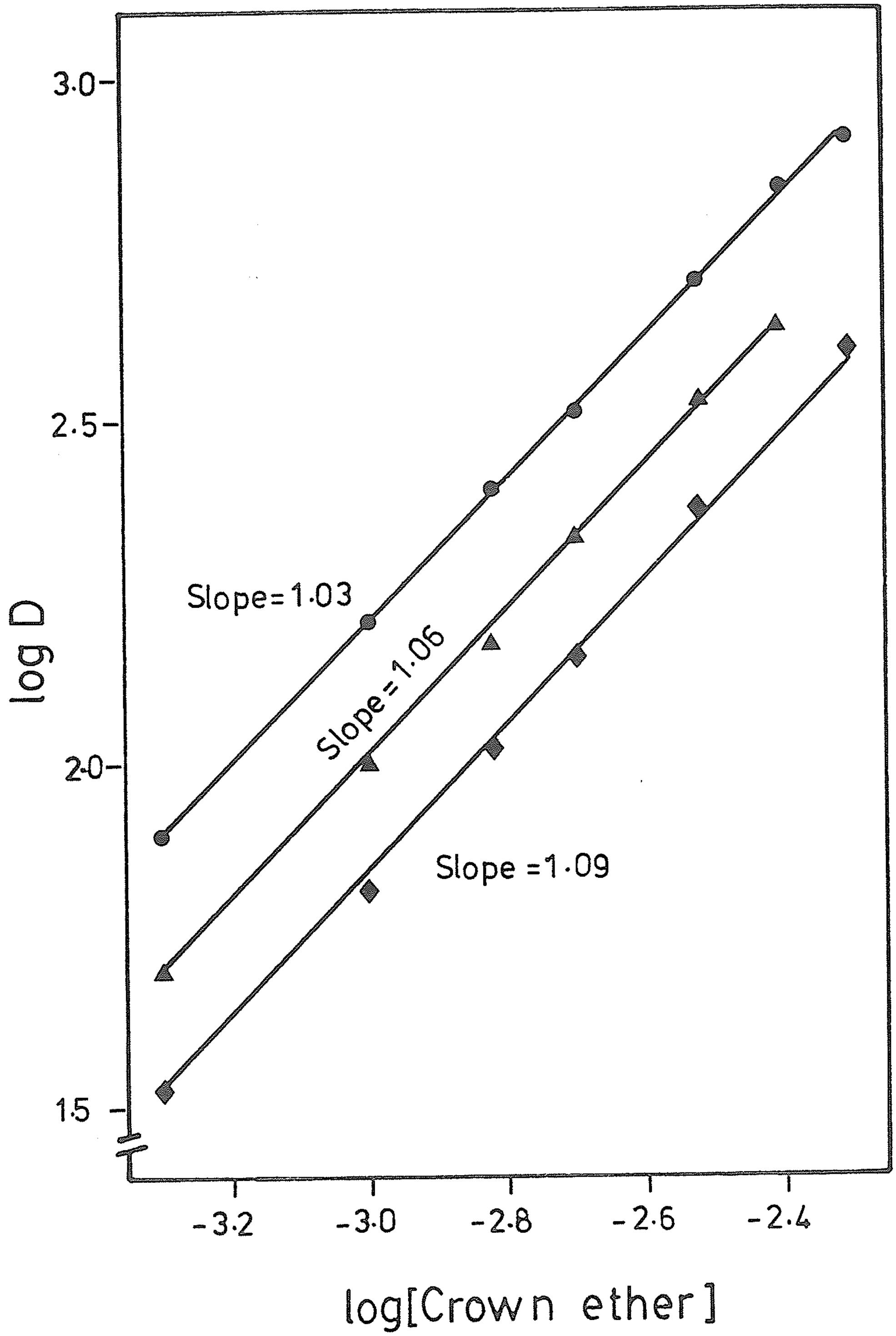
[Potassium]	1×10^{-4} M
Solution volume	40 mL
Foam weight	0.20 ± 0.01 g
Temperature	25.00 ± 0.05°C

Notes:

(◆) 2×10^{-3} M picric acid

(▲) 4×10^{-3} M picric acid

(●) 8×10^{-3} M picric acid


3.0
2.5
2.0
1.5
log D
Slope=1.03
Slope=1.06
Slope =1.09
-3.2
-3.0
-2.8
-2.6
-2.4
log[Crown ether]

5. Extraction of Monovalent Cations Other Than Alkali Metals

Since the complexing ability of DCHC-6 is not limited to the alkali metals, the use of polyester foam has also been extended to the extraction of silver and thallium-crown ether complexes. The results of preliminary experiments have demonstrated the ability of polyester foam to extract Ag^+ and $T\ell^+$ picrates by DCHC-6. The extraction of Ag^+ and $T\ell^+$ has been studied more thoroughly under varied crown ether concentrations in order to establish the stoichiometry of the complex formed between crown ether and cation. Figure 21, in which log D is plotted against initial concentration of crown ether, presents the results of these experiments. Here, the extraction of cation (Ag^+ or $T\ell^+$) was studied by equilibrating foam cubes (0.20 ± 0.01 g) for six hours with a 40 mL volume of solutions initially containing a constant amount of metal cation (0.5×10^{-4}) and picric acid (4×10^{-3} M) with various amounts of DCHC-6. Samples were taken after six hours and analyzed by atomic absorption spectrometry. The log D vs log [C] plot in Figure 21 shows a linear relationship with a slope of nearly unity for both cations indicating that DCHC-6 forms a 1:1 complex with both Ag^+ and $T\ell^+$.

Figure 21

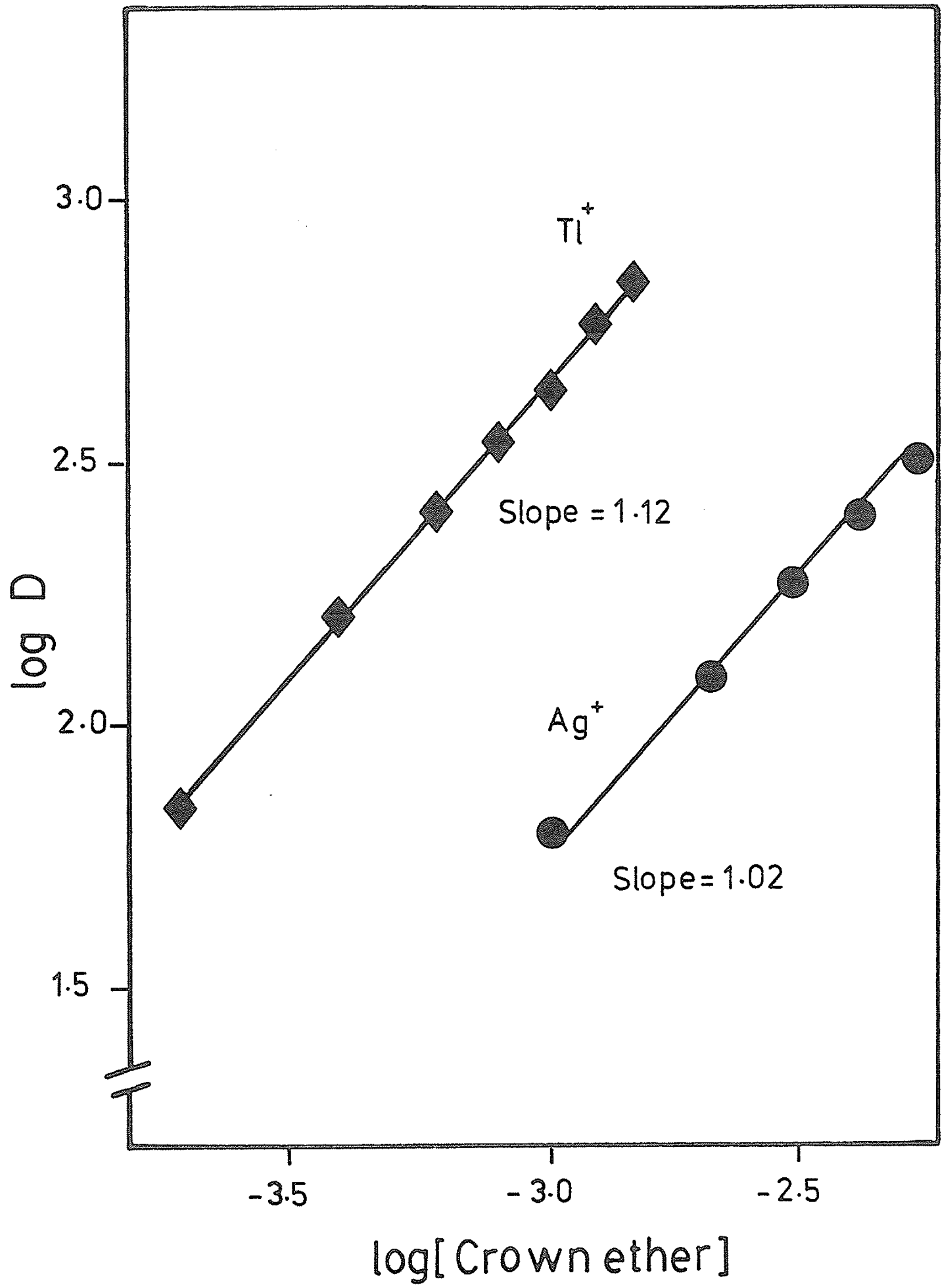
Plots of log D vs log of initial crown ether concentration for the distribution of Ag^+ and Tl^+ between polyester foam and aqueous solution.

Initial solution conditions:

[Cation]	5×10^{-5} M
[Picric acid]	4×10^{-3} M
Solution volume	40 mL
Foam weight	0.20 ± 0.01 g

Notes:

Ag^+ (●)
Tl^+ (◆)


3·0
2·5
2·0
1·5
log D
Tl$^+$
Slope = 1·12
Ag$^+$
Slope = 1·02
-3.5
- 3.0
- 2.5
log[Crown ether]

6. Effect of Foam Type and Comparison with Solvent Extraction

As has been mentioned earlier, the objective of this study was not only to explore the use of polyurethane foam for the extraction of several species but also to compare the results of "Foam Extraction" with those of "Solvent Extraction". It is obvious from the results of the present study that polyester foam behaves exactly like an organic solvent for the extraction of alkali metal picrates in the presence of DCHC-6, whereas polyether foam acts quite differently. In order to examine the differences in the extraction behaviour of polyurethane foams, the extraction of potassium by polyether foam is plotted as a function of initial concentration of DCHC-6 in Figure 22 (curve a) along with the results of a similar study for polyester foam (curve b). The comparison of these curves indicates several differences in the extraction behaviour of polyether and polyester foams.

i. The most obvious difference between the extraction behaviour of polyether and polyester for the extraction of potassium is that curve b passes through the origin whereas curve a has a positive intercept.

ii. Another striking feature of Figure 22 is that curve a and curve b intersect each other indicating that although polyether is a poor extractor of potassium at higher concentrations of crown ether, it is certainly a better extractor in the presence of low concentrations of crown ether. Similar behaviour is also observed for the extraction of silver from the aqueous solution of DCHC-6 and picric acid by polyurethane foams (see Figure 23).

In the previous section, the dissociation of the extracting species

Figure 22

Comparison of potassium-picrate sorption as a function of DCHC-6 from aqueous solutions by polyether and polyester-based polyurethane foam.

Initial solution conditions:

[K^+]	1×10^{-4} M
[Picric acid]	4×10^{-3} M
Solution volume	40 mL
Temperature	25.00 ± 0.05°C
Foam weight	0.20 ± 0.01 g

Notes:

Polyester foam(▲)
Polyether foam(●)

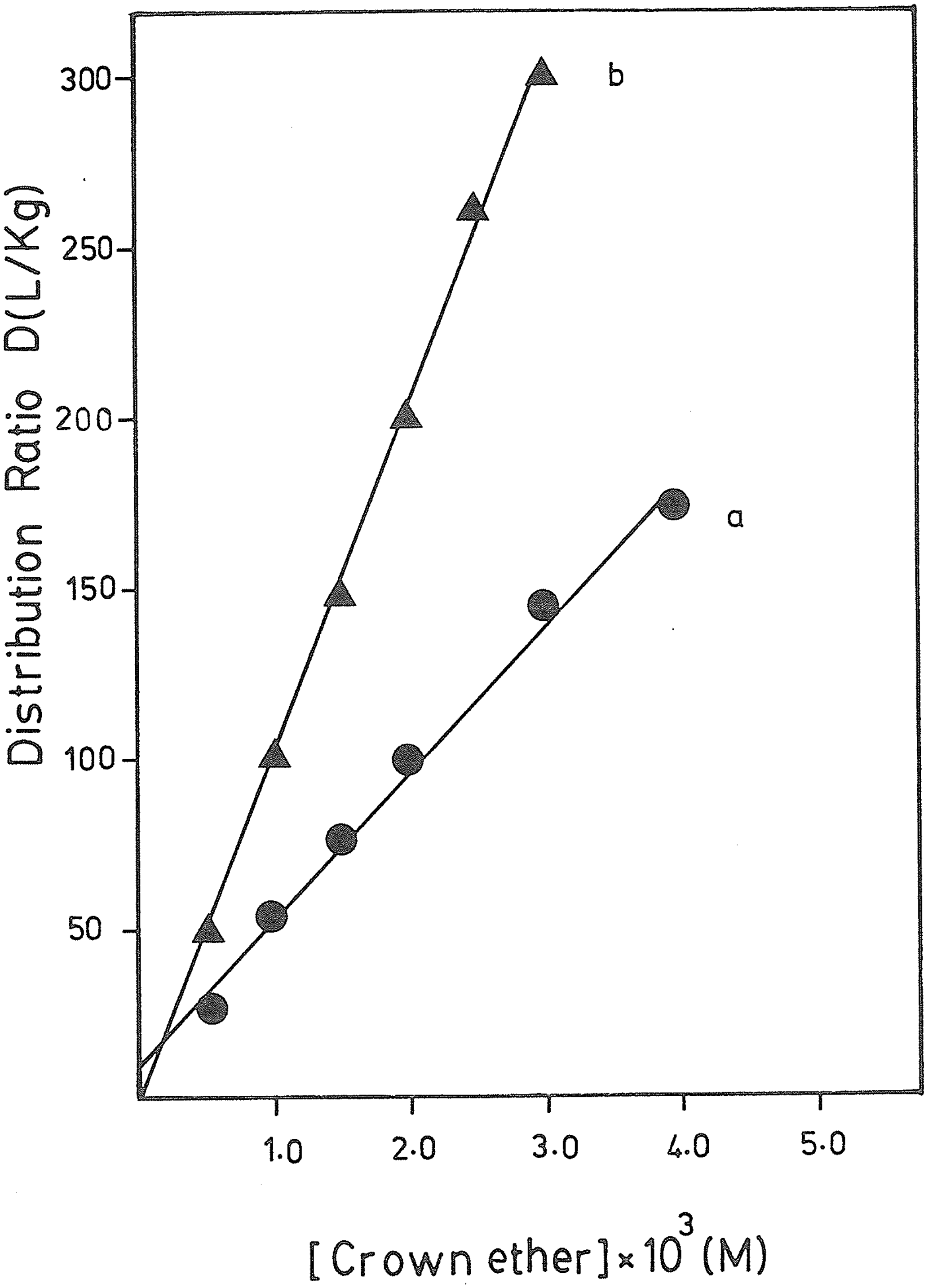

Distribution Ratio D(L/Kg)
300
250
200
150
100
50
1.0
2.0
3.0
4.0
5.0
[Crown ether] × 10^3 (M)
b
a

Figure 23

Comparison of silver-picrate sorption as a function of DCHC-6 from aqueous solutions by polyether and polyester-based polyurethane foam.

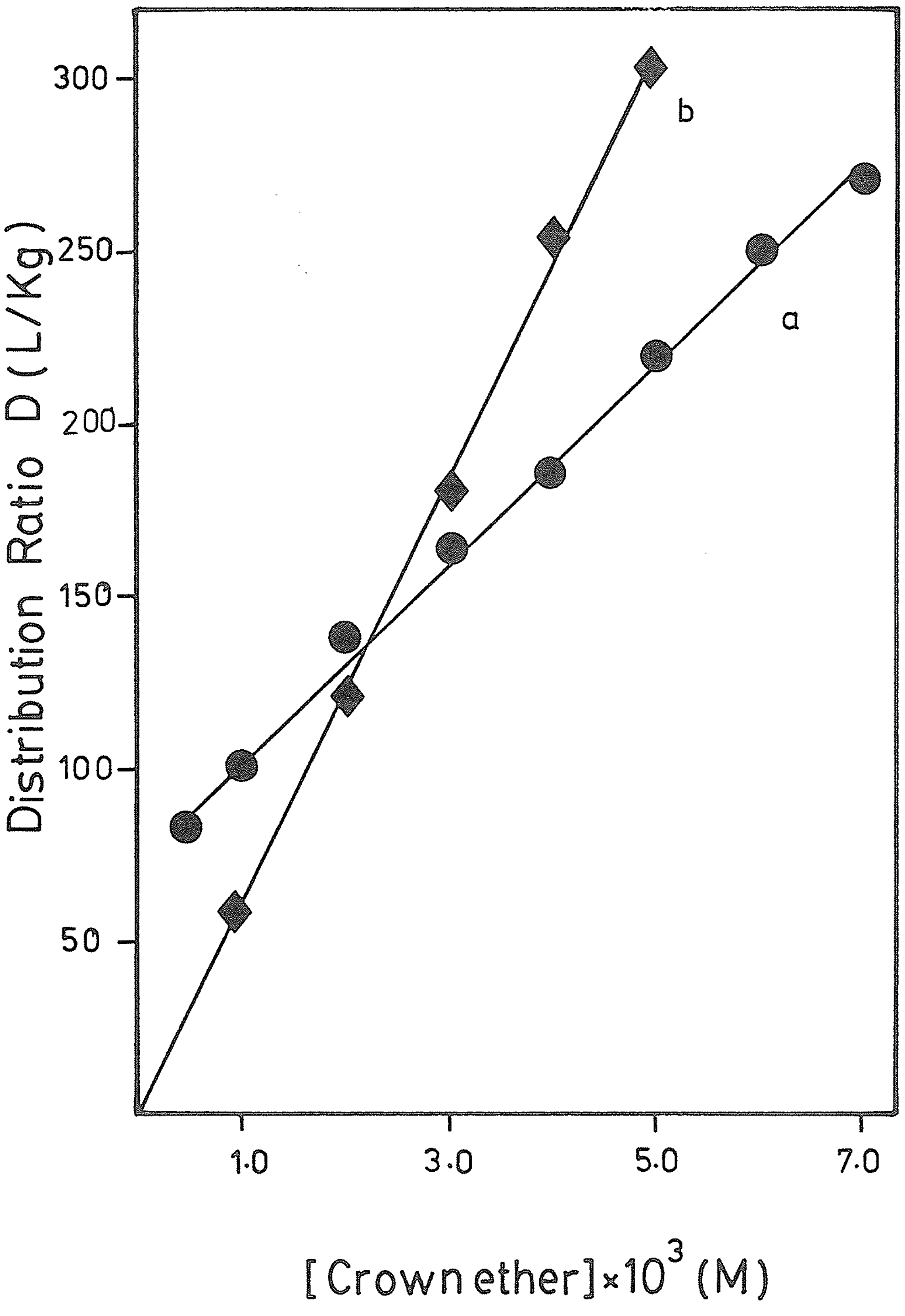
Initial solution cations:

[Ag^+]	5×10^{-5} M
[Picric acid]	4×10^{-3} M
Solution volume	40 mL
Temperature	25.00 ± 0.05°C
Foam weight	0.20 ± 0.01 g

Notes:

Polyester foam (◆)

Polyether foam (●)


Distribution Ratio D (L/Kg)
300
250
200
150
100
50
1.0
3.0
5.0
7.0
[Crownether] × 10^3 (M)
a
b

in the polyether foam has been regarded as the cause of a positive intercept for curve a. However, comparing the results of polyether with those of polyester (i.e. curve a with curve b) this explanation seems most unlikely since the extraction of potassium into a more polar phase, the polyester foam, has no intercept. If the intercept was due to the dissociation of extracting species in the polyether foam, one would have expected a large intercept for the polyester foam.

An alternative and more logical explanation for the intercept of curve a and which can also explain very well the intersection of the two extraction curves, is that two different species containing M^+ are probably extracted by polyether. One species may be predominant at a low concentration of crown ether while the other is most abundant at higher concentrations. On the other hand, polyester would apparently be extracting only one species over the entire range of crown ether concentration. The nature of the species involved in the polyester system has already been established and it is most likely that polyether foam is also extracting the same species (i.e. MCr^+A^-) at higher concentrations of crown ether. The positive value of intercepts for curve a (Figures 22 and 23) suggest that polyether is extracting a metal species which does not contain crown ether. The extraction of M^+ by polyether-based polyurethane foam in the presence of excess of a bulky anion can be justified by considering the sorption of the M^+A^- ion-pair (A^- = picrate or ANS). The extraction of alkali metal picrates into nitrobenzene has been reported by Iwachido et al(64). Their model involves the formation of ion-pairs in the aqueous phase with subsequent extraction. They have also reported the aqueous association constants of these ion-pairs which are given in Table 4.

We have neglected the formation and extraction of M^+Pic^- in the derivation of equation (53) since the alkali metal picrate solutions have been reported to be strong electrolytes in water$^{(65)}$. Furthermore, we have also observed no detectable extraction of potassium in the absence of crown ether by polyether foam. However, the results shown in Figure 22 and 23 strongly suggest that an equilibrium exists between an aqueous solution of monovalent metal cations, M^+, bulky anions, A^- (e.g. picrate) crown ether, Cr and polyether-based polyurethane foam involving the following equilibria.

i. Distribution of free crown ether between the foam and aqueous phases

$$\mathrm{Cr} \xrightleftharpoons{K_{1ex}} \mathrm{Cr}_f \qquad (15)$$

$$K_{1ex} = [\mathrm{Cr}]_f/[\mathrm{Cr}] \qquad (16)$$

ii. Distribution of picric acid between the two phases

$$\mathrm{HA} \xrightleftharpoons{K_{2ex}} \mathrm{HA}_f \qquad (17)$$

$$K_{2ex} = [\mathrm{HA}]_f/[\mathrm{HA}] \qquad (18)$$

iii. Dissociation of picric acid

$$\mathrm{HA} \xrightleftharpoons{K_{3d}} \mathrm{H}^+ + \mathrm{A}^- \qquad (19)$$

$$K_{3d} = [\mathrm{H}^+][\mathrm{A}^-]/[\mathrm{HA}] \qquad (20)$$

iv. Ion-pair formation (M^+A^-)

$$\mathrm{M}^+ + \mathrm{A}^- \xrightleftharpoons{K_3} \mathrm{MA} \qquad (55)$$

$$K_3 = [MA]/[M^+][A^-] \tag{56}$$

v. Distribution of the ion-pair between the two phases

$$MA \xrightleftharpoons{K_{3ex}} MA_f \tag{57}$$

$$K_{3ex} = [MA]_f/[MA] \tag{58}$$

vi. Metal-crown complexation

$$M^+ + Cr \xrightleftharpoons{K_4} MCr^+ \tag{21}$$

$$K_4 = [MCr^+]/[M^+][Cr] \tag{22}$$

vii. Ion-pair formation (MCrA)

$$MCr^+ + A^- \xrightleftharpoons{K_5} MCrA \tag{23}$$

$$K_5 = [MCrA]/[MCr^+][A^-] \tag{24}$$

viii. Distribution of ion-pairs between the two phases

$$MCrA \xrightleftharpoons{K_{5ex}} MCrA_f \tag{25}$$

$$K_{5ex} = [MCrA]_f/[MCrA] \tag{26}$$

According to equation (27), the distribution coefficient

$$D = \frac{\text{Total metal on foam per unit weight of foam}}{\text{Total metal in solution per unit volume of solution}}$$

Thus, using the above-mentioned equilibria

$$D = ([MCrA]_f + [MA]_f)/([M^+] + [MA] + [MCr^+] + [MCrA]) \tag{59}$$

$$D = \frac{K_4 \cdot K_5 \cdot K_{5ex}[M^+][Cr][A^-] + K_3 \cdot K_{3ex}[M^+][A^-]}{[M^+] + K_3[M^+][A^-] + K_4[M^+][Cr] + K_4 \cdot K_5[M^+][Cr][A^-]} \qquad (60)$$

$$D = \frac{K_4 \cdot K_5 \cdot K_{5ex}[Cr][A^-] + K_3 \cdot K_{3ex}[A^-]}{1 + K_3[A^-] + K_4[Cr] + K_4K_5[Cr][A^-]} \qquad (61)$$

Since for all experiments the initial concentration of picrate $[A_T]$ is always large compared to metal concentration $[M_T]$ the $[A^-]$ can be approximated to $[A_T]$. The value of [Cr] can be calculated according to equation (51) as follows:

$$[Cr] = [Cr_T]/(1 + K_{1ex}\, w/v)$$

Substituting the appropriate values of K_4, K_5, [Cr] and $[A^-]$ it can be seen that the denominator in equation (61) can be approximated to $1 + K_3[A_T] + K_4\,[Cr]$

$$D \simeq \frac{K_4 \cdot K_5 \cdot K_{5ex}[Cr][A_T] + K_3K_{3ex}[A_T]}{1 + K_3[A_T] + K_4[Cr]} \qquad (62)$$

If we plot $D(1 + K_3[A_T] + K_4[Cr])$ vs [Cr], then

$$\text{intercept} = K_3 \cdot K_{3ex}[A_T]$$

$$\text{slope} = K_4 \cdot K_5K_{5ex}[A_T]$$

Thus, from the slope and intercept obtained for a particular cation, we can calculate the values of K_{3ex} and K_{5ex} using the other constants given in Table 4. Such plots for Na^+, K^+, Rb^+ and Cs^+ extraction into polyether foam are shown in Figure 24, and the values of K_{3ex} and

Figure 24

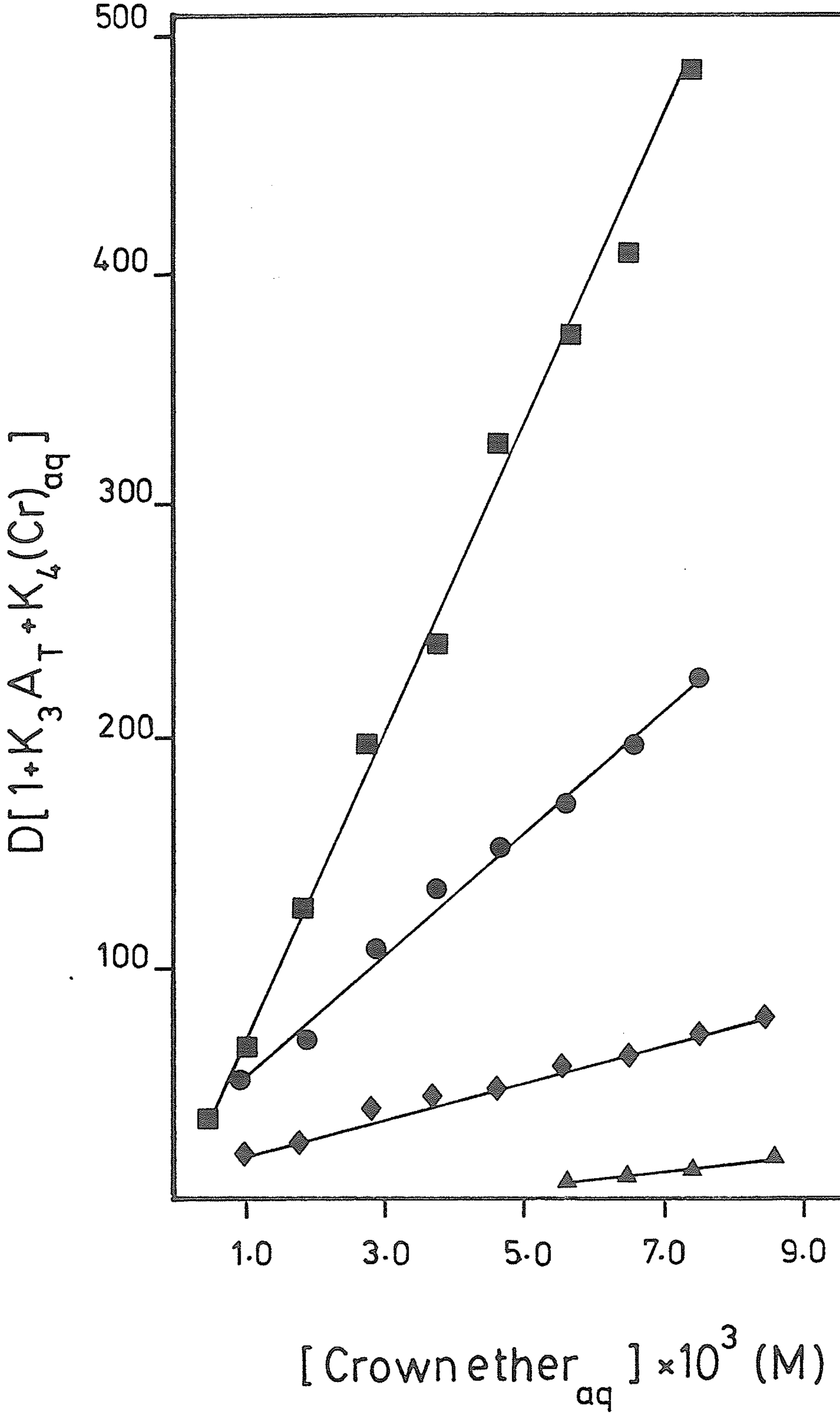
Effect of varying the initial concentration of crown ethers on the distribution ratio for the sorption of alkali metal-picrates from aqueous solutions by polyether foam.

Initial solution conditions:

[Cation]	1×10^{-4} M
[Picric acid]	4×10^{-3} M
Solution volume	40 mL
Foam weight	0.20 ± 0.01 g
Temperature	25.00 ± 0.05°C

Notes:

Na^+ (▲)
K^+ (■)
Rb^+ (●)
Cs^+ (◆)



500
400
300
200
100
$D[1+K_3A_T+K_4(Cr)_{aq}]$
1.0
3.0
5.0
7.0
9.0
$[\text{Crownether}_{aq}] \times 10^3$ (M)

TABLE 4 THE EQUILIBRIUM CONSTANTS, K, FOR ALKALI METAL ION-CROWN ETHER-PICRATE ION PAIR EXTRACTION INTO POLYETHER-BASED POLYURETHANE FOAM

Cation	K_3+ $L\ mol^{-1}$	K_{3ex} $L\ Kg^{-1}$	K_4‡ $L\ mol^{-1}$	$K_5 \cdot K_{5ex}$ $L^2 mol^{-1} Kg^{-1}$	K_{ex} $L^3 mol^{-2} Kg^{-1}$
Na^+	24	5.2	25	3.39×10^4	8.47×10^5
K^+	44	62.5	63	2.5×10^5	1.57×10^7
Rb^+	87	86.1	8	8.15×10^5	6.52×10^6
Cs^+	117	27.8	8	2.38×10^5	1.90×10^6

+Reference 64.

‡Reference 46.

$K_5 . K_{5ex}$ estimated from these plots are summarized in Table 4. The values of overall extraction constant, K_{ex}, are calculated according to equation (54), from these constants and also given in Table 4.

Since polyester foam does not extract any metal picrates in the absence of crown ether, we can neglect the equilibrium $\mathrm{MPic} \xrightleftharpoons{K_{3ex}} \mathrm{MPic}_f$. Considering then the overall extraction equilibrium of alkali metals into polyester foam from aqueous solutions containing DCHC-6 and picric acid, the distribution coefficient can be given by

$$D \simeq \frac{K_4 . K_5 K_{5ex} [A_T][Cr]}{1 + K_3[A_T] + K_4[Cr]} \tag{63}$$

and the plot of $D(1 + K_3[A_T] + K_4[Cr])$ against $[Cr]$ at constant picric acid concentration will be a straight line. Such plots for Na^+, K^+, Rb^+ and Cs^+ extraction into polyester foam are shown in Figure 25. The values of $K_5 . K_{5ex}$ have been estimated from the slopes of each plot and are summarized in Table 5. The values of overall extraction constant, K_{ex}, are also calculated according to equation 54. Furthermore, the plots of $\log D(1 + K_3[A_T] + K_4[Cr])$ vs $\log [Cr]$ (Figure 26) yield straight lines with slopes of near to unity further confirming the 1:1 stoichiometry of complex between metal and crown ether. The slope of unity also indicates that the extraction of alkali metal cations into polyurethane foam from aqueous solutions of bulky anions using DCHC-6 can be well represented by equation (62).

Figure 25

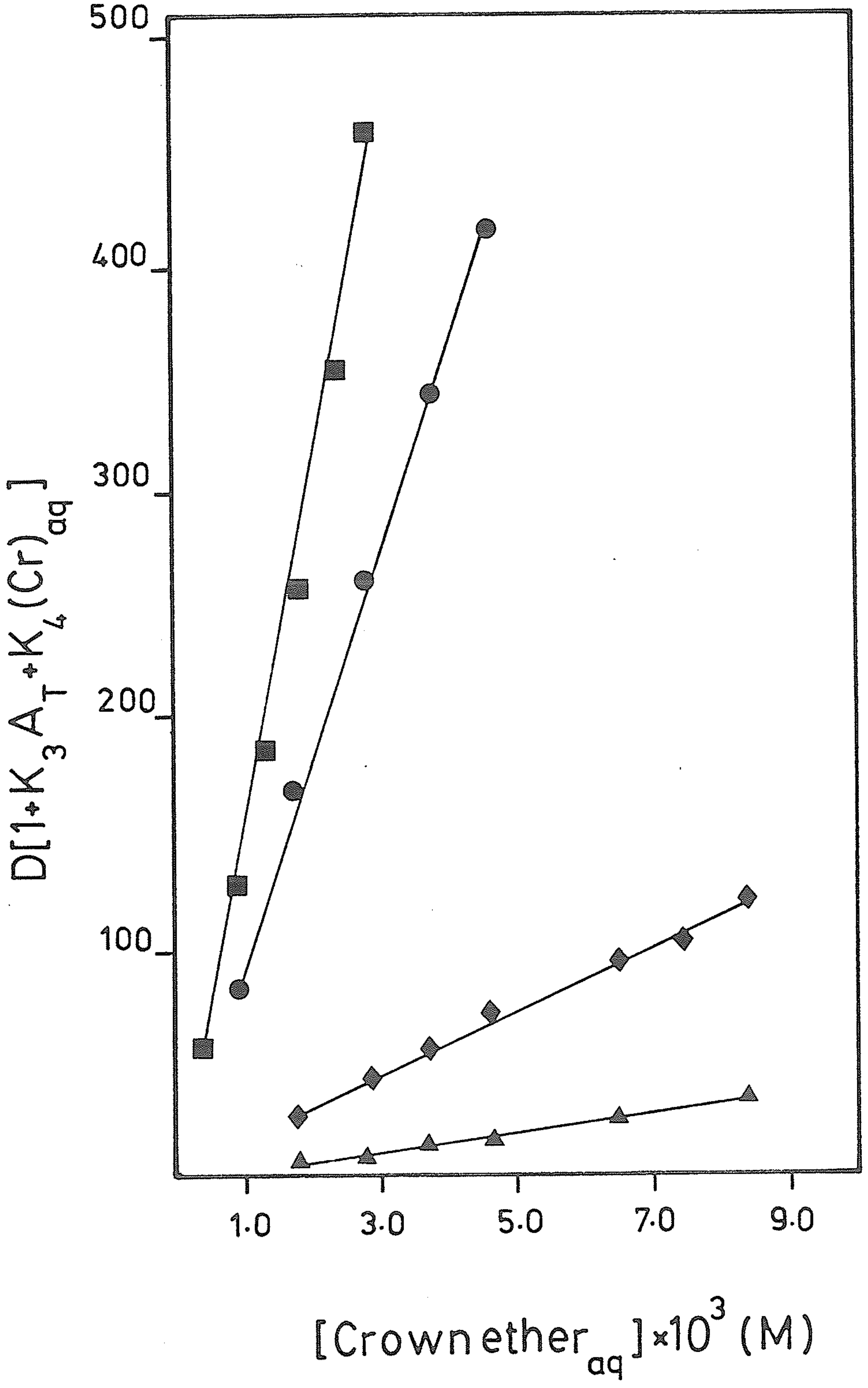
Effect of varying the initial concentration of crown ether on the distribution for the extraction of alkali metal-picrates from aqueous solution by polyester foams.

Initial solution conditions:

[Cation]	1×10^{-4} M
[Picric acid]	4×10^{-3} M
Solution volume	40 mL
Foam weight	0.20 ± 0.01 g
Temperature	25.00 ± 0.05°C

Notes:

Na^+	(▲)
K^+	(■)
Rb^+	(●)
Cs^+	(◆)



$D[1+K_3A_T+K_4(Cr)_{aq}]$
500
400
300
200
100
1·0
3·0
5·0
7·0
9·0
$[\text{Crownether}_{aq}]\times10^3$ (M)

Figure 26

Plots of $\log [D (1 + K_3A_T + K_4Cr)]$ vs log [crown ether] for the extraction of alkali metal picrates from aqueous solutions by polyester foam.

Initial solution conditions:

[Cation]	1×10^{-4} M
[Picric acid]	4×10^{-3} M
Solution volume	40 mL
Foam weight	0.20 ± 0.01 g
Temperature	25.00 ± 0.05°C

Notes:

Na^+	(▲)
K^+	(■)
Rb^+	(●)
Cs^+	(◆)

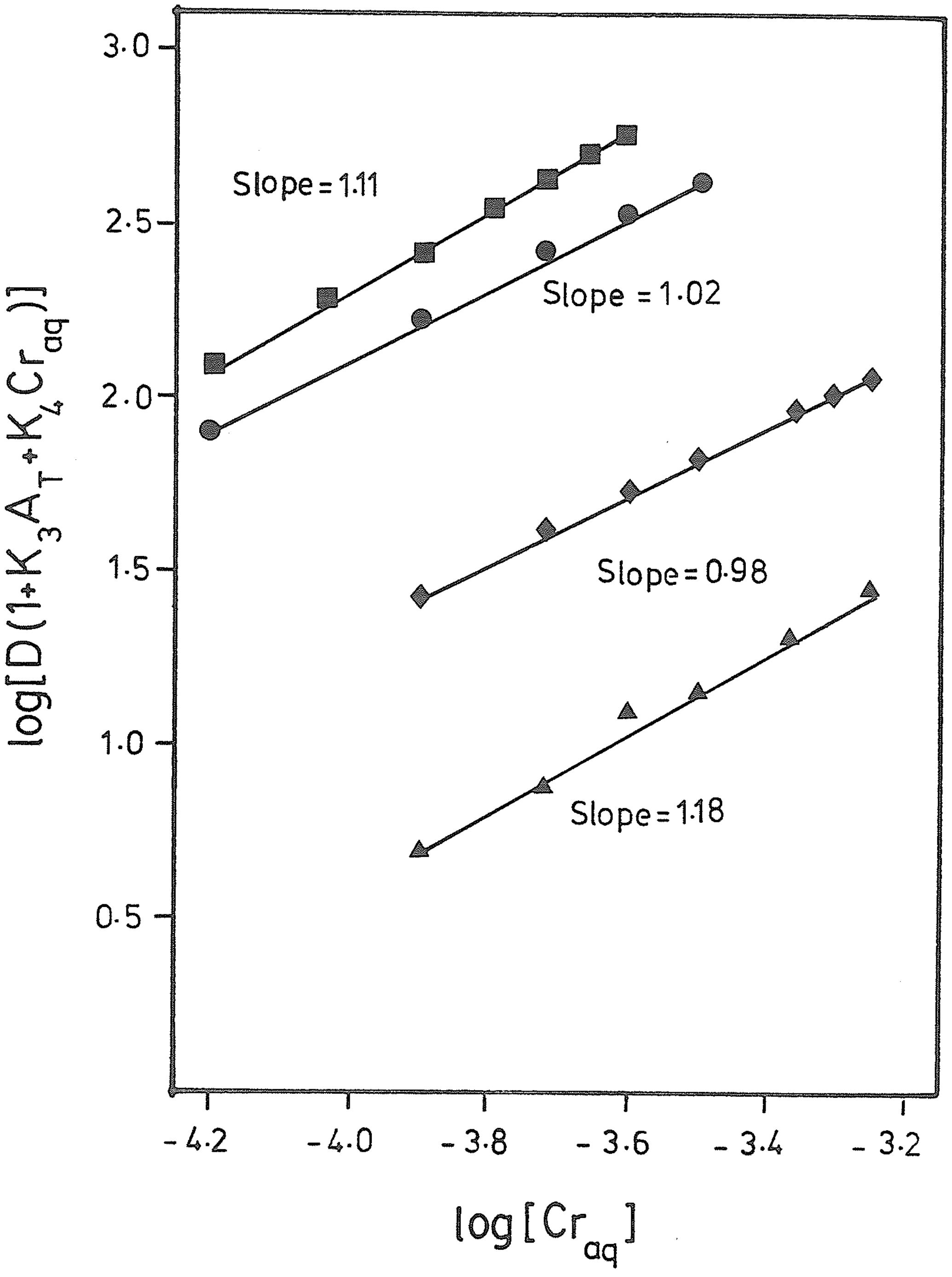

3·0
2·5
2·0
1·5
1·0
0·5
$\log[D(1+K_3A_T+K_4Cr_{aq})]$
Slope = 1·11
Slope = 1·02
Slope = 0·98
Slope = 1·18
- 4·2
- 4·0
- 3·8
- 3·6
- 3·4
- 3·2
$\log[Cr_{aq}]$

TABLE 5 THE EQUILIBRIUM CONSTANTS K, FOR ALKALI METAL ION-CROWN ETHER-PICRATE ION-PAIR EXTRACTION INTO POLYESTER-BASED POLYURETHANE FOAM.

Cation	K_4‡ / $L\ mol^{-1}$	$K_5 . K_{5ex}$ / $L^2 mol^{-1}\ Kg^{-1}$	K_{ex} / $L^3 mol^{-2}\ Kg^{-1}$
Na^+	25	4.41×10^4	1.1×10^6
K^+	63	6.7×10^5	4.22×10^7
Rb^+	8	2.9×10^6	2.33×10^7
Cs^+	8	4.42×10^5	3.54×10^6

‡Reference 46.

D. CONCLUSION

This study clearly demonstrates the ability of both polyether and polyester foams to extract alkali metal cations from aqueous solution using DCHC-6 in the presence of bulky anions. Similar to solvent extraction, it is efficient only in the presence of bulky and more hydrophobic anions. The efficiency of extraction further depends on the nature of the organic phase, with extraction into the more polar polyester foam being greater. The same order of K_{ex} of alkali metals obtained for both polyether and polyester foams suggests that although the degree of extraction may depend on the nature of organic phase, the order of extractability is most probably governed by the ratio of the cation size to that of crown ether cavity. Similar results have been reported for the ion-pair extraction of MCrA in various organic solvents(42,48,51). This similarity tends to suggest that the extraction of alkali metals from an aqueous solution by polyurethane foam in the presence of crown ether and a bulky anion can be considered as ion-pair extraction of MCrA by an organic solvent. However, in contrast to previous reports(22) that polyether is a better extractor than is polyester foam, it is clear from the K_{ex} values (Tables 4 and 5) that the opposite is true here. This study further reveals that polyether foam has an ability to extract metal-picrates (MPic) whereas polyester foam does not show any such characteristic. In the next chapter, this special ability of polyether foam has been further exploited to accomplish the extraction of mono and divalent cations from aqueous solutions containing bulky anions. These studies have been undertaken with the hope that they might lead us to a better understanding of the mechanism of foam extraction.

CHAPTER III. EXTRACTION OF MONO AND DIVALENT CATIONS BY POLYETHER-BASED POLYURETHANE FOAM

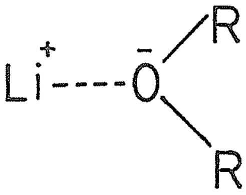
A. INTRODUCTION

Complexing Ability of Ethers

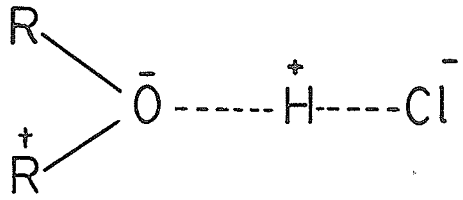
A short review of metal-ether interactions is included here to give a better insight into the subject.

Ethers, like water and alcohols, can interact with a wide variety of Bronsted and Lewis acids through lone pairs of electrons on oxygen atoms. In fact, most of their reactions proceed through intermediate complexes, and their solvent properties as well have been solely attributed to their complexing ability. The types of forces which may lead to the complexation of ethers with electron acceptors are discussed below:

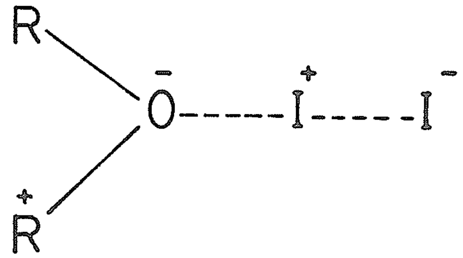
a) Ion-Dipole Interaction. The solvation of most salts is due mainly to this type of interaction.



b) Dipole-Dipole Interaction such as that of acid with ethers.



c) Dipole-Induced Dipole Interaction. Halogen ether complexes are the best examples of such an interaction.



What actually happens is that in all these interactions, the negative charge on oxygen induces a polarization in the species with which it interacts. This effect would be expected to be greater for easily polarizable molecules or ions (HCl for example) and smaller for ions like Li^+. In turn, the ether itself is polarized by the interacting species. Thus, in addition to the above mentioned interactions, the complexes of ethers and Bronsted or Lewis acids are also held together by the Induced Dipole-Induced Dipole interactions.

A strong interaction between an ether and a Lewis acid may dissociate the acid, producing an oxonium salt by the transfer of cation. This type of interaction depends mainly on the strength of the acid but, the natures of the anion and of the medium also play an important role. For example, the reaction of ether with nitric acid results in the formation of dialkyloxonium nitrates whereas the reaction of hydrochloric acid with ether produces only a weak hydrogen bonded complex.

Metal halide complexes in an acidic system interact with ethers to give protonated oxonium salts. These are the etherates of the complex halogen acid, HMX_n, where X and M represent halogen and metal atoms, respectively, and several such have been reported. A typical etherate has the formula $HMX_n.R_2O$ where X = Cl; M = Sb(V), Fe(III), or Al(III) etc. and the ether could be methyl, ethyl, isopropyl ether or tetrahydrofuran. These etherates are white or yellow crystalline compounds. Klages(66a,b) has formulated these compounds as oxonium salts, $R_2OH^+MCl_n^-$, on the basis of their observed high conductivity in liquid sulphur dioxide. Another molecule of ether interacts with these etherates resulting in the formation of a dietherate of the general formula $HMX_n.2R_2O$. These dietherates generally have intense colours and are low melting crystalline solids or viscous oily liquids. Dietherates are ionic in nature as they are very soluble in polar solvents and the resulting solutions are good conductors of electricity(67).

Like the proton, several other cations have also been reported to interact with ethers in a way similar to the hydration of cations. Interaction of ethers with metallic salts usually results in the formation of molecular complexes which will be discussed later. On the other hand, an ether-solvated cation would result with small cations such as lithium and sodium, which do not have a tendency to form complexes.

The extremely high solubility of lithium perchlorate in ethyl ether (i.e. 44 mole percent at 25°C) provides the most striking example of metallooxanium ion formation(68). The existence of ether-solvated lithium ion has been confirmed by measurements of the electrical conductance of the solution. Sillen and coworkers(69) have shown after studying the vapour pressure of complexes that the ether to lithium molecular ratio is 1:2. A high degree of solubility of lithium perchlorate has also been observed in various other ethers (e.g. n-butyl ether and tetrahydrofuran). Such unusually high solubility has been attributed to the ability of ethers to solvate the Li^+ ion. The importance to solubility of direct interaction between ether oxygen and the metal ion has further been confirmed by the poor solubility of hydrated lithium perchlorate in ethers.

Evidence of ether coordination with sodium has been reported by Aftandilian *et al*(70) who isolated the etherates of substituted sodium borohydride salts. An indirect proof of sodium solvation has also been reported by Day and coworkers(71), who observed approximately tenfold enhancement in the conductance of sodium tetraethyl aluminum in toluene by the addition of ethyl ether. Coates(72), based on the electrical conductance, has also proposed the solvation of the metal cation and hydrocarbon anion in the ethereal solution of sodium naphthalene. Wilkinson and his coworkers(78) drew a similar conclusion from the effect of various ethers in dissolving sodium and potassium.

Etherates of beryllium and magnesium halides have been known for a long time. Turova *et al*(74,75) have reported the synthesis of several dietherates of beryllium chloride and bromide with methyl ether, ethyl ether, tetrahydrofuran and tetrahydropyran. These compounds are solids of well defined melting points. Several etherates of magnesium bromide and iodide have also been isolated(76). Magnesium iodide has been reported to form tetra-, tri-, and dietherates with ethyl ether. These etherates are stable below 8°C, 17°C and 23°C respectively. Di- and trietherates of magnesium bromide have been reported(77) as well.

In addition to well-characterized etherates of boron fluorides, the etherates of aluminum, gallium and indium compounds have also been isolated. The interaction of ether with aluminum chloride has been studied in detail. It has been reported(78) that due to the dimeric nature of aluminum chloride, the complexation of ethers generally involves two equilibria; first, the cleavage of only one Al-Cl-Al bond resulting in the formation of $R_2OAl\text{-}Cl_3\text{-}AlCl_3$ and second, the complete rupture of the dimeric chloride to produce R_2OAlCl_3. Stable 1:1 adducts of gallium trichloride and tribromide with methyl and ethyl ethers have been isolated(79). In later reports(80) the formation of less stable dietherates such as $GaCl_3.2Et_2O$ has also been mentioned.

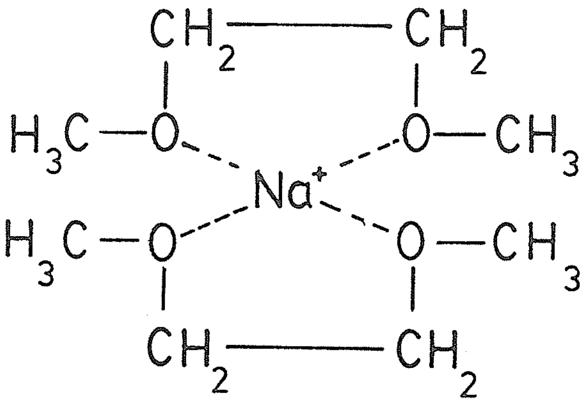
Ethers frequently interact with compounds of heavy metals which have the ability to form additional bonds e.g. the interaction of $AuCl_3$ and $HgCl_2$ with ethyl ether and dioxane yields the complexes $AuCl_3.Et_2O$ and $HgCl_2.C_4H_8O_2$ respectively(81). Stannic chloride has been reported to form stable complexes of the general formula $SnCl_4.2R_2O$ when allowed to react with ethers. Germanium and silicon tetrachlorides, however, do not complex with ethers appreciably(82).

Dietherates of both titanium and zirconium tetrachlorides with several ethers have been isolated(83). Fairbrother and coworkers(84) have recently isolated a number of etherates of niobium and tantalum pentachlorides and pentafluorides. These etherates, of general formula $MX_5.R_2O$, are liquids or low melting solids. Dietherates, although less stable than monoetherates, have also been prepared by the same authors(85).

Dietherates of molybodic oxide and tungsten pentachloride(86) with ethyl ether have been reported. Walton and coworkers(87) have reported the synthesis and spectral properties of several etherates of transition metal salts with tetrahydrofuran, having formula $MX_2.5C_4H_8O$ where M = Mn, Fe, or Co and X = Cl, Br, or I. In another study, Walton and coworkers(88) have described the synthesis of 1:1 and 2:1 adducts of 1,4-dioxane with manganese(II), iron(II), cobalt(II), and nickel(II) halides.

The formation of etherates (e.g. $HMX_n.nR_2O$) is important in the extraction of several metals from haloacidic solutions. The species involved in the extraction of iron(III)(89) and gallium(III)(90) into ether from acidic chloride media have been described as the etherates of molecular formula $HMCl_4.R_2O$(M = Ga(III) and Fe(III)). Etherates have also been involved in the extraction of several metals from other systems, e.g. extraction of Co(II) from the perchloric acid-thiocyanate system(91). The ether extraction of plutonium(IV)(92) from nitric acid solution and that of polonium(IV) from hydrochloric and nitric acid solutions has also been described to involve the etherates of these metal complexes(93). The extraction of uranium from the nitrate solution has been reported(94) to involve the mono- and dietherates of uranyl nitrate, i.e. $UO_2(NO_3)_2.3H_2O.Et_2O$ and $UO_2(NO_3)_2.2H_2O.2Et_2O$. In another study(95), it has been concluded from the infra red study that ether molecules are attached to the water molecules through hydrogen bonding.

Having described the interactions of monoethers with Lewis and Bronsted acids, the attention will now be focused on the complexing abilities of acyclic polyethers (which one would expect to form even more stable complexes due to chelation effect). A survey of the literature reveals many reports of complexation by polyethers. For example, the fact that $LiClO_4$ is highly soluble in polypropylene oxide is attributed to the solvating ability of the polyether$^{(96)}$. Diethyleneglycol has been noted$^{(97)}$ to complex sodium more strongly and more effectively than does ethyl ether. Zook and Russo$^{(98)}$ have reported both higher solubility and higher conductivity of n-butyrophenone and diphenylacetophenone in dimethyl ethers of ethylene glycol and diethylene glycol as compared to those in ethyl ether. In addition, the greater rate of alkylation of the above mentioned enolates with ethyl bromide in these polyethers also confirms the greater ionization. On the basis of these observations, authors have proposed the existence of tetracoordinated sodium ion such as is shown below:



The importance of sodium solvation has also been noticed during the addition of sodium to naphthalene as it takes place faster in polyethers(72,99), particularly in dimethyl and diethyl ethers of diethylene glycol. The e.s.r. study of the above system has also confirmed the existence of solvated metal cation(100). A higher rate of isomerization of 3-butenyl benzene to 1-butenyl benzene with potassium-t-butylate in polyethers compared to that in monoethers has been reported by Ugelstad _et al_(101). These authors have also observed that the rate of reaction increases markedly with increasing chain length of the polyethers and have concluded that the rate is mainly dependent on the ability of polyethers to solvate potassium ions.

In 1959 F. Cafasso and B. R. Sundhen(102) reported the solubilization of alkali metals in polyethers after studying several properties of these solutions (electrical conductance, e.p.r., and ultraviolet and visible spectra, etc.). The authors projected the idea of cavity formation and suggested the possibility of a well-defined negative cavity (i.e. the oxygen atoms directed towards the hole) for complexation of the positive ion. They have also concluded that this property is peculiar to polyethers.

Changes in the physical properties of polyethers caused by the addition of alkali metal salts have been attributed to the interaction of metal salts with the polyether chains. For example, pure polyethylene oxide has a very sharp melting point (65°C) while it has been observed that introduction of increasing amounts of potassium iodide progressively lowers the melting point of the polymer to produce an elastomeric composition at room temperature in the presence of 30 to 40% potassium iodide. Furthermore, an increase from -70°C to 40°C in the glass transition temperature (G.T.T.) of polypropylene oxide has been observed by the addition of $LiClO_4$. Such an exceptionally high increase in the G.T.T. of the polymer has been attributed to the formation by the polymer of a helical structure with $LiClO_4$ at the core of the helix(104). Subsequently D. B. James et al(105) have reported an increase in the G.T.T. of polypropylene oxide by the addition of several transition metal salts (e.g. $ZnCl_2$, $HgCl_2$, $CoCl_2$, and $FeCl_3$).

It has been reported by Bailey and coworkers(103,106) that methanol (which is normally a poor solvent for poly(ethylene oxide)) becomes a very good solvent for those polymers by the addition of small amounts of certain metal halides. The authors have determined the association constants of various metal salts (KCl, KBr, KI, KF, RbCl, RbI and NH_4Cl) with poly(ethylene oxide) polymer in methanol.

It is interesting to note here that a "salting in" phenomenon of polyethers in the presence of metal salts had been reported in 1950 by Doscher et al(107). The decrease in the turbidity of aqueous solutions of Triton X-100 caused by the addition of $CaCl_2$ was attributed by the same authors to the coordination of the Ca^{2+} ion by ether oxygen atoms of the polyethylene oxide chain.

The preparation of the polyethylene oxide complex of mercuric chloride has also been reported in 1964 by A. Blumberg et al(108,109) who observed that the complex is rigid, brittle, and insoluble in water although the pure polymer is both flexible and water soluble.

It is evident from these studies that the complexing ability of mono and acyclic polyethers was known long before Pedersen reported(40) the synthesis and complexing ability of crown ethers. However, it is only recently in connection with the present interest in the chemistry of macrocyclic polyethers that systematic investigation has been carried out to further explore the complexing ability of noncyclic polyethers. The dual aim of these studies has been both to learn more about the mechanism of cation complexation by these cylic and noncyclic polyethers, and to synthesize inexpensive noncyclic polyethers which can mimic their expensive cyclic analogues. Attention has also been directed toward exploiting the unique properties of noncyclic polyethers in the analytical areas for metal separation, preparation of ion selective electrodes and other uses.

Numerous publications have appeared in the last few years concerning the synthesis and structure of crystalline polyether complexes with metal cations. Fenton _et al_(110) have reported the synthesis in methanolic solution of complexes of poly(ethylene oxide) containing one mole of sodium iodide, sodium thiocyanate, or potassium thiocyanate and four moles of ethylene oxide repeating units. These crystalline complexes have well-defined and elevated melting points (200°C for NaI and 170°C both for KSCN and NaSCN complexes as compared to 65°C for the pure polymer). The authors have also observed marked differences between the X-ray and infrared spectra of such complexes and those of the pure polymer.

J. Smid and coworkers(111) have reported that polyglycol dimethyl ethers (glymes) having the general formula $CH_3O(CH_2-CH_2O)_xCH_3$ (where $1 \leq x \leq 6$) form complexes with lithium, sodium and potassium salts of carbanions in solvents of low dielectric constant such as tetrahydrofuran and dioxane. The equilibrium constant (K_i) for the following reaction has been studied by optical absorption spectrophotometry:

$$M^+F^- \quad + \quad G \quad \underset{}{\overset{K_i}{\rightleftharpoons}} \quad M^+GF^-$$

where M^+ is the alkali metal cation, F^- some carbanion and G the glyme. It has also been observed by the same authors that one mole of glyme 5(x = 4), glyme 6(x = 5) or glyme 7(x = 6) is required to form a glyme separated ion-pair with sodium but that two moles of glyme 4(x = 3) or glyme 3(x = 2) are required to solvate the sodium ion. On the other hand, with the potassium salt, only glyme 6 and glyme 7 yield glyme separated 1:1 complexes, and 1:1 mole ratio of salt to glyme is required to form complexes of K^+ with glyme 5 and glyme 4. On the basis of these observations, the authors have concluded that the formation of glyme separated ion-pairs depends mainly on the chain length and on the cation size. The authors have also estimated the complexation constants for Li^+, Na^+ and K^+ complexes with various glymes and have found that these constants increase rapidly with increasing numbers of oxygen atoms in the chain, but level off after a certain value of x, depending on the size of the cation. The conclusion that the stability constant increases with increasing numbers of oxygen atoms in the chain has also been drawn by L. Favretto(112) in studying the complexation of alkali metal cations by poly(ethylene oxide) derivatives ($RO(CH_2-CH_2O)_xR$ where R = phenyl) both in aqueous and in methanolic solutions. He has also reported that for a given value of x, the stability constants for alkali metal cations have the order: $K^+ > Rb^+ > Na^+ > Li^+$.

The interaction of different ammonium salts with ethylene glycol in aqueous solution of polyether containing various amounts of the ethylene glycol, has also been reported(113). The results show that for a particular composition of ethylene glycol-water the magnitude of interaction in solutions of ammonium chloride, ammonium bromide and ammonium nitrate has the order: $NH_4Br > NH_4NO_3 > NH_4Cl$.

G. Chaputet et al(114) have determined the association constants in methanol of 1:1 complexes of monovalent cations (Na^+, K^+, Cs^+ and Tl^+) with polyethylene glycols and their derivatives. A reduction in the complexing ability of polyethers after the replacement of the terminal methoxy group by amide or ester has been noted. The authors have also mentioned that the formation of 1:1 complexes of the type NaL^+ and KL^+ can take place only when the number of repeating units of ethylene oxide in the ligand, L, is greater than five and smaller than eight.

In a series of papers, Yanagida and coworkers(115a,b,c) have published results obtained by various techniques to study the interactions of alkali and alkaline earth metals with poly(ethylene oxide) and its derivatives. In the first paper, solvent extraction of metal cations using poly(ethylene oxide) and its derivatives has been used as a measure of the complexing ability of these polyethers. Extraction of KSCN in methylene chloride revealed that polyethers containing more than twenty-three ethylene oxide units have extraction ability comparable to that of 18-crown-6. On the other hand, polypropylene glycols proved to be weak extracting agents. A series of block copolymers of polypropylene oxide and polyethylene oxide showed a progressive increase in their extracting power with increases in the number of ethylene oxide units suggesting that $-CH_2-CH_2O-$ unit is the governing factor. Moreover, the extraction of potassium was observed only with the polyethers containing more than seven ethylene oxide units and, like the 18-crown-6 system, was efficient only with bulky anions such as I^- or SCN^- and not with smaller ones such as Cl^-, Br^-, and NO_3^-. Interestingly, the authors did not observe any remarkable differences between 18-crown-6 and the derivatives of polyethylene glycols studied for the selective extraction of alkali metals.

The interaction of metal cations with acyclic polyethers has also been studied by P.M.R. spectroscopy by the same authors(15b). Splitting in the signal of the oxyethylene protons has been used as the criterion for complexation of polyethers with metal cations and the results have been compared with those obtained from similar studies on crown ethers. On this basis, it has been inferred that octaethylene glycol complexes significantly with K^+, Rb^+, Cs^+, Sr^{2+} and Ba^{2+}; heptaethylene glycol interacts with Sr^{2+} and all alkali metals except Li^+, but hexaethylene glycol is complexed only with sodium ion. It has also been reported that Li^+ and Mg^{2+} do not cause any change in the P.M.R. spectra either of crown ethers (15-crown-5 and 18-crown-6) or of the glycols. On the basis of these results, the authors have concluded that hexaethylene glycol is a better complexing agent for sodium ion and that heptaethylene glycol forms stable complexes with K^+, Rb^+ and Cs^+. Among the alkaline earth cations Ca^{2+}, Ba^{2+} and Sr^{2+} interact strongly with various polyethers. The authors have also reported stronger interactions of Ca^{2+} with hexaethylene glycol and weaker interactions with octa- and hepta ethylene glycols compared to that with 15-crown-5. On the other hand, hexaethylene glycol monoethyl ether showed splitting of the main signal suggesting the role played by the terminal hydroxyl groups in complexation of the cation.

The "terminal group" concept has been projected by F. Vogtle and coworkers(116) who synthesised a variety of polyethylene oxide derivatives with terminal chelating groups. These derivatives have shown remarkable complexing properties with metal cations. Apart from alkali and alkaline earth metal cations, several other cations (e.g. lanthanoids, uranyl, zinc, mercury, silver as well as ammonium ion) also form stable complexes with the PEO derivatives. However, later reports by others(117,118) and also from the same laboratories(119) have shown that the polyether chains containing five to seven repeating ethylene oxide units with terminal groups incapable of acting as ligands also form stable complexes with a variety of metal cations. On the other hand, in a detailed investigation of the interaction of metal cations with polyetheylene glycol (PEG) and its derivatives, Yanagida et al(115c) have concluded that the role of terminal groups in the complexation of metal cations by polyethers varies both with the properties of the metal cations and with the polarity of the solvents. For example, the terminal hydroxy groups of PEG play an important role in the complexation of Li^+ and Mg^{2+} in acetone, but not in the complexation of Na^+ with PEG derivatives in that solvent. The terminal group also does not significantly influence the complexation of K^+ with PEG derivatives in acetonitrile.

Numerous reports have appeared in the last few years concerning the synthesis and structure of complexes of polyethylene glycol and its derivatives with transition metals (e.g. Fe^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+} and Cd^{2+}). X-ray analysis of the complexes of the last two cations has also been reported(120,121). Y. Hirashima and J. Shiokawa(122) have reported the complexation of polyethylene glycol and its derivatives with lanthanoid salts.

Like diethyl ether, the use of polyethers as extrants has also been known for a long time. In 1961, for example, Max Ziegler(123) described the use of polyethylene glycol for the extraction of Au^{3+} from acidic chloride media. The use of polyethers has also been investigated(124,125) for the extraction of several other metal ions. However, it is only after the discovery of the unique ability of polyethers to complex metal cations that several studies have been carried out with the ultimate aim of exploiting the peculiar property of the polyethers (for the extraction of metal cations). J. Rais *et al*(126) have reported strong enhancement in the extraction of Sr^{2+}, Ba^{2+}, and Ca^{2+} by nitrobenzene in the presence of ethylene glycol. Subsequently, the same authors have investigated in detail the extraction of Sr^{2+}/dicarbolide ion-pair (dicarbolide = $[(\pi\text{-}(3)\text{-}1,2,B_9C_2H_{11})_2Co^-]$ into nitrobenzene using polyethylene glycol(127).

In a series of investigations Sotobayashi and coworkers(128) have demonstrated the extractive ability of polyethylene glycol and its derivatives for various metal cations from thiocyanate and iodide solutions. The extraction has been reported to be enhanced with increases in the polyethylene oxide content in polyether chains also containing propylene oxide units. The following order of extraction for various transition metals from thiocyanate solution has been reported: Zn(II) > Mo(V) > Co(II) > Fe(III) > V(IV) > Cu(I) > Hg(II) > Cd(II) > Pb(II) > Ni(II).

Recently, S. Yanagida et al(129) have reported the synthesis of polyethylene oxide resin beads. They have also demonstrated the use of these beads for the extraction and separation of alkali metal salts. It has been reported that beads with more than five ethylene oxide units are more efficient for the extraction of KSCN than they are for the extraction of NaSCN. For beads containing seven ethylene oxide units, the selectively order of the alkali metal cations in the presence of the same anion is $K^+ > Rb^+ > Cs^+ > Na^+$ while anions in the presence of potassium cation follow the order $SCN > I^- > Br^- > Cl^-$.

On the basis of conclusions drawn from the above mentioned studies, it is evident that, like cyclic polyethers, non-cyclic polyethers containing repeating ethylene oxide units (CH_2-CH_2-0-) are also able to form complexes with several cations. It was expected, therefore, that polyether-based polyurethane foam might also be capable of complexing some cations. Extraction was selected as a convenient method for the purpose of investigating this possibility as it has already been widely used in similar studies, for cyclic(130) as well as noncyclic(131,132) polyethers. The main objective of the present study is to assess the complexing ability of polyether-based polyurethane foam for various mono- and divalent cations from the distribution of these cations between water and polyurethane foam in the presence of bulky anions e.g. picrate and sulphonate. It was also hoped that information obtained from this study might help us to clear up some of the puzzling aspects of the extraction mechanism of various other anionic complexes such as $M(SCN)_4^{2-}$ ($M = Co^{2+}$, and Pd^{2+}) by polyether-based polyurethane foam.

B. EXPERIMENTAL

Apparatus and Reagents

Perkin-Elmer model 306 atomic absorption spectrophotometer
Varian Techtron hollow-cathode lamps
Varian model 634 S UV-visible spectrophotometer
Evans Electro Selenium Ltd. Flame Photometer
Baird-Atomic model 530A single channel gamma ray spectrometer
    fitted with a Harshaw well-type NaI (Tl) detector
Fisher Accumet model 520 pH meter
Glass and saturated calomel reference electrodes
Perkin-Elmer model 337 grating infrared spectrometer
Extraction cells (Figure 27)
Multiple automatic squeezer (Figure 28)

The following reagent grade chemicals were obtained from Fisher Scientific Co. unless otherwise indicated

Silver Nitrate
Thallium Chloride
Lead Nitrate
Barium Nitrate
Zinc Chloride
Cobalt Chloride
Magnesium Nitrate
Calcium Nitrate
Strontium Nitrate

Figure 27

Extraction cell for equilibrating polyurethane foam with solution.

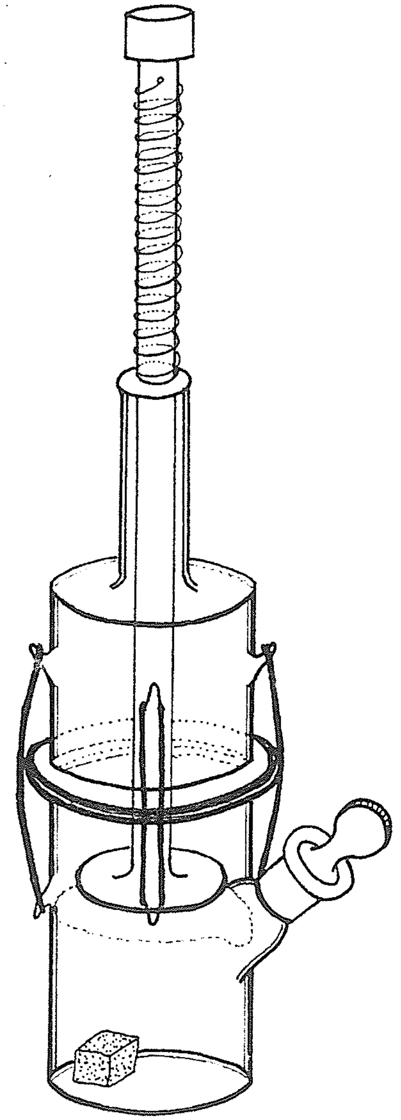
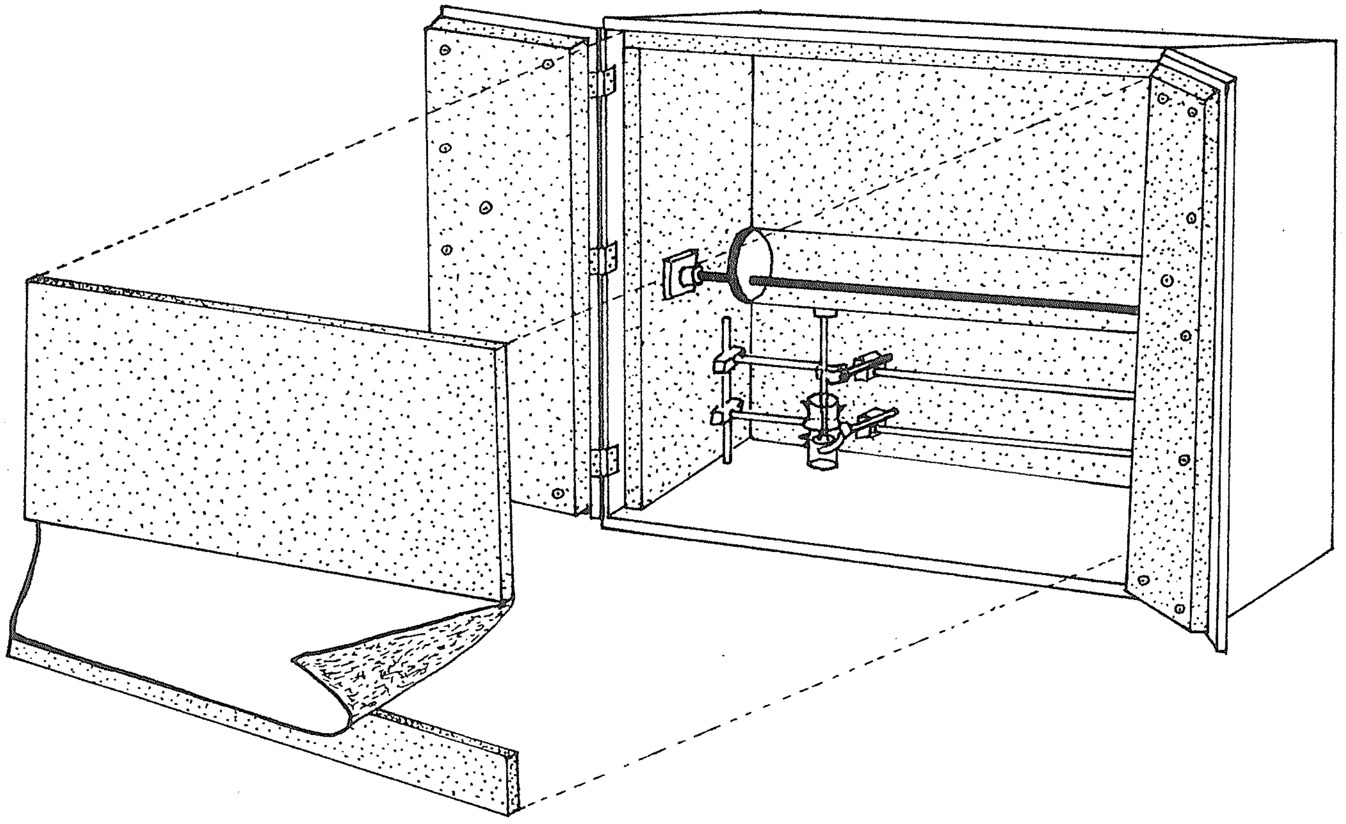


Figure 28

Thermostated automatic squeezing apparatus.



Lithium Chloride

Sodium Chloride

Potassium Chloride

Lithium perchlorate

Picric Acid Hydrate (BDH England)

8-Anilino Napthalene Sulphonic Acid as Magnesium salt
(Eastman Kodak Co.)

Barium - 133 (New England Nuclear Canada Ltd.)

Cobalt - 60 (New England Nuclear Canada Ltd.)

Foams:

Polyether type polyurethane foam (#1338 M) was obtained from G. N. Jackson Ltd.(Winnipeg, Manitoba). Polyester type polyurethane foam (Dispo) used in this study was the product of Scientific Products (McGraw Park, Illinois) and distributed by Canlab (Winnipeg). "Hypol" foam (another polyether-type foam) was obtained from W. R. Grace and Co. (Baltimore, Maryland).

General Procedure:

Preparation of Standard and Sample Solutions

0.01 M Solutions of $AgNO_3$, TlCl, $PbNO_3$ and $BaNO_3$ were prepared by dissolving the appropriate weight of each salt in water.

The standard solutions of picric acid and 8-anilino napthalene sulphonate were prepared by the procedure described in Chapter II.

A series of ten solutions was prepared in separate 100 mL volumetric flasks for each experiment by diluting sufficient volumes of the above standard solutions to give the required concentrations.

Washing of the Foams

Foams were washed and dried according to the procedure described in chapter II.

The Extraction of Species from Aqueous Solution by Foam

For each experiment, 100 mL of sample solution and the foam cube were equilibrated from ten to twelve hours in the extraction cell shown in Figure 27. The squeezing was performed by a thermostated automatic squeezing apparatus at 25°C. No attempt was made to absolutely calibrate the thermometer but the temperature was maintained within ± 0.05°C. The apparatus, capable of handling up to ten samples, was designed by Hamon(22) for the automatic squeezing of foam cubes at a rate of 30 strokes per minute over extended periods of time (Figure 28).

Methods of Analysis

Atomic absorption spectrophotometry and radioactive tracer techniques were used for the analysis of metal cations. The former method was used for the analysis of silver, thallium, lead and zinc. The precision of the method was ± 1% estimated by the repeated analysis of the standard solutions. The radioactive tracer technique was applied for barium and cobalt. The precision of the method was better than 0.5% and evaluated by counting ten identical samples of cobalt. On the other hand, UV-visible spectrophotometry was employed for the analysis of picrate and ANS with a precision of ± 3%.

Radioactive Tracer Techniques

The sample solutions containing the required amounts of all reagents were spiked with sufficient amount of metal tracer (^{60}Co or ^{133}Ba) to give a count rate of approximately 200 counts per second for 15 mL of sample.

A test tube of 15 mm internal diameter containing 15 mL aliquot of a sample solution was placed in the well of NaI detector and counted for 100 seconds. The activity of each sample was determined from the average of five successive counts. The average activity was corrected for the background activity before the calculation of distribution ratio. The background activity was obtained from the average of ten counts of 100 second duration.

Determination of Percentage Extraction by Tracer Technique

The comparison of the equilibrium activity of the sample solution to that existing prior to contact with polyurethane foam allowed the indirect calculation of the percentage extraction (%E).

$$\%E = \frac{\text{Activity}_{\text{before Extraction}} - \text{Activity}_{\text{after extraction}}}{\text{Activity}_{\text{before extraction}}} \times 100$$

The distribution coefficient was calculated using percentage extraction according to the equation 12 of Chapter 2.

$$D = \frac{\%E}{100-\%E} \times \frac{V}{W}$$

V is the volume of solution and W is the weight of the foam.

An error analysis of all data indicates an average of ± 3 percent for the distribution ratio "D". The values of D used in calculation and plotting and graphs are the average values of three closely agreeing runs.

Preparation of Polyurethane Film:

The polyurethane foam material was used in the form of thin films in order to obtain its infra red spectra, because severe light scattering made the measurement of spectra directly on foam quite difficult. Therefore, 0.1 g of 1338 BFG polyurethane foam was dissolved in 5 mL of refluxing m-cresol, and 0.2 mL aliquot of the resulting solution was transferred to the face of 1.5 x 3.0 cm sodium chloride plate. The m-cresol was then removed by overnight gentle heating under vacuum. To eliminate the possibility of any complexation by free $-NH_2$ or OH groups (that might have resulted from the above mentioned treatment) the films were allowed to react at room temperature with 0.1 gram of phenyl isocyanate in 100 mL of hexane for 18 hours. In order to get rid of the excess reactant, the plate containing the film was then soaked in fresh hexane for two days followed by evaporation of solvent under vacuum. The resulting plate was then soaked for eighteen hours in 50 mL of a saturated sodium chloride solution which was 50 ppm in Co(II), 0.1 M in NaSCN. The solution was saturated with sodium chloride in order to prevent dissolution of the plate. Spectra of the film and sorbed species were then measured directly.

C. RESULTS AND DISCUSSION

II. Extraction of Monovalent Cations by Polyether-Based Polyurethane Foam

1. Preliminary Studies

Preliminary experiments were carried out to check the extractibility of several monovalent cations by polyether foam from aqueous picrate solution. The results indicate that only Ag^+ and Tl^+ are effectively extracted, whereas no detectable amount of alkali metals is extracted even from 5×10^{-2} M picric acid solution. Experiments were also carried out to determine the time required to establish the equilibrium. A polyether foam cube weighing approximately 0.4 g was squeezed in 100 mL solution which was 1×10^{-4} M in metal cation (Ag^+ or Tl^+) and 5×10^{-3} M in picric acid, for one half hours when the solution was analyzed for cation. The same experiment was repeated for different squeezing times ranging from one half hour to twenty four hours. The results obtained show that the extraction increases sharply during the first hour of squeezing then starts to level off and becomes almost constant after four hours of squeezing indicating the establishment of equilibrium. For further studies, the foam cubes were squeezed for eight to twelve hours in order to ensure the achievement of equilibrium.

2. Effect of Metal Concentration on the Distribution Coefficient

In order to investigate the formation and extraction of polynuclear species, the extraction of metal picrates was studied at different initial concentrations of metal cation. A series of 100 mL solutions of 0.02 M picric acid containing various concentrations of silver ranging from 5 x 10^{-5} M to 2 x 10^{-3} M were equilibrated with foam cubes each weighing 0.30 ± 0.01 g for ten hours. The samples were then analyzed for silver by atomic absorption spectrophotometry. The results are shown in Figure 29 where the log of the distribution coefficient is plotted as a function of the log of metal concentration at equilibrium. As can be seen, the distribution coefficient remains practically constant up to 7 x 10^{-4} M initial concentration of silver. The "D" value starts to decline above this initial concentration of silver with a resulting slope of 0.4. Such a small value of slope can neither be attributed to the dissociation of the extracting species (Ag^+Pic^-) in the polyether foam, nor to the capacity of the foam. On the other hand, this drop in the "D" value may be due to the continuous decrease in the metal to picrate ratio with the increase of metal concentration. This idea is further substantiated by the fact that when a similar study was carried out with a higher initial concentration of picric acid (3 x 10^{-2} M), the "D" values remained constant up to a higher concentration of silver (Figure 29).

The sorption of thallium from aqueous picrate solution into polyurethane foam was also studied as a function of metal concentration. Foam cubes each weighing 0.30 ± 0.01 g were squeezed for about ten hours in a series of 100 mL solutions of 0.02 M picric acid, containing various initial concentrations of thallium(I) ranging from

Figure 29

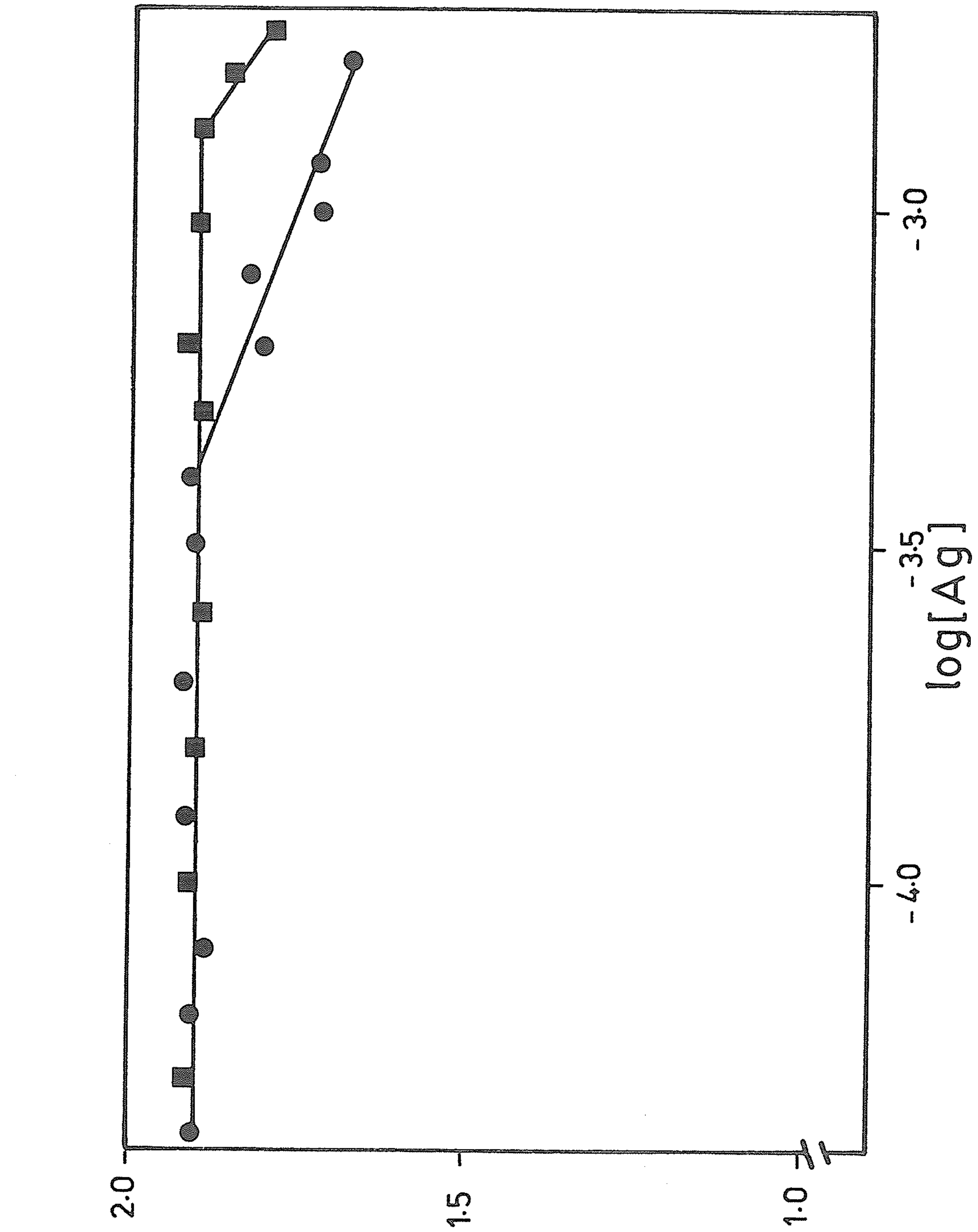
Effect of equilibrium solution silver concentration on the extraction of silver from aqueous picrate solution.

Initial solution conditions:

Solution volume	100 mL
Foam weight	0.30 ± 0.01 g
Temperature	25.00 ± 0.05°C

Notes:

(●) 2 x 10^{-2} Picric acid
(■) 3 x 10^{-2} M Picric acid


log D
2.0
1.5
1.0
- 4.0
- 3.5
- 3.0
log[Ag]

5×10^{-5} to 2×10^{-3} M. The results (Figure 30) indicate that the extraction of thallium remains almost constant up to 5×10^{-3} M initial concentration of thallium and then starts to decrease, most likely due to insufficient amounts of picrate.

From the results of these studies, it is obvious that the extraction of metal picrates is independant of metal concentration, most likely over the entire range of metal concentration studied, but certainly up to 1×10^{-2} M for silver and 0.5×10^{-2} M for thallium. These results suggest that the formation and extraction of any polynuclear species can be ruled out under these conditions.

The possibility of the existence of a polynuclear species was also examined by studying the extraction of metal picrates by polyether based polyurethane foam as a function of picrate concentration for three different initial concentrations of metal cation. A series of 100 mL solutions with 2.5×10^{-4} to 2×10^{-2} M in picric acid and 5×10^{-5} M in Tl^+, were equilibrated with polyether foam cubes for ten hours. The results are shown in Figure 31, along with the results of two other similar experiments but with 1×10^{-4} and 2.5×10^{-4} M initial concentrations of thallium. The plots between "D" and picrate concentration for three different initial concentration of thallium are coincident, indicating the absence of polynuclear species. The cation concentration for further experiments was kept within the above concentration range.

Figure 30

Effect of equilibrium solution thallium concentration on the sorption of thallium from aqueous picrate solution.

Initial solution conditions:

[Picric acid]	2×10^{-2} M
Solution volume	100 mL
Foam weight	0.30 ± 0.01 g
Temperature	25.00 ± 0.05°C

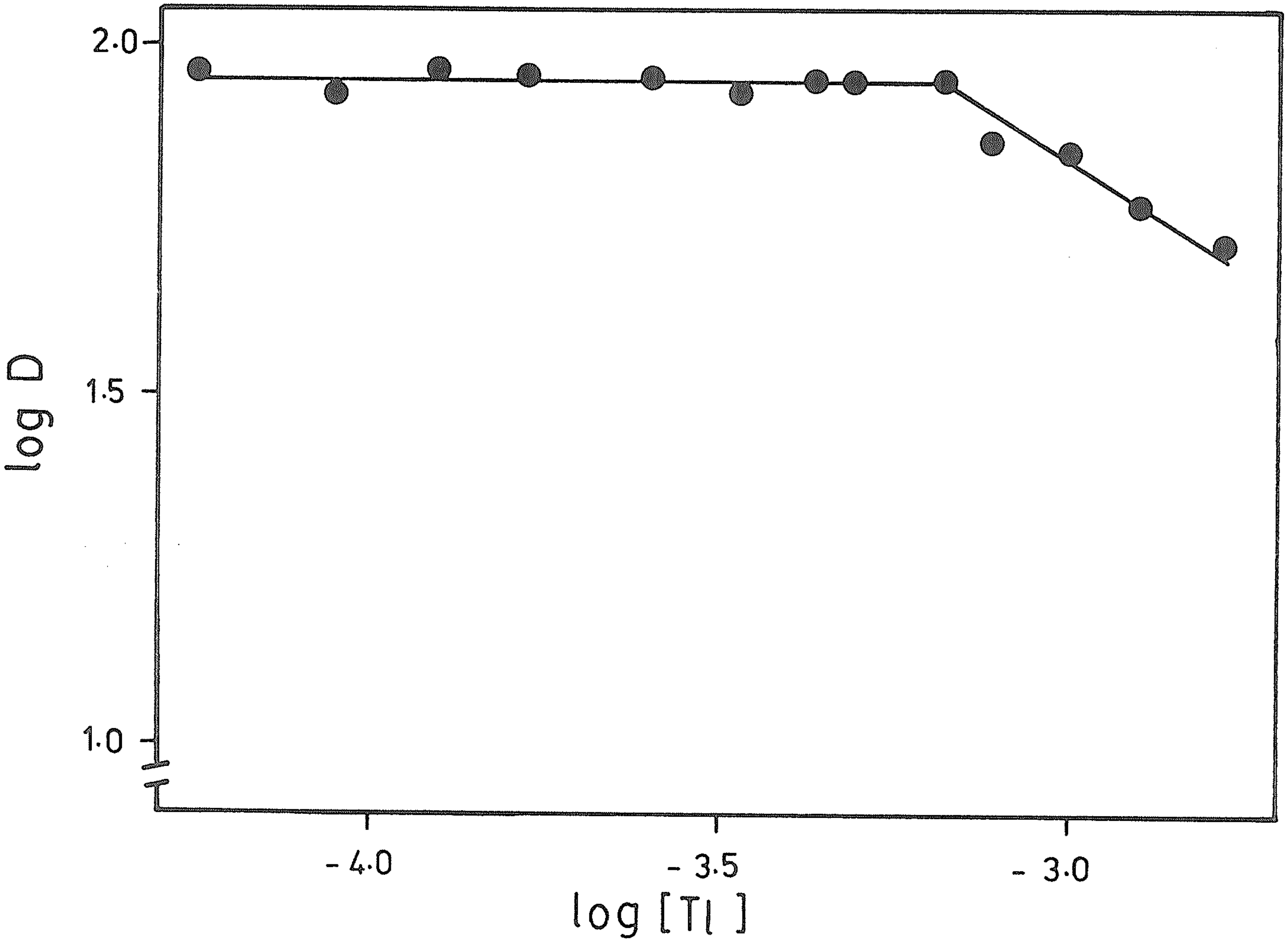

2.0
1.5
1.0
log D
-4.0
-3.5
-3.0
log [Tl]

Figure 31

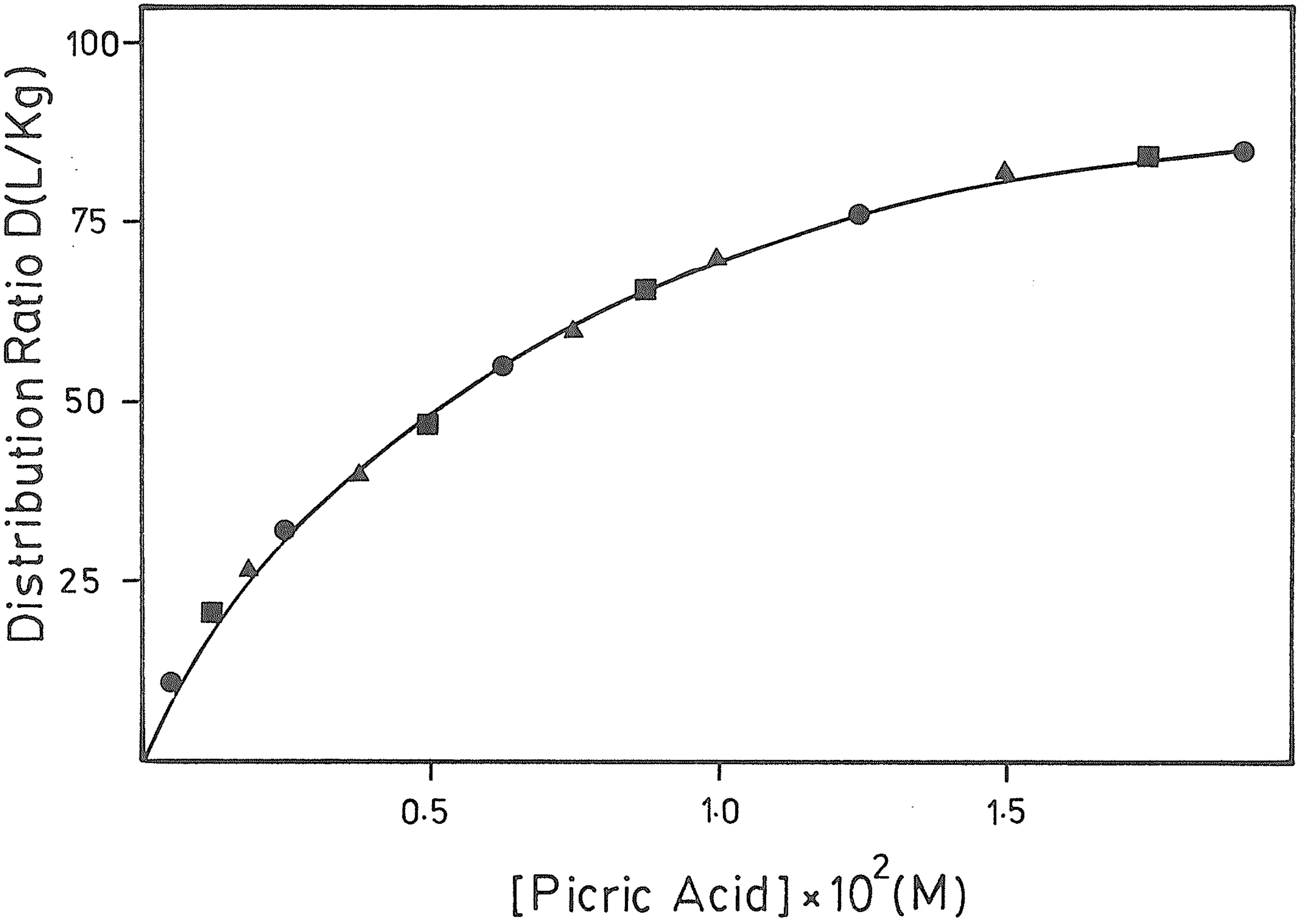
Distribution ratio as a function of initial concentration of picric acid at different concentrations of thallium.

Initial solution conditions:

Solution volume	100 mL
Foam weight	0.30 ± 0.01 g
Temperature	25.00 ± 0.05°C

Notes:

(●) 5 x 10^{-5} M Tl^{+}
(■) 1 x 10^{-4} M Tl^{+}
(▲) 2.5 x 10^{-4} M Tl^{+}


100
75
50
25
Distribution Ratio D(L/Kg)
0.5
1.0
1.5
[Picric Acid] × 10^2(M)

3. Effect of Aqueous/Foam Phase Ratio on the Extraction of Metal Picrates

In order to confirm the validity of assumption that "D" (distribution coefficient) is independent of the relative amounts of solution and foam, the extraction of Tl^+ was determined over a wide range of aqueous/foam phase ratios. Different aqueous/foam phase ratios were obtained by changing the foam weight, since the design of the extraction cell did not allow enough alteration in the volume used (small volumes result in the splashing of solution).

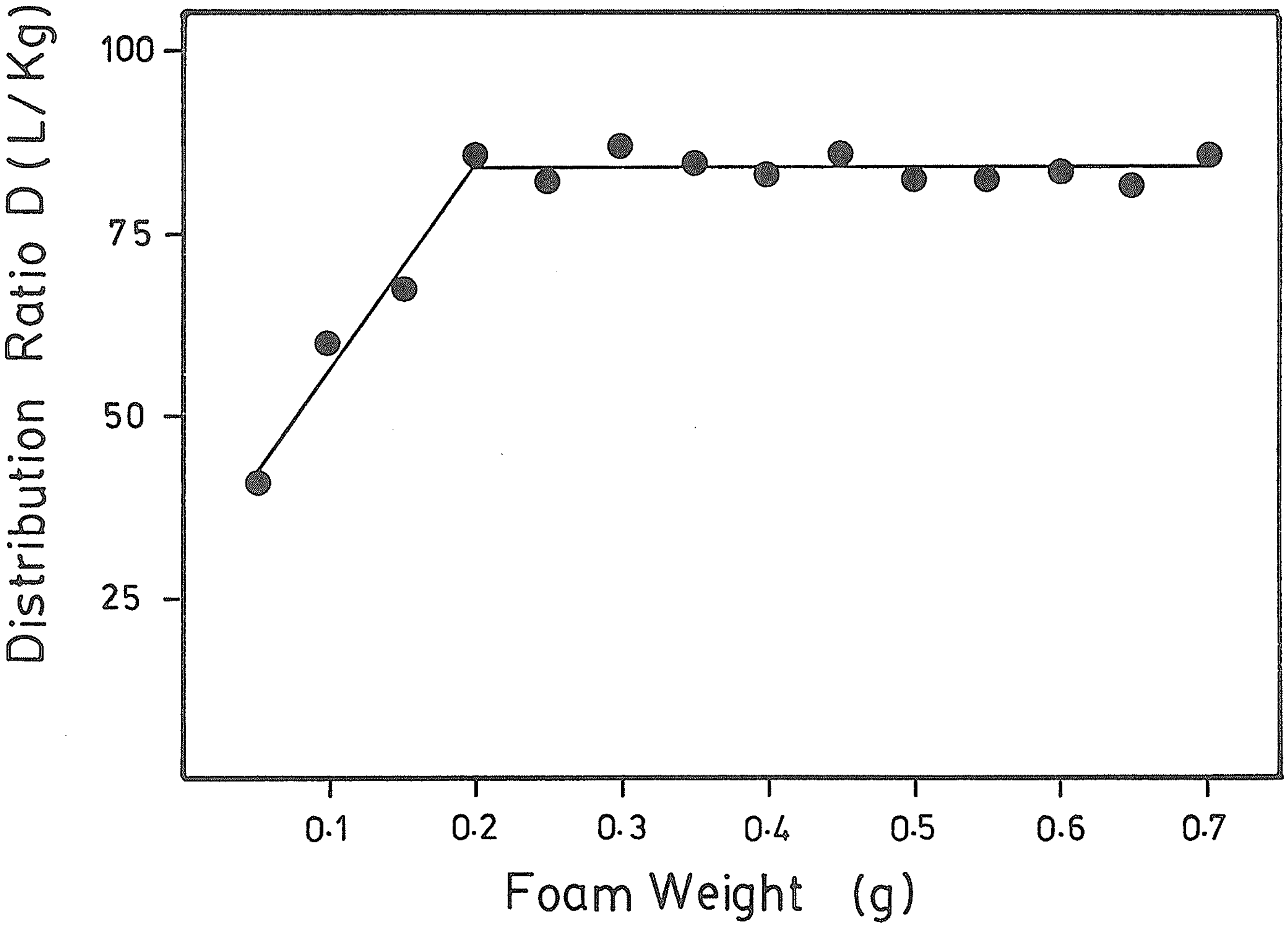
Foam cubes of different weights ranging from 50 mg to 700 mg were squeezed for twelve hours in a series of 100 mL solutions of 0.02 M picric acid and 1×10^{-4} M Tl^+. Samples were then taken and analyzed for thallium by atomic absorption spectrophotometry. Results of the experiments are shown in Figure 32 where the distribution coefficient "D" is plotted as a function of foam weight. As can be seen, the distribution ratio "D" remains constant over a wide range of foam weight and then starts to drop at higher aqueous/foam phase ratios (i.e. at lower foam weight since volume is constant). The lower "D" values resulting from small foam weights are most likely due to the low percentage ($< 5\%$) of extraction, and a minor change in the aqueous/foam phase ratio (e.g. evaporation of the aqueous phase) therefore would result in a large drop in the "D" values. Furthermore, the "D" values obtained from such a low percentage of extraction are also subject to a considerable error. In addition to these, the low "D" values may be the result of ineffective squeezing of the small foam cubes.

Figure 32

Distribution ratio as a funciton of foam weight.

Initial solution conditions:

[Picric acid]	2×10^{-2} M
[Tl^+]	1×10^{-4} M
Solution volume	100 mL
Temperature	25.00 ± 0.05°C


Distribution Ratio D (L / Kg)
100
75
50
25
0·1
0·2
0·3
0·4
0·5
0·6
0·7
Foam Weight (g)

4. Effect of Various Types and Concentration of Anions on the Distribution Ratio

As has been mentioned earlier, the electrostatic cation-anion interactions depend not only on the concentration, but also on the nature of the anion e.g. the solubility properties of the anion are extremely important for the extraction of the ion-pair in a non-aqueous phase of low polarity. Large and soft inorganic or preferably organic anions strongly increase the extraction. The hydrophobic character is also of importance. The distribution coefficient of silver was studied as a function of picrate concentration, in order to establish the effect of anion concentration on the extraction of silver into polyether foam from picric acid solution.

Foam cubes weighing 0.40 ± 0.02 g were squeezed for twelve hours in a series of 100 mL solutions 2.5×10^{-4} M to 2.5×10^{-2} M in picric acid and containing 1×10^{-4}M silver. The samples were then analyzed for silver. The results are shown in Figure 33, where the distribution coefficient is plotted as a function of initial concentration of picric acid. On the basis of the law of mass action, it is quite reasonable to expect an increase in the concentration of the extracting species (most likely $Ag^+ Pic^-$) and thus a corresponding increase in the distribution ratio. The effect of picrate concentration was also studied for thallium (Tl^+) in a similar fashion and the results are shown in Figure 34. Like the Ag^+/picrate system, the extraction of Tl^+ increases with increasing anion concentration up to 2×10^{-2} M concentration of picric acid and then levels off.

Figure 33

Effect of varying the initial concentration of picric acid on the extraction of silver.

Initial solution conditions:

$[Ag^+]$	1×10^{-4} M
Solution volume	100 mL
Foam weight	0.40 ± 0.02 g
Temperature	25.00 ± 0.05°C

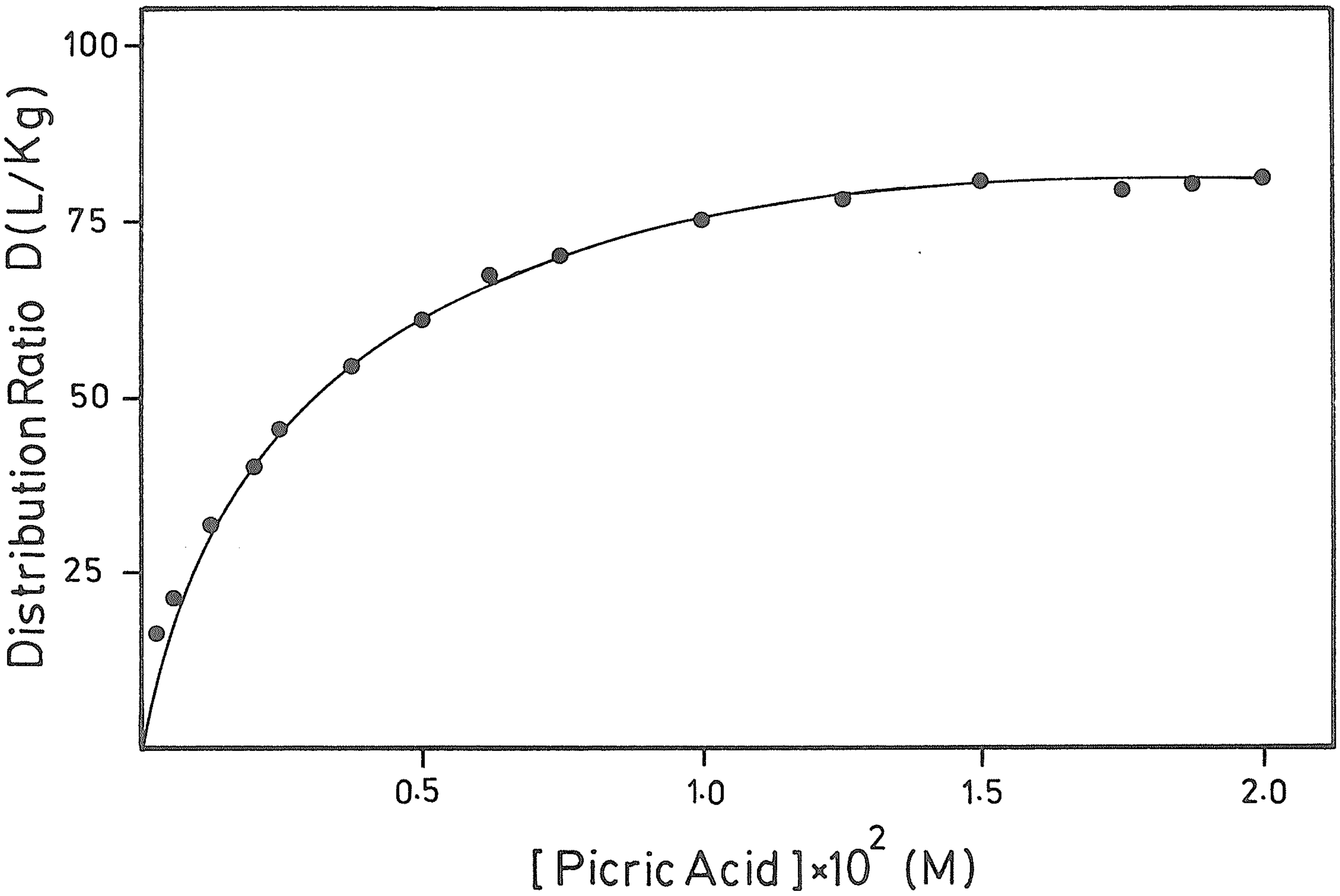
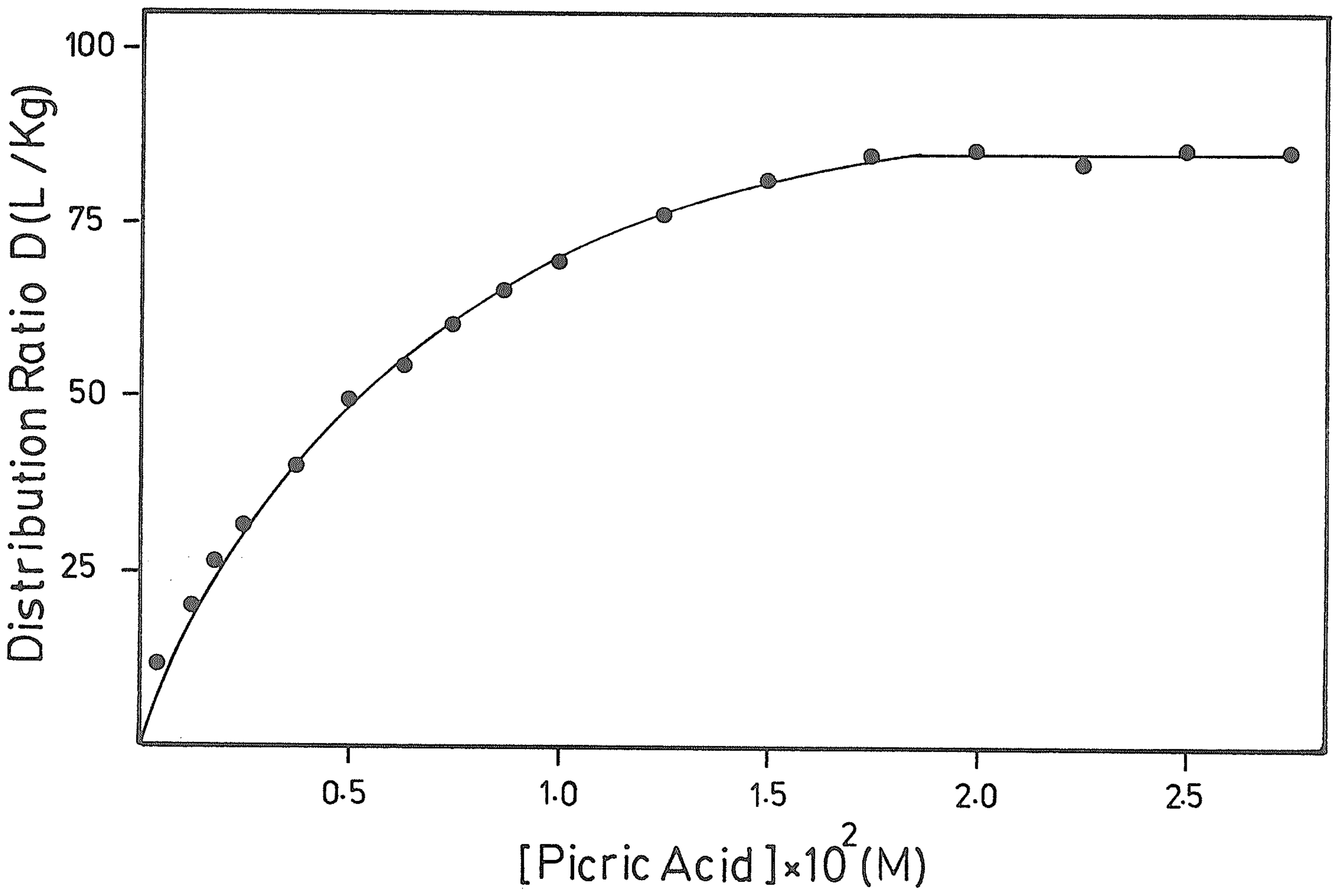

100
75
50
25
Distribution Ratio D(L/Kg)
0.5
1.0
1.5
2.0
[Picric Acid] ×10^2 (M)

Figure 34

Effect of varying the initial concentration of picric acid on the sorption of thallium.

Initial solution conditions:

$[Tl^+]$	1×10^{-4} M
Solution volume	100 mL
Foam weight	0.40 ± 0.02 g
Temperature	25.00 ± 0.05°C


Distribution Ratio D(L /Kg)
100
75
50
25
0.5
1.0
1.5
2.0
2.5
[Picric Acid]×10^2(M)

Experiments were carried out to study the effect of various anions on the extraction of silver. No detectable extraction of silver was observed either from 0.01 M solution of NO_3^- or from 0.004 M aqueous solution of 2,4 or 2,6 dinitrophenolate. A distribution ratio as high as 40 ± 5 was obtained from 0.01 M ClO_4^- solution.

The effect of ANS concentration on the sorption of silver and thallium was also studied. A series of 100 mL solutions 5×10^{-4} to 5×10^{-3} M in thallium were extracted for eight hours with 0.40 ± 0.02 g polyether foam cubes. The results are presented in Figure 35, along with the results of a similar study with picric acid. As expected, the extraction of thallium is improved with bulkier ANS. The increase in distribution coefficient in going from picrate to ANS is most likely due to the decreasing hydration of the anion in the aqueous phase.

The extraction of silver was also studied as a function of ANS. A series of solutions, 1×10^{-4} M in silver and containing various amounts of ANS ranging from 5×10^{-4} M to 5×10^{-3} M, were equilibrated with foam cubes weighing 0.40 ± 0.02 g for ten hours. The results are shown in Figure 36. The results of a similar study with picric acid are also included for comparison. As can be seen, the extraction of silver is enhanced in the presence of a bulkier anion. Comparing these results with those obtained from similar studies for thallium (and also those for lead and barium which will be discussed later), it is obvious that the magnitude of the increase in distribution coefficient in the case of silver is far greater than expected. Such a large increase in silver extraction cannot be solely attributed to

Figure 35

Extraction of thallium as a function of initial concentration of anions.

Initial solution conditions:

$[Tl^+]$	1×10^{-4} M
Solution volume	100 mL
Foam weight	0.40 ± 0.02 g
Temperature	25.00 ± 0.05°C

Notes:

Picric acid	(◆)
ANS	(●)

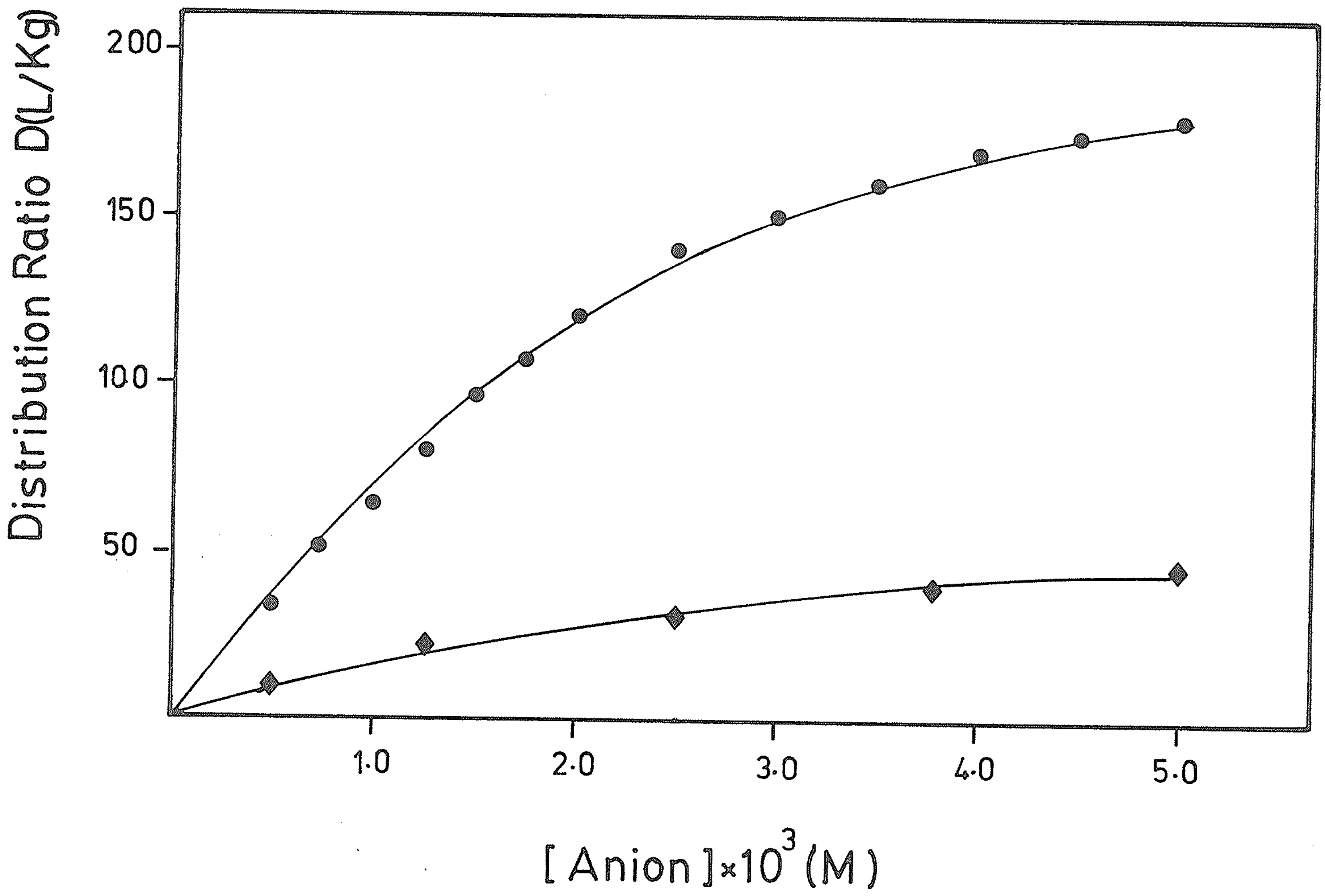

Distribution Ratio D(L/Kg)
200
150
100
50
1·0
2·0
3·0
4·0
5·0
[Anion]×10³ (M)

Figure 36

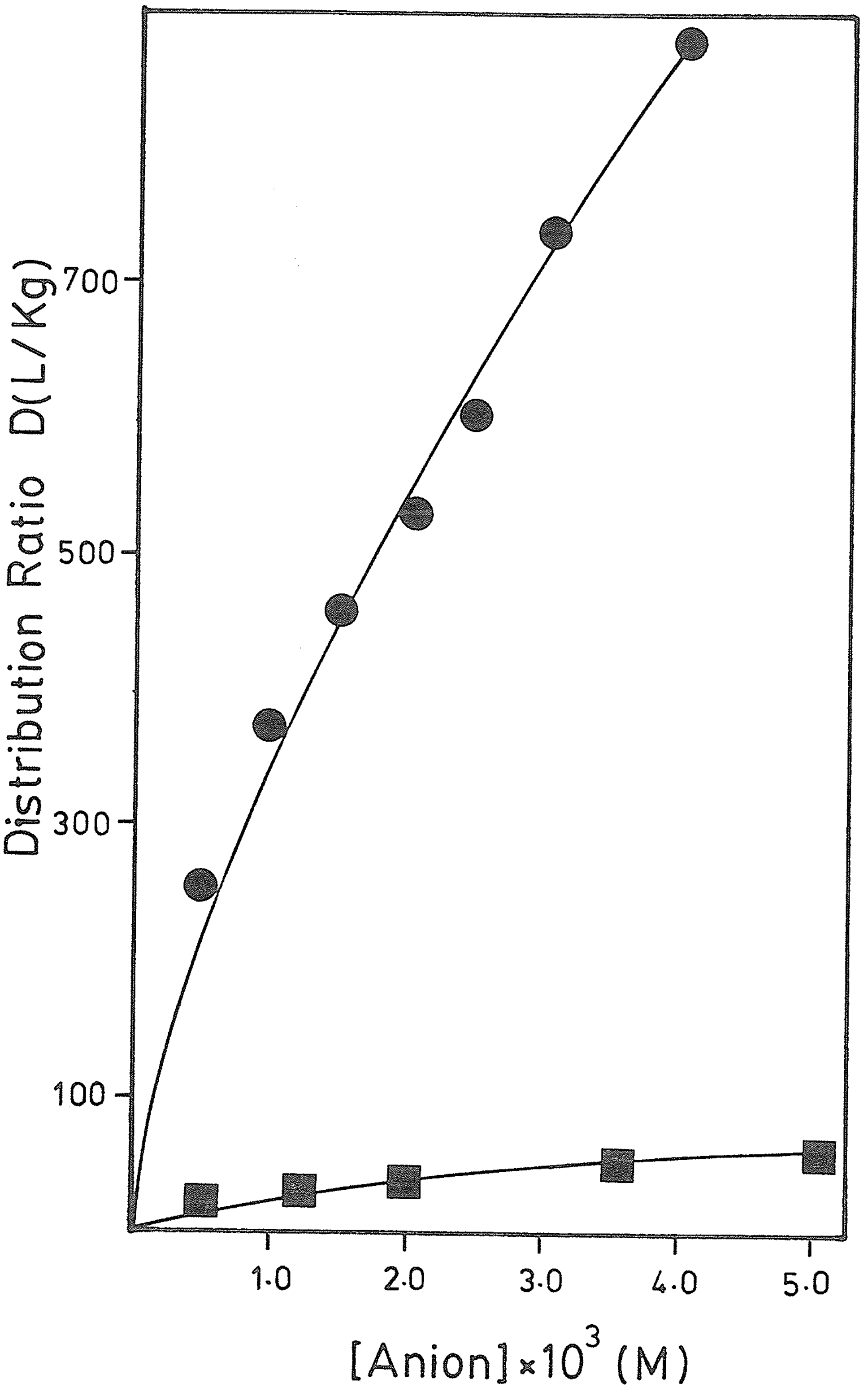
Effect of anions on the extraction of silver.

Initial solution conditions:

$[Ag^+]$	1×10^{-4} M
Solution volume	100 mL
Foam weight	0.40 ± 0.02 g
Temperature	25.00 ± 0.05°C

Notes:

ANS	(●)
Picrate acid	(■)


Distribution Ratio D(L/Kg)
700
500
300
100
1.0
2.0
3.0
4.0
5.0
[Anion] × 10^3 (M)

the large size of the ANS, but can possibly be explained by considering the formation of a highly extractable complex between silver and ANS. This assumption seems reasonable in view of the fact that ANS can act as a ligand through the lone-pair of electrons on nitrogen atom. It is also well documented(133) that silver forms very stable complexes with nitrogen donor ligands.

5. Extraction of Thallium Picrate into Various Organic Solvents

It is well established(134) that ion pair extraction is greatly affected by the dielectric constant of the non aqueous phase. The ability of various organic phases for the extraction of thallium from aqueous picrate solution was studied in order to establish the mechanism of ion-pair extraction by polyether based polyurethane foam.

Experiments were carried out to establish the role of dielectric-constant of the organic phase in the extraction of thallium from picrate solution. Several organic solvents (50 mL each) ranging in polarity from hexane to methylene chloride were equilibrated with 50 mL solutions of 0.02 M picric acid and 1×10^{-4} M Tl^{+1} in separatory funnels for 30 min. (initial experiments showed that ten minutes are enough to establish the equilibrium). After that both aqueous and organic layers were analyzed for thallium. The results of these experiments are given in Table 6. It is evident from these that none of the organic solvents used in this study extract any appreciable amount of thallium. Thus, it is reasonable to assume that dielectric constant of the organic phase is not playing any significant role in the extraction of thallium-picrate, and that the extraction of Tl^+ (and also of Ag^+) can not be treated as a simple solvent-like ion-pair extraction.

Experiments were also carried out to test the use of some other types of polyurethane foam for the extraction of thallium-picrate from aqueous solution. Different types of foam used in the present study are; i) regular polyether-based polyurethane foam (#1338 M); ii) #1338 B.F. a polyether-based polyurethane foam, which is believed

TABLE 6 EXTRACTION OF THALLIUM PICRATE INTO VARIOUS ORGANIC PHASES

Organic Phase	Dielectric Constant (202)	Distribution Ratio D
Hexane	1.89	< 0.01
Benzene	2.28	< 0.01
Ether	4.335	< 0.01
Chloroform	4.8	< 0.01
Methylene Chloride	9.02	0.02
Polyester Foam	-	$7 \pm 2^*$
Polyether Foam	-	$85 \pm 5^*$

*D in L Kg^{-1} for Polyurethane Foams

Conditions: 50 mL solution 1×10^{-4} M in Tl^+ and 2×10^{-2} M in picric acid; 50 mL organic solvent or 0.30 gram of foams.

to have same major constituents as those of regular foam but may differ in minor additives; iii) Hypol, another polyether foam, and iv) Dispo a polyester-based polyurethane foam.

In the preliminary experiments it was observed that under similar experimental conditions all polyether-based polyurethane foams extract thallium picrate to some extent (i.e. "D" values are almost constant for all polyether foams). The only polyester-based polyurethane foam, Dispo, behaves quite differently for the extraction of thallium picrate. On the basis of these results a study was carried out to compare the relative abilities of polyether (1338 M) and polyester foams for the extraction of thallium as a function of picrate concentration. For this study 100 mL solutions, containing 1×10^{-4} M thallium and various concentrations of picric acid ranging from 2.5×10^{-3} M to 2.5×10^{-2} M, were equilibrated with polyester foam cubes each weighing approximately 0.4 g for ten hours. The samples were then taken and analyzed for thallium. A similar experiment using polyether foam was also performed. The results of these experiments are shown in Figure 37, where distribution coefficients are plotted as a function of initial concentration of picric acid. As can be seen from the figure, the polyether is a better extractor than polyester foam for Tl-picrate. Similar results are also obtained for silver-picrate system. The superiority of polyether foam has been reported by other workers as well(5,22). However, these results are not in accordance to our early results where we observed a higher extraction of metal-crownether-picrate (MCrA) ion-pairs by polyester than that by polyether foam. Since the extraction of MCrA by polyester foam has been

Figure 37

Comparison of thallium extraction from aqueous picrate solution by polyether and polyester-based polyurethane foam.

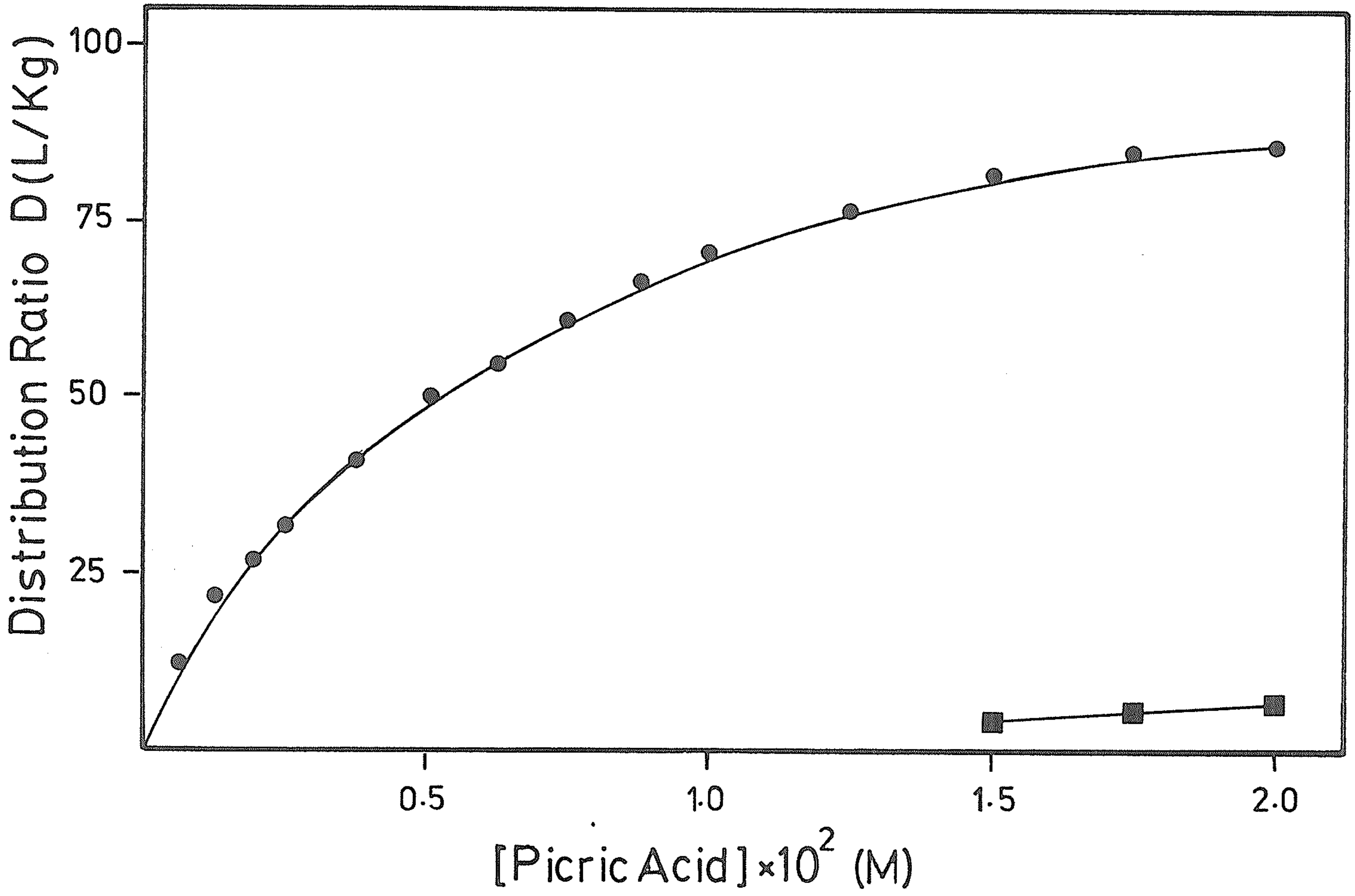
Initial solution conditions:

$[\mathrm{Tl}^+]$	1×10^{-4} M
Solution volume	100 mL
Foam weight	0.4 ± 0.02 g
Temperature	25.00 ± 0.05°C

Notes:

Polyether foam (●)

Polyester foam (■)


Distribution Ratio D(L/Kg)
100
75
50
25
0.5
1.0
1.5
2.0
[Picric Acid]×10² (M)

successfully analyzed in terms of a simple solvent-like ion-pair extraction mechanism, it is reasonable to assume that this mechanism can not solely account for the sorption of Ag^+/Tl^+ by polyether foam in the presence of bulky anions. If this mechamism did hold in this case, we would have observed a higher extraction of these ion-pairs by polyester foam.

Based on the fact that polyether and polyester foams differ mainly in the polyol portion of the polymer$^{(1,2)}$, the following can be said about the sorption of Ag/Tl by polyurethane foam; firstly that polyol portion of the polymer is playing the most important role in the extraction of metal-picrates and secondly that the common units of the polyurethane foams i.e. urea and urethane linkages are not of any significant importance in the extraction of metal picrates.

6. Extraction Equilibria

The equilibrium between an aqueous solution containing the monovalent metal cation M^+, the picrate anion A^- and polyether-based polyurethane foam can be written as:

$$M^+ + A^- \overset{K_{ex}}{\rightleftharpoons} MA_f \qquad (1)$$

$$K_{ex} = [MA]_f/[M^+][A] \qquad (2)$$

where MA denotes the ion-pair, the molar concentrations are given in brackets, the subscript "f" indicates the foam phase and the absence of subscipt denotes the aqueous phase. The overall extraction equilibrium can be analyzed in terms of the following constituent equilibria:

i) Ion-pair formation in aqueous solution:

Since the ion-pair formation constants have been reported for the alkali metal picrate systems$^{(64)}$ it is quite reasonable to assume the ion-pair formation of Ag^+ and Tl^+ cations with picrate in aqueous solutions.

$$M^+ + A^- \overset{K_1}{\rightleftharpoons} MA \qquad (3)$$

$$K_1 = [MA]/[M^+][A^-] \qquad (4)$$

ii) Extraction of the ion-pairs into foam:

$$MA \overset{K_{1ex}}{\rightleftharpoons} MA_f \qquad (5)$$

$$K_{1ex} = [MA]_f/[MA] \qquad (6)$$

Considering the low polarity of the organic phase (foam), equilibria such as dissociation and aggregation of the ion-pair in the foam have been ignored.

The distribution coefficient for metal is expressed as:

$$D = \frac{\text{Total metal ion on foam per unit weight of foam}}{\text{Total metal ion in aqueous phase per unit volume of solution}} \quad (7)$$

Using equations 3 to 6

$$D = [MA]_f/[M^+] + [MA] \quad (8)$$

Substituting for $[MA]_f/$ and $[MA]$ from equations 4 and 6 in equation 8 yields:

$$D = K_1 . K_{1ex}[M^+][A^-]/[M^+] + K_1[M^+][A^-] \quad (9)$$

$$D = K_1 . K_{1ex}[A^-]/1 + K_1[A^-] \quad (10)$$

$$\text{or } D(1 + K_1[A^-]) = K_1 . K_{1ex}[A^-] \quad (11)$$

The values of K_{ex} and K_1 can be determined as follows:

a) at higher concentration of anion one can assume that $[MA] >> [M^+]$

Equation 9 can be written as follows:

$$D \simeq K_1 K_{1ex}[M^+][A^-]/K_1[M^+][A^-] \quad (12)$$

$$D \simeq K_{1ex} \quad (13)$$

b) on the other hand, it is reasonable to assume that at low concentration of anion $[M^+] >> [MA]$ and thus equation 9 can be approximated to:

$$D \simeq K_1 K_{1ex}[M^+][A^-]/[M^+] \quad (14)$$

$$D \simeq K_1 . K_{1ex}[A^-] \tag{15}$$

The plot of D vs $[A^-]$ at low concentration of anion yields a slope equal to product of K_1 and K_{1ex}, substituting the value of K_{1ex} which can be obtained from the same plot according to equation 13 $D = K_{1ex}$ at higher concentration of A^-, the value of K_1 can be determined.

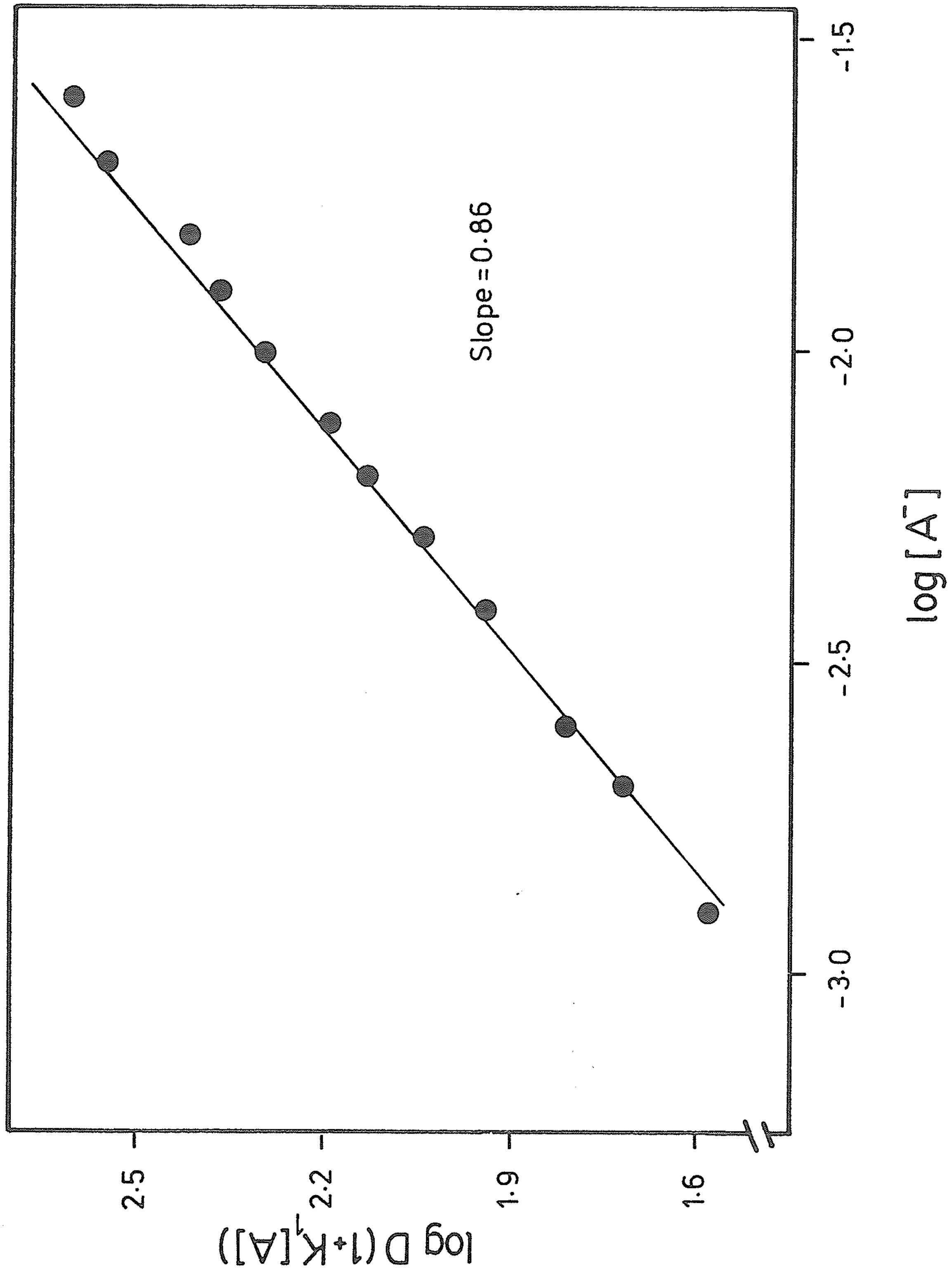
The values of K_1 and K_{1ex} for silver and thallium picrate system have been determined from Figure 38 and 39 according to above method and are given in Table 7. If the assumptions used are reasonable, theplots of log D $(1 + K_1[A^-]$ vs log $[A^-])$ should be straight lines with a slope of unity. Such plots (Figure 38 and 39) for silver and thallium are indeed straight lines with slopes close to unity, (0.86 for Ag^+ and 0.95 for Tl^+) thus confirming the validity of the assumptions.

Figure 38

Plot of log D $(1 + K_1[A])$ vs log [A] for silver/picrate system.

Initial solution conditions:

$[Ag^+]$	1×10^{-4} M
Solution volume	100 mL
Foam weight	0.40 ± 0.02 g
Temperature	25.00 ± 0.05°C



Slope = 0.86
2.5
2.2
1.9
1.6
log D (1+K1[A])
-3.0
-2.5
-2.0
-1.5
log [A⁻]

Figure 39

Plot of log D $(1 + K_1[A])$ vs log [A] for thallium/picrate system.

Initial solution conditions:

$[Tl^+]$	1×10^{-4} M
Foam weight	0.40 ± 0.02 g
Solution volume	100 mL
Temperature	25.00 ± 0.05°C

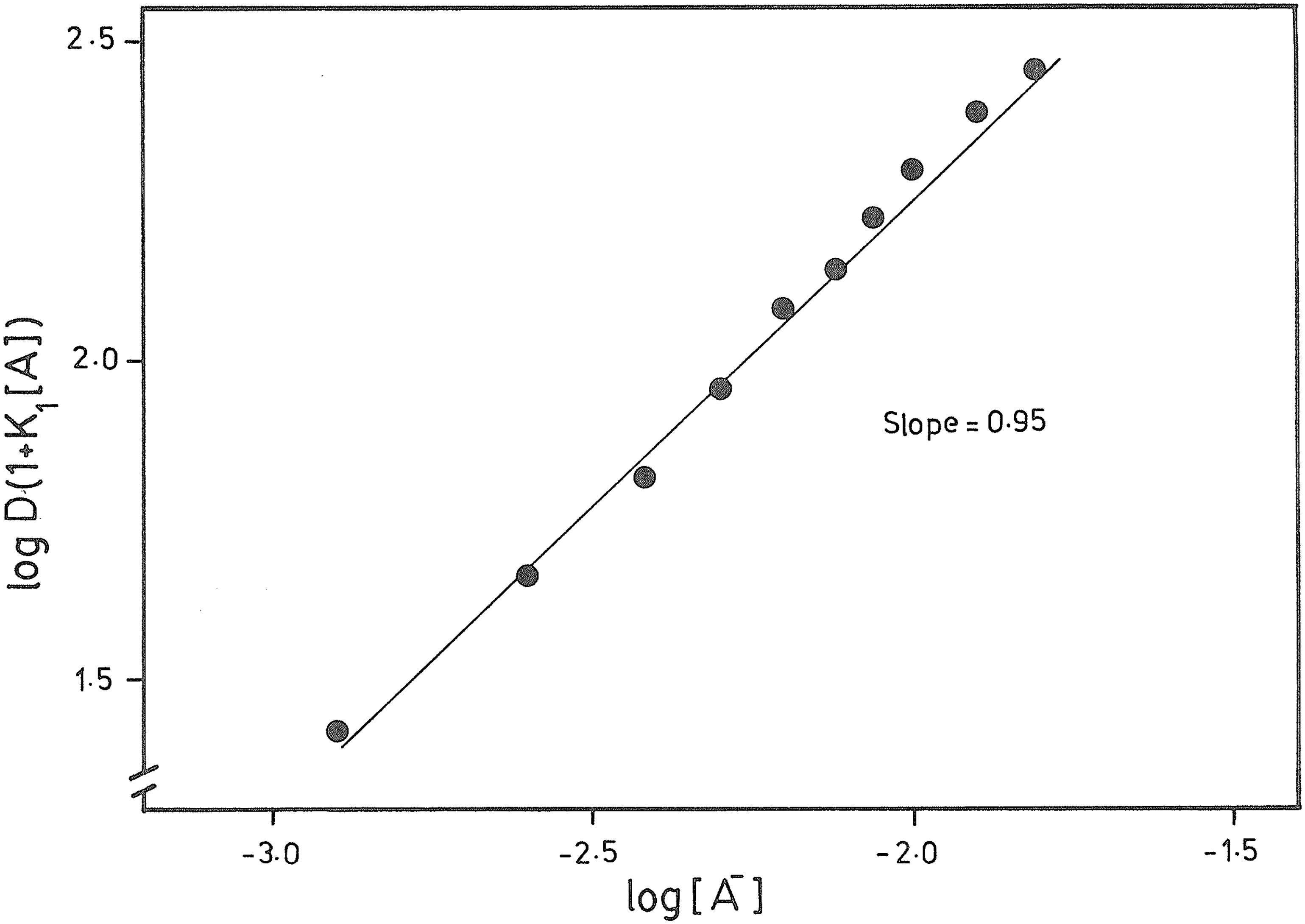

2.5
2.0
1.5
-3.0
-2.5
-2.0
-1.5
log[A⁻]
log D(1+K₁[A⁻])
Slope = 0.95

TABLE 7 THE EQUILIBRIUM CONSTANTS K FOR SILVER, THALLIUM-PICRATE ION-PAIR EXTRACTION INTO POLYETHER-BASED POLYURETHANE FOAM

Cation	K_1 / $L\ mol^{-1}$	K_{1ex} / $L\ Kg^{-1}$	K_{ex} / $L^2\ mol^{-1}\ Kg^{-1}$
Ag^+	195	80	1.56×10^4
Tl^+	155	85	1.32×10^4

7. Effect of Temperature on the Extraction of Silver Picrate

It is difficult to predict the specific effect of temperature on the extraction. In the literature, there are data on the negative influence of temperature on extraction and it is generally believed that an increase in temperature most frequently results in a decrease in the distribution ratio. On the other hand, data are also available that suggest a negligible influence of temperature on the extraction(136), or even an enhancement of extraction(137). Thus, the existing data show that no general conclusion can be drawn and that only experimental evidence on a specific system can give the proper picture of its temperature dependence.

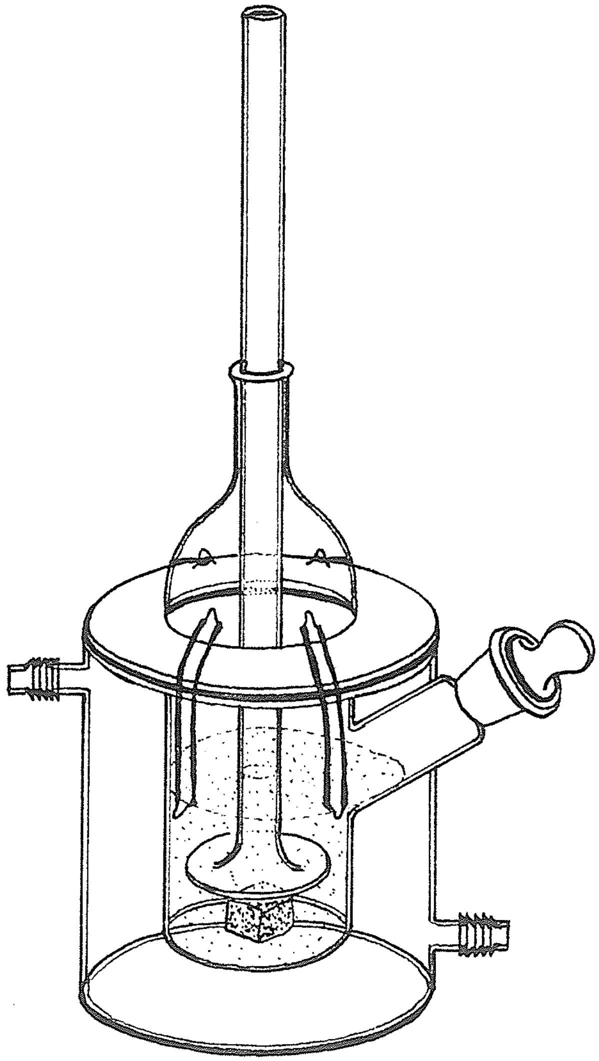
The extraction of silver picrate by polyether foam was studied at different temperature to establish the effect on this system. The extraction was carried out in a well isolated double-walled cell (Figure 40) with the required temperature maintained by recirculating the water from a thermostatic bath around the cell containing experimental solution. A foam cube weighing ~0.4 g was squeezed by a single automatic squeezer for eight hours in order to establish the equilibrium. Similar experiments were performed at different temperatures ranging from 5° to 30°C. The results of experiments carried out at temperatures higher than 30°C were discarded due to very low extractions, which leads to a considerable error in the "D" values.

The thermodynamic parameters of a reaction are related to the equilibrium constant by Van't Hoff equation:

$$\log K = \frac{\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303R} \qquad (16)$$

Figure 40:

Water-jacketed distribution cell for equilibrating foam with solution at selected temperatures.



where T and R are absolute temperature and universal gas constant respectively. Assuming that ΔS and ΔH are independant of temperature, the plot of log K vs $\frac{1}{T}$ will be a straight line with a slope equal to $\frac{-\Delta H}{2.303R}$ and intercept equal to $\frac{\Delta S}{2.303R}$.

The extraction of silver (Ag^+) from picrate solution involves the following equilibria:

i. formation of ion pair

$$Ag^+(aq) + Pic^-(aq) \underset{\substack{\Delta H_1 \\ \Delta S_1}}{\overset{K_1}{\rightleftharpoons}} AgPic(aq) \tag{17}$$

ii. distribution of ion-pair between aqueous and foam phase

$$AgPic(aq) \underset{\substack{\Delta H_{ex} \\ \Delta S_{ex}}}{\overset{K_{ex}}{\rightleftharpoons}} AgPic(f) \tag{18}$$

It is obvious that a change in temperature will affect both equilibria and thus, in general the plot of log D vs $\frac{1}{T}$ will not be a straight line. However, if the initial conditions are such that $AgPic \gg Ag^+$ in aqueous phase (i.e. $D \simeq K_{1ex}$ according to equation 13) the plot of log D vs $\frac{1}{T}$ will obey the Vant Hoff relation and the slope and intercept could be used to determine ΔH and ΔS of extraction.

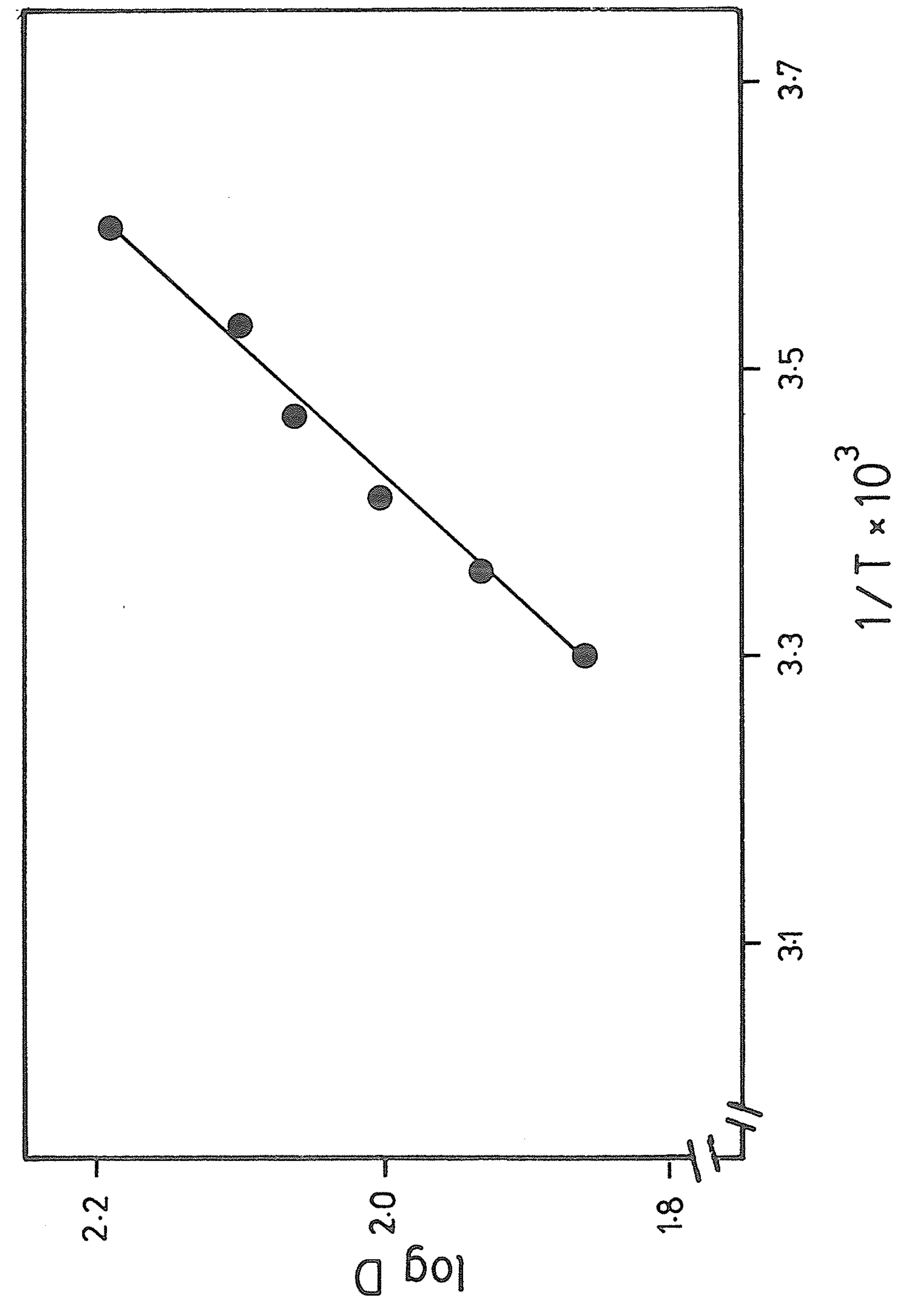
Since the experimental conditions for this study were such that AgPic was the most favoured species ($Pic \gg Ag^+$) the plot of log D vs $\frac{1}{T}$, as expected, yielded a straight line (Figure 41). The values

Figure 41

Variation of log of distribution ratio as a function of 1/T.

Initial solution conditions:

$[Ag^+]$	1×10^{-4} M
[Picric acid]	2×10^{-2} M
Solution volume	100 mL
Foam weight	0.40 g


log D
2·2
2·0
1·8
3·1
3·3
3·5
3·7
1/T × 10^3

of ΔH(-4.9 ± 1.1 Kcal/mole) and ΔS(-7.5 ± 1.7 cal/mole deg) of extraction have been calculated from the intercept and slope of the curve. Although not much can be inferred from these values of ΔH and ΔS it is obvious that the extraction process is exothermic, furthermore, the linear relationship between log D and $\frac{1}{T}$ supports the earlier assumption that $Ag^{+}Pic^{-}$ is the predominant species at higher concentration of picrate.

II. Extraction of Divalent Cations by Polyether-Based Polyurethane Foam

1. Preliminary Studies

After successfully employing the polyether based polyurethane foam for the extraction of monovalent cations from picrate and sulphonate media, the use of polyether foam was extended to divalent cations. The results of preliminary experiments indicated that polyether foam can effectively extract lead (Pb^{2+}), barium (Ba^{2+}), and mercury (Hg^{2+}) from picrate solution, whereas no measurable amounts of calcium (Ca^{2+}) magnesium (Mg^{2+}), zinc (Zn^{2+}), and cadmium (Cd^{2+}) are extracted. Based on these observations the experiments were carried out to study the effects of various parameters on the extraction of lead and barium. A few experiments were also carried out for the extraction of mercury.

As with the Tl^+ and Ag^+ systems, the formation and extraction of polynuclear species were examined by studying the dependence of distribution ratio on the metal concentration. This was achieved by studying the extraction of lead as a function of picrate for three different initial concentrations of lead (Pb^{2+}).

Foam cubes each weighing 0.40 ± 0.02 g were squeezed in a series of 100 mL solutions of 5×10^{-5}M Pb^{2+} and containing 2.5×10^{-3} to 4×10^{-2} M picric acid. The samples were withdrawn after eight hours and analyzed for lead. The same experiment was repeated for two different initial concentrations of lead (1×10^{-4} and 3×10^{-4} M),

Figure 42

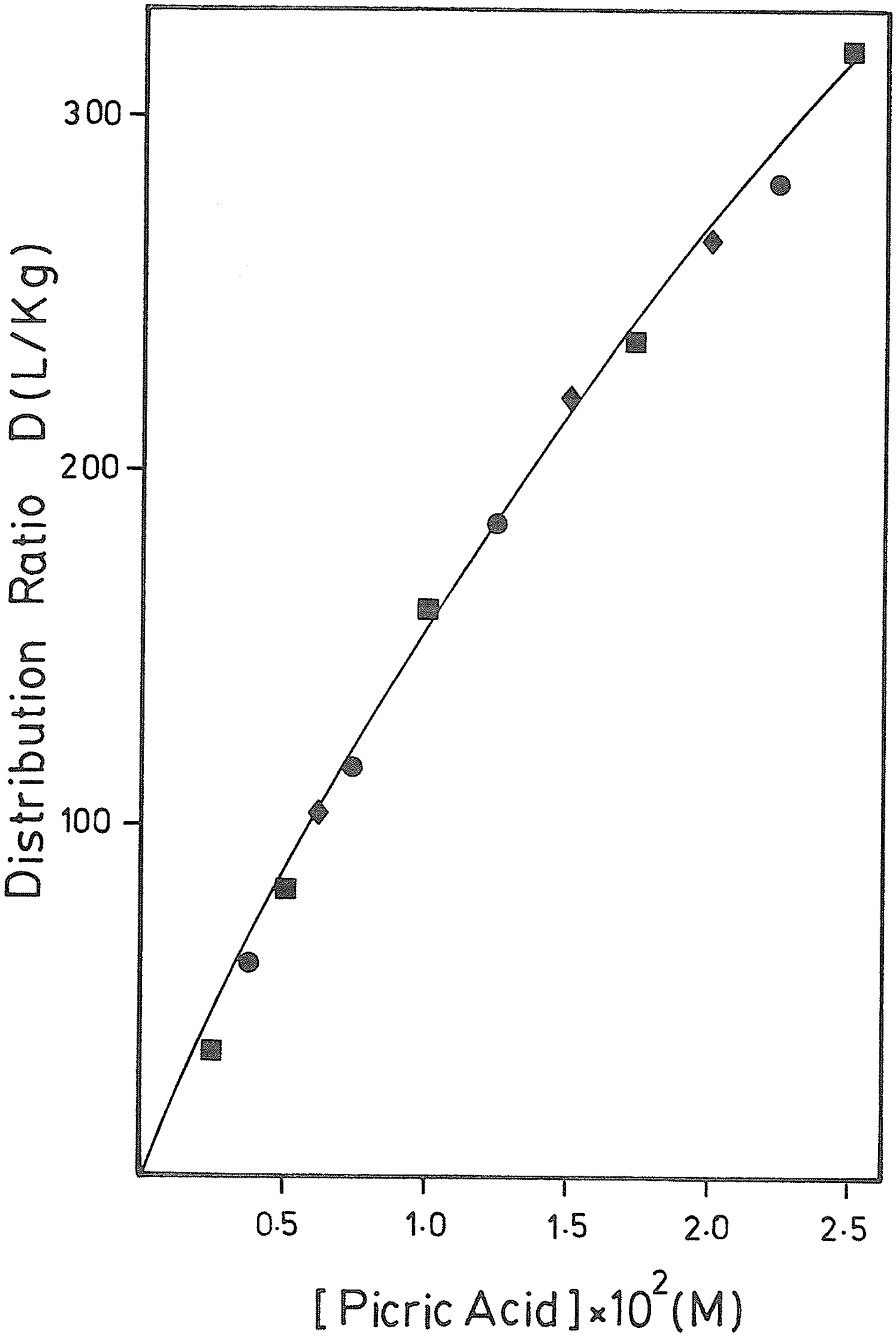
Distribution ratio as a function of initial concentrations of picric acid at different concentrations of Pb^{2+}.

Initial solution conditions:

Solution volume	100 mL
Foam weight	0.40 ± 0.02 g
Temperature	25.00 ± 0.05°C

Notes:

(■) 5×10^{-5} M Pb^{2+}
(●) 1×10^{-4} M Pb^{2+}
(◆) 3×10^{-4} M Pb^{2+}



300
200
100
Distribution Ratio D (L/Kg)
0.5
1.0
1.5
2.0
2.5
[Picric Acid] × 10^2 (M)

the results of which are also shown in Figure 42 were D values are plotted as a function of picric acid. As can be seen the plots of all three experiments are coincident i.e. the extraction is independent of metal concentration, indicating the absence of polynuclear species in the system. The cation concentrations for further experiments were kept within the above concentration range.

2. Effect of Anion Type and Concentration on the Extraction of Metal Cations

Since the efficiency of the ion-pair extraction can be improved, by adjusting the concentration of counter ion or by changing the nature of counter ion, the extraction of lead and barium was studied as a function of anion concentration for different counter ion in order to optimize the extraction.

A series of 100 mL solutions with 2.5×10^{-3} to 4×10^{-2} M of picric acid and 1×10^{-4} M in lead were extracted for ten hours with 0.40 ± 0.03 g of foam cubes. The results are presented in Figure 43. The general trend of the extraction curve is similar to those of silver and thallium picrate systems i.e. the extraction increases with increasing picric acid concentration up to 2×10^{-2} M and becomes practically constant at 3.0×10^{-2} M or greater picric acid.

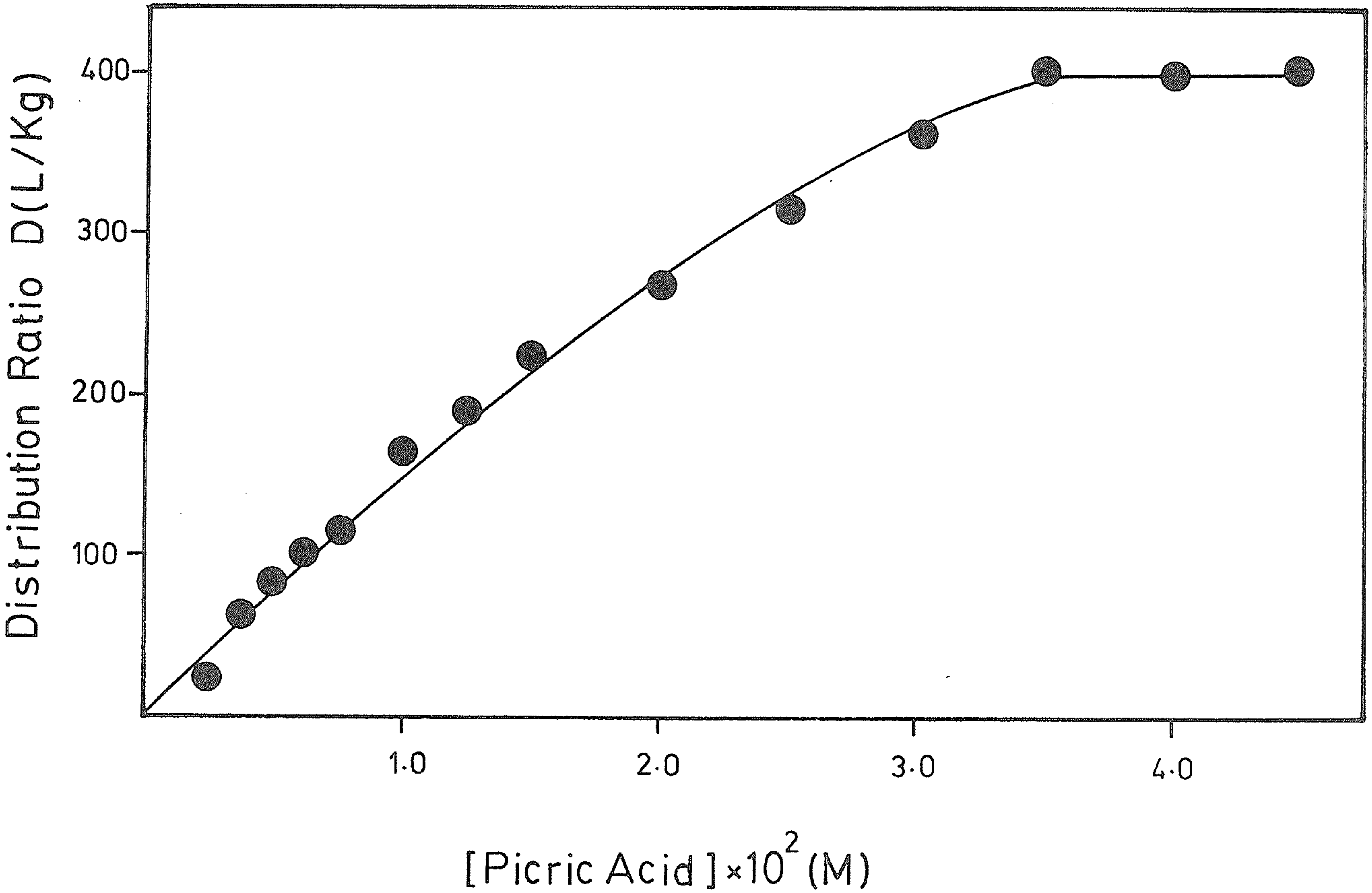
The extraction of barium into polyether foam was also studied as a function of picric acid concentration in order to improve the extraction of barium (from aqueous picrate solution). A series of 100 mL solutions of 1×10^{-4} M barium and various amounts of picric acid from 2.5×10^{-3} M to 3.5×10^{-2} M, were equilibrated with polyether foam cubes each weighing approximately 0.4 g for twelve hours. Samples were then withdrawn and analyzed for barium. The results are shown in Figure 44. The shape of the extraction curve is characteristic of the metal picrate extraction as discussed previously. The extraction increases with the addition of picric acid up to 2.0×10^{-2} M concentration above which it remains practically constant. However, comparing the extraction curve of Ba/Picrate with that of Pb/Picrate

Figure 43

Effect of varying the initial concentration of picric acid on the extraction of Pb^{2+} from aqueous solution by polyether foam.

Initial solution conditions:

$[Pb^{2+}]$	1×10^{-4} M
Solution volume	100 mL
Foam weight	0.40 ± 0.03 g
Temperature	25.00 ± 0.05°C



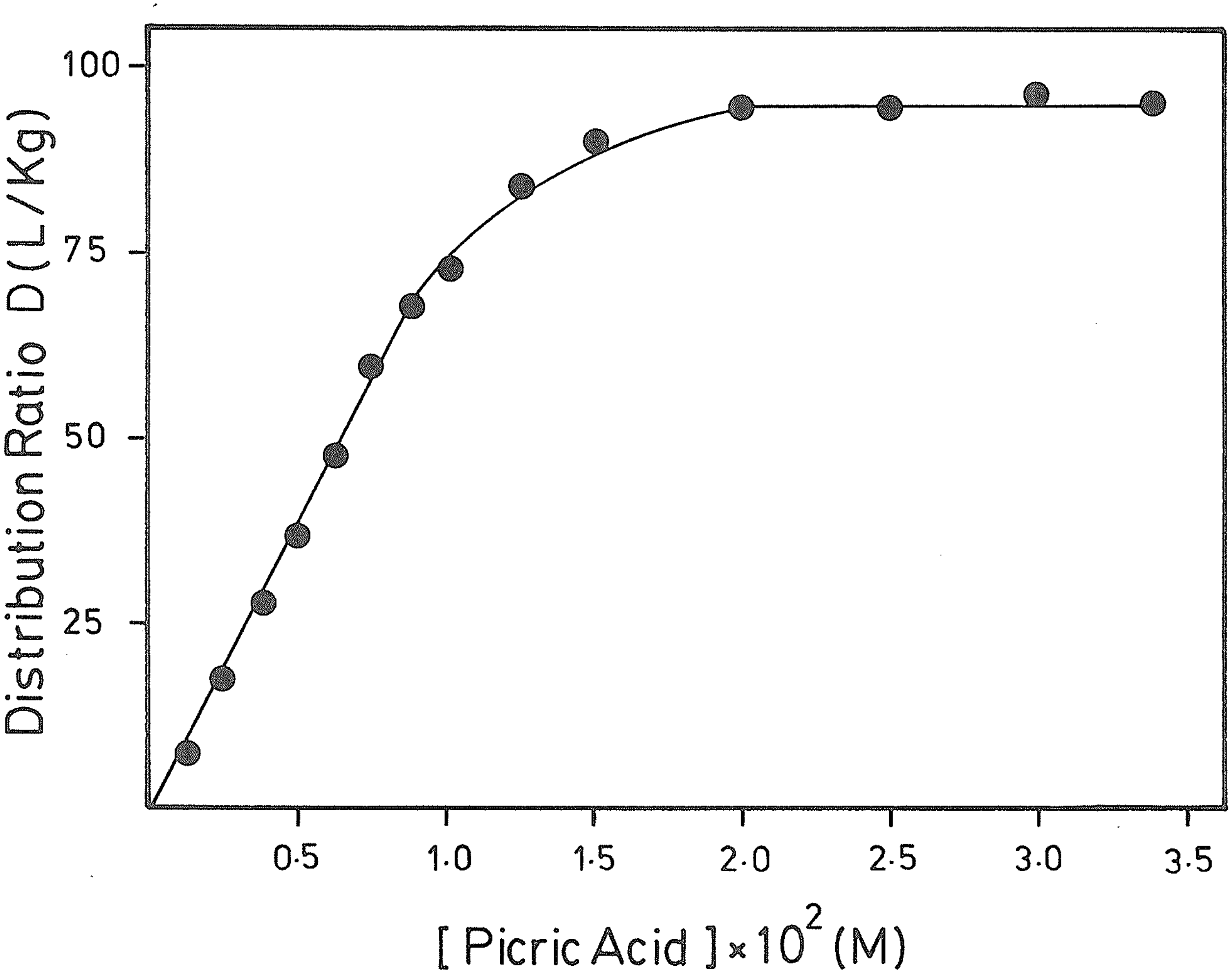
Distribution Ratio D(L/Kg)
400
300
200
100
1.0
2.0
3.0
4.0
[Picric Acid] ×10^2 (M)

Figure 44

Effect of varying the initial concentration of picric acid on the sorption of barium from aqueous solution.

Initial solution conditions:

$[Ba^{2+}]$	1×10^{-4} M
Solution volume	100 mL
Foam weight	0.40 ± 0.02 g
Temperature	25.00 ± 0.05°C


Distribution Ratio D (L / Kg)
100
75
50
25
0·5
1·0
1·5
2·0
2·5
3·0
3·5
[Picric Acid] × 10^2 (M)

it is clear that smaller sized Pb^{2+} (1.2 Å) extracts to a greater extent into polyether foam than does the larger sized Ba^{2+}(1.35 Å), in contrast to the general rule of ion-pair extraction according to which, the increase in the cation size leads to an increase in the extraction(138,139).

The sorption of Hg^{2+} (1.1 Å) from the aqueous picrate solution into polyether was also studied and a distribution coefficient of 190 ± 10 was obtained for Hg^{2+}/picrate system, higher than that of large sized barium (D = 100 ± 5) but lower than that of medium sized Pb^{2+} (D = 400 ± 18).

As has been observed earlier during the extraction of monovalent cations, and has also been reported by other workers(139), the ion-pair extraction can be improved by increasing the size of the counter ion. Therefore the extraction of both Ba^{2+} and Pb^{2+} was studied using larger anion (ANS), with the hope of improving the extraction. Foam cubes each weighing approximately 0.3 g were squeezed in 100 mL solutions of 1×10^{-4} M Pb^{2+} and various amounts of ANS ranging from 5×10^{-4} M to 5×10^{-3} M, for twelve hours to ensure the establishment of equilibrium. The results of this study along with that of a similar study done using picric acid are shown in Figure 45. As can be seen, a higher extraction of lead resulted from the bulky ANS anion solution.

The effect of bulkier anion (ANS) on barium sorption was also studied. A series of 100 mL solutions containing a constant amount of barium (1×10^{-4} M) and 5×10^{-4} to 5×10^{-3} M of ANS were equilibrated with 0.40 ± 0.02 g of polyether foam cubes for ten hours. The

Figure 45

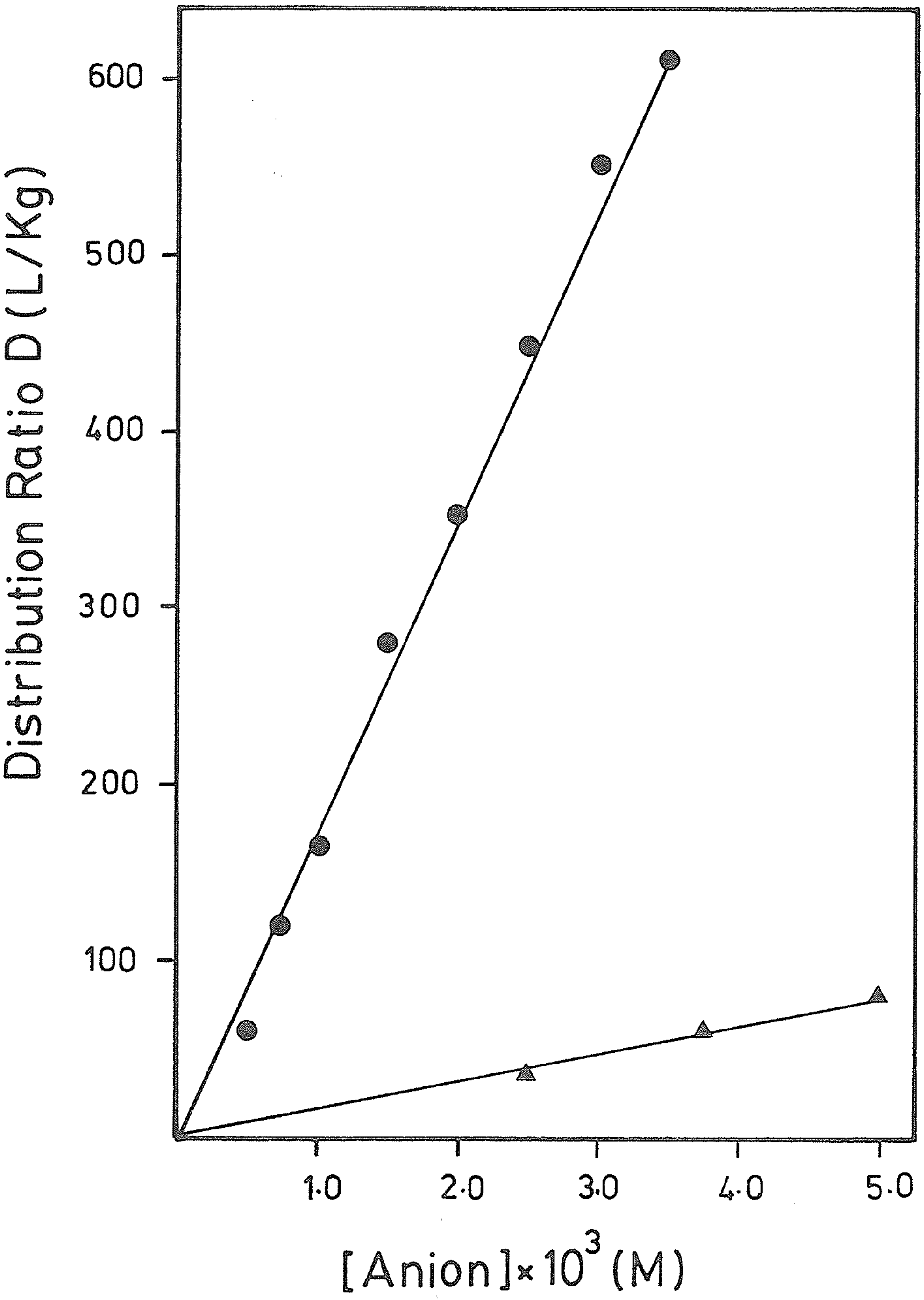
Distribution ratio as a function of initial concentration of anions.

Initial solution conditions:

[Pb]	1×10^{-4} M
Solution volume	100 mL
Foam weight	0.30 ± 0.01 g
Temperature	25.00 ± 0.05°C

Notes:

ANS	(●)
Picric acid	(▲)


Distribution Ratio D (L/Kg)
600
500
400
300
200
100
1·0
2·0
3·0
4·0
5·0
[Anion] × 10^3 (M)

samples were then analyzed for barium. The results are shown in Figure 46, where for comparison the results of a similar study, using picrate as a counter anion, are also included. As expected, the figure shows that the extraction of barium increases in the presence of bulky anion. This can be attributed to the fact that ANS due to its large size, has a low charge density which results in a low free hydration energy and thus enhances the extraction of accompanying cations into the organic phase.

Figure 46

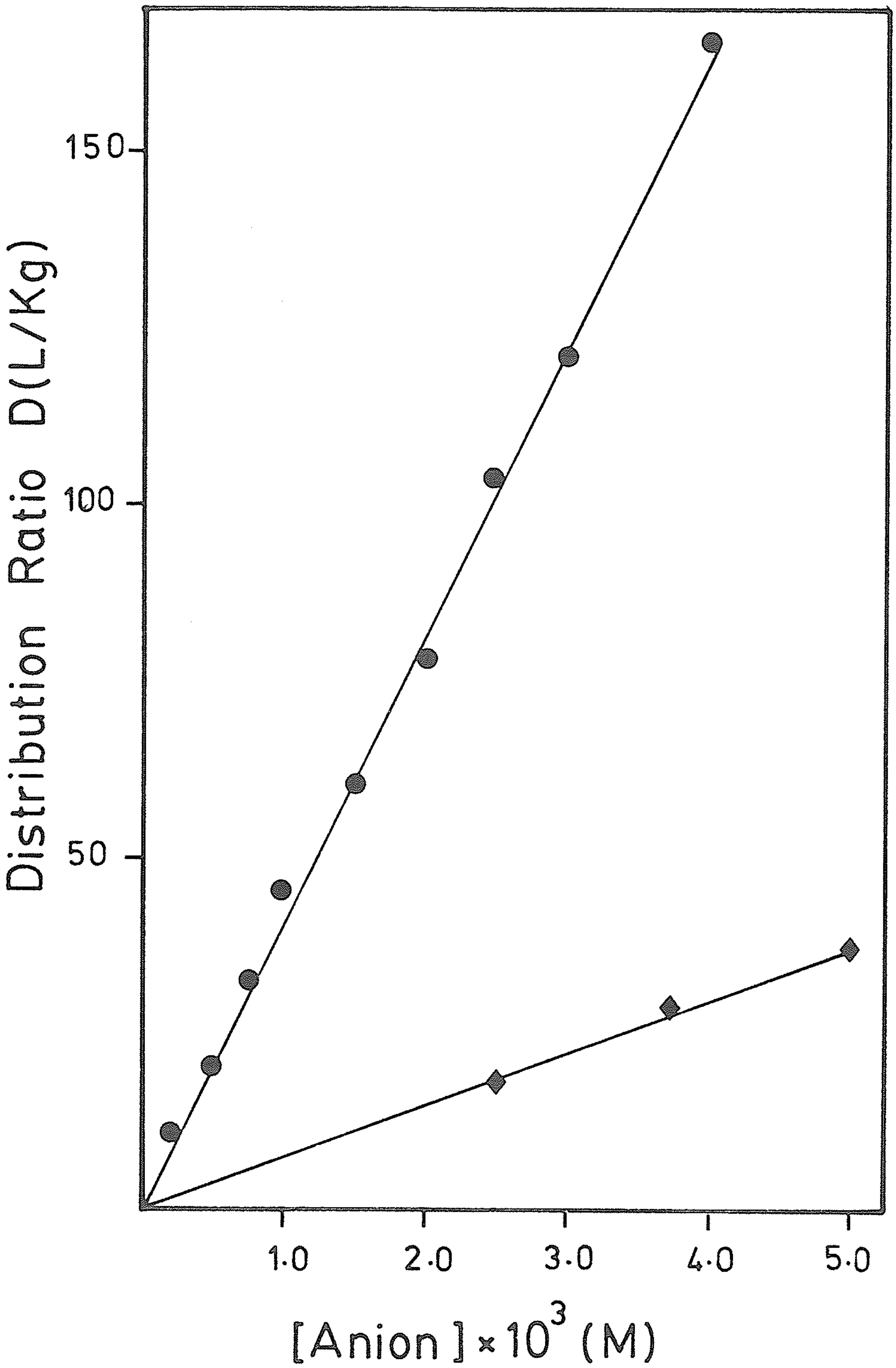
Effect of varying the initial concentration of anions on the extraction of Ba^{2+}.

Initial solution conditions:

$[Ba^{2+}]$	1×10^{-4} M
Solution volume	100 mL
Foam weight	0.40 ± 0.02 g
Temperature	25.00 ± 0.05°C

Notes:

ANS	(●)
Picrate acid	(◆)


Distribution Ratio D(L/Kg)
150
100
50
1·0
2·0
3·0
4·0
5·0
[Anion] × 10^3 (M)

3. Effect of Alkali Metal Salts on the Extraction of Lead Picrate

The ionic strength has been reported to have significant influence on the extraction of several species(22,23) into polyether foams. Experiments were carried out to study the effect of salts on the extraction of lead from picrate solution. Since the addition of ions ties up water molecules in the coordination shell, it would reduce the number of "free" water molecules available to solvate the ion-pair. Furthermore, the addition of salt also lowers the dielectric constant of the aqueous phase(140) and hence favours the formation of ion-pairs. It was therefore hoped that the extraction of lead picrate would increase with the addition of salts.

Foam cubes weighing 0.40 ± 0.02 g were equilibrated for ten hours with a series of 100 mL solutions 1×10^{-4} M in lead, 2×10^{-2} M in picric acid and containing 0.05 to 0.5 M of lithium chloride. The samples were then taken and analyzed for lead. The results of this study are shown in Figure 47. One would have expected an increase in the extraction of lead for the reasons outlined above but as can be seen, the extraction of lead drops to almost zero with the addition of lithium. Sodium and potassium interfere more severely in the extraction of lead picrate. The interference and also the order of interference i.e. $Li^+ < Na^+ < K^+$, can be explained as follows. It is quite resonable to assume that alkali metal cations are competing with lead for picrate and subsequently these ion-pairs most probably also compete for the sorption in the polyether foam. Since larger cations can compete more effectively with lead both for the ion-pair formation and for the extraction into foam, the large cation (K^+) would interfere more strongly with the extraction of lead from picrate solution.

Figure 47

Effect of alkali metal chlorides on the distribution of lead between polyether foam and aqueous picrate solution.

Initial solution condition:

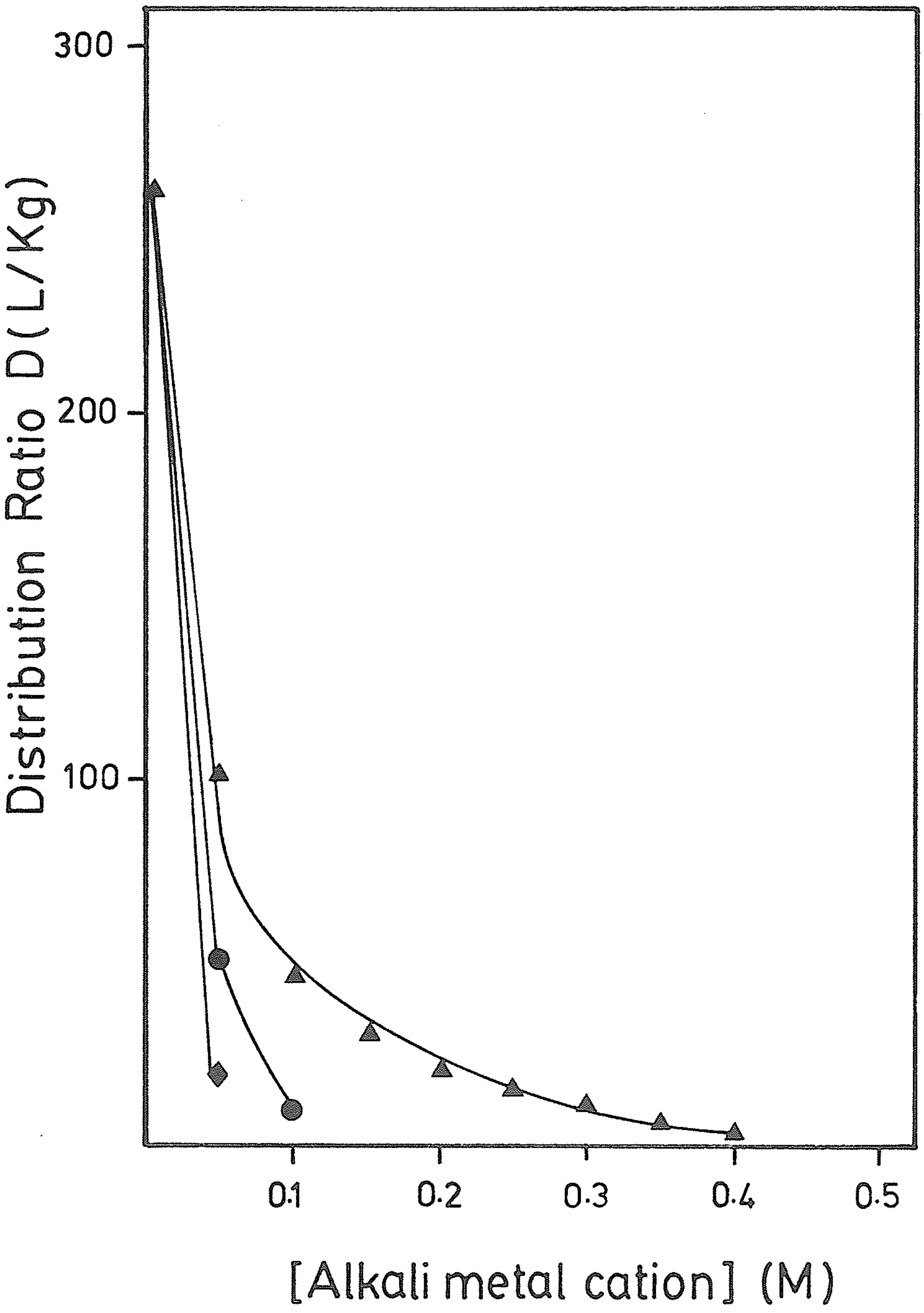
[Pb]	1×10^{-4} M
[Picrate acid]	2×10^{-2} M
Solution volume	100 mL
Foam weight	0.40 ± 0.02 g
Temperature	25.00 ± 0.05°C

Notes:

LiCl (▲)

NaCl (●)

KCl (◆)


Distribution Ratio D (L / Kg)
300
200
100
0.1
0.2
0.3
0.4
0.5
[Alkali metal cation] (M)

4. Extraction of Lead Picrate by other Organic Phases

The ability of different organic solvents, varying in polarity to extract lead-picrate was investigated. Since the similar study for Tl- picrate has revealed that dielectric constant of the non aqueous phase is not playing any significant role in the extraction, it was expected that results of this study would throw further light on the role of the dielectric constant of the organic phase in the extraction of metal-picrate.

A series of 50 mL aqueous solutions initially containing 1×10^{-4} M lead and 4.0×10^{-2} M picric acid were equilibrated with 50 mL of several organic solvent for half hour, after which both phases were analyzed for lead. The results are given in Table 8. It is clear that none of these solvents which differ in polarity, has any significant ability to extract lead picrate. This further confirms that the dielectric constant of the organic phase is not playing any important role in the extraction of metal picrates which therefore, cannot be treated as a simple solvent-like ion-pair extraction.

Different types of foam were also employed for the extraction of divalent metal cations from aqueous picrate solutions. Initial experiments showed that lead picrate extracts to the same extent by all types of polyether-based polyurethane foams (three-different types of polyether foam were tested). On the other hand, the polyester-based polyurethane foam,Dispo,appeared to be a poor extractor of lead-picrate under the same experimental conditions. Experiments were performed to compare the two types (polyether and polyester) of foam for the extraction of Pb-picrate.

TABLE 8 EXTRACTION OF LEAD PICRATE INTO VARIOUS ORGANIC PHASES

Organic Phase	Dielectric Constant (202)	Distribution Ratio D
Hexane	1.89	0.03
Benzene	2.28	< 0.01
Ether	4.325	< 0.01
Chloroform	4.8	< 0.01
Methylene Chloride	9.02	0.04
Polyester Foam b	-	$45 \pm 3^*$
Polyether Foam b	-	$400 \pm 18^*$

*D in $L\ Kg^{-1}$ for Polyurethane Foams

Conditions: 50 mL solution 1×10^{-4} M in Pb^{2+} and 4×10^{-2} M in picric acid; 50 mL of organic solvent or 0.40 gram of foam.

A series of 100 mL solutions, 1.25×10^{-3} to 1.25×10^{-2} M with picric acid and 1×10^{-4} M in lead were equilibrated for twelve hours with 0.40 ± 0.02 g of polyester foam cubes. Similar experiments were also carried out using polyether type foam. The results of these experiments are presented in Figure 48 where superiority of the polyether-based polyurethane foam is evident. Since both types of polyurethane foam differ mainly in the polyol portion of the polymer, and all types of polyether foam which differ in minor additives behave similarly for the extraction of metal picrates, it can be concluded that the ability of polyether foams to extract metal picrates is related most likely to the polyol portion of the polyether foam.

Figure 48

Comparison of Pb^{2+} extraction from aqueous picrate solution by polyether and polyester foams.

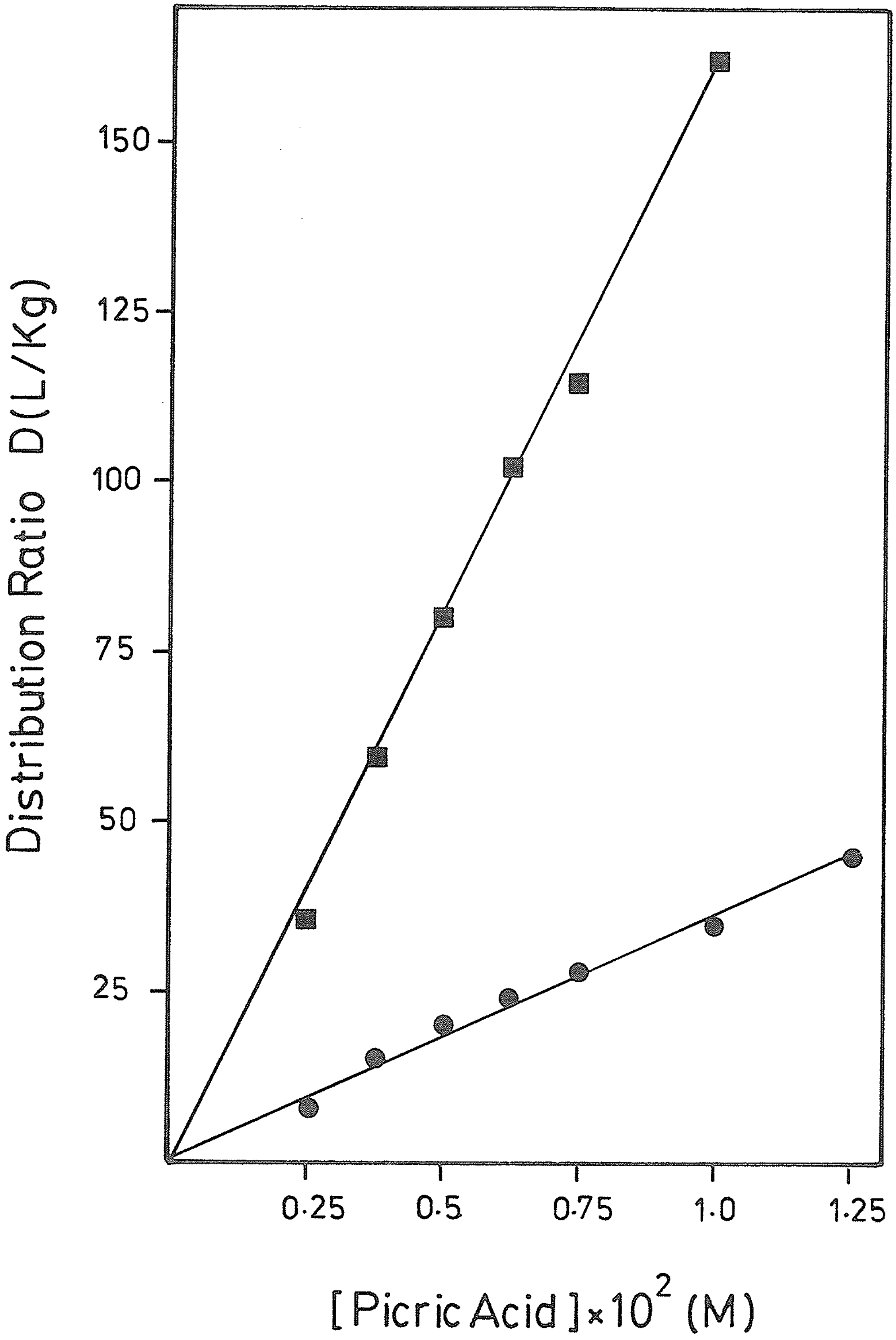
Initial solution conditions:

[Pb]	1×10^{-4} M
Solution volume	100 mL
Foam weight	0.40 ± 0.02 g
Temperature	25.00 ± 0.05°C

Notes:

Polyester foam (●)

Polyether foam (■)


Distribution Ratio D(L/Kg)
150
125
100
75
50
25
0.25
0.5
0.75
1.0
1.25
[Picric Acid]×10^2 (M)

5. Effect of Foam Weight on the Extraction of Lead Picrate

To establish the optimum aqueous foam phase ratio the extraction of lead was studied as a function of foam weight since the design of the extraction cell did not allow enough alteration in the volume used.

A series of 100 mL solutions containing 1×10^{-4} M Pb^{2+} and 2.5×10^{-2} M picric acid were equilibrated with foams of different weights ranging from 50 mg to 600 mg, for twelve hours. The results of the experiment are given in Table 9 and are also shown in Figure 49 where distribution ratio is plotted as a function of foam weight. It is evident that the distribution ratio remains constant over a wide range of foam weights. However, lower "D" values are obtained for small weights of foam and are most likely due to a large change in the aqueous to foam ratio, which results due to evaporation of the solution (Preliminary experiments showed about 2% loss in the solution volume over a period of twelve hours). Similar results were obtained for monovalent cations and have also been reported by Hamon(22) for the extraction of Co^{2+}/SCN system, and have been attributed to the change in the aqueous to foam ratio. However, when "D" values were calculated (Table 9) using the corrected aqueous to foam ratio, the situation did not improve significantly and the "D" values were still lower for small foam cubes. Thus, the decrease in distribution ratio cannot be attributed solely to the change in the aqueous to foam phase ratio. Whether the low "D" values represent ineffective squeezing of the small foams or non attainment of the equilibrium is not clear, but considering the reported(22) value of foam capacity (approximately

Figure 49

Distribution of lead between polyether foam and aqueous picrate solution as a function of foam weight.

Initial solution conditions:

[Pb^{2+}]	1×10^{-4} M
[Picric acid]	2.5×10^{-2} M
Solution volume	100 mL
Temperature	25.00 ± 0.05°C

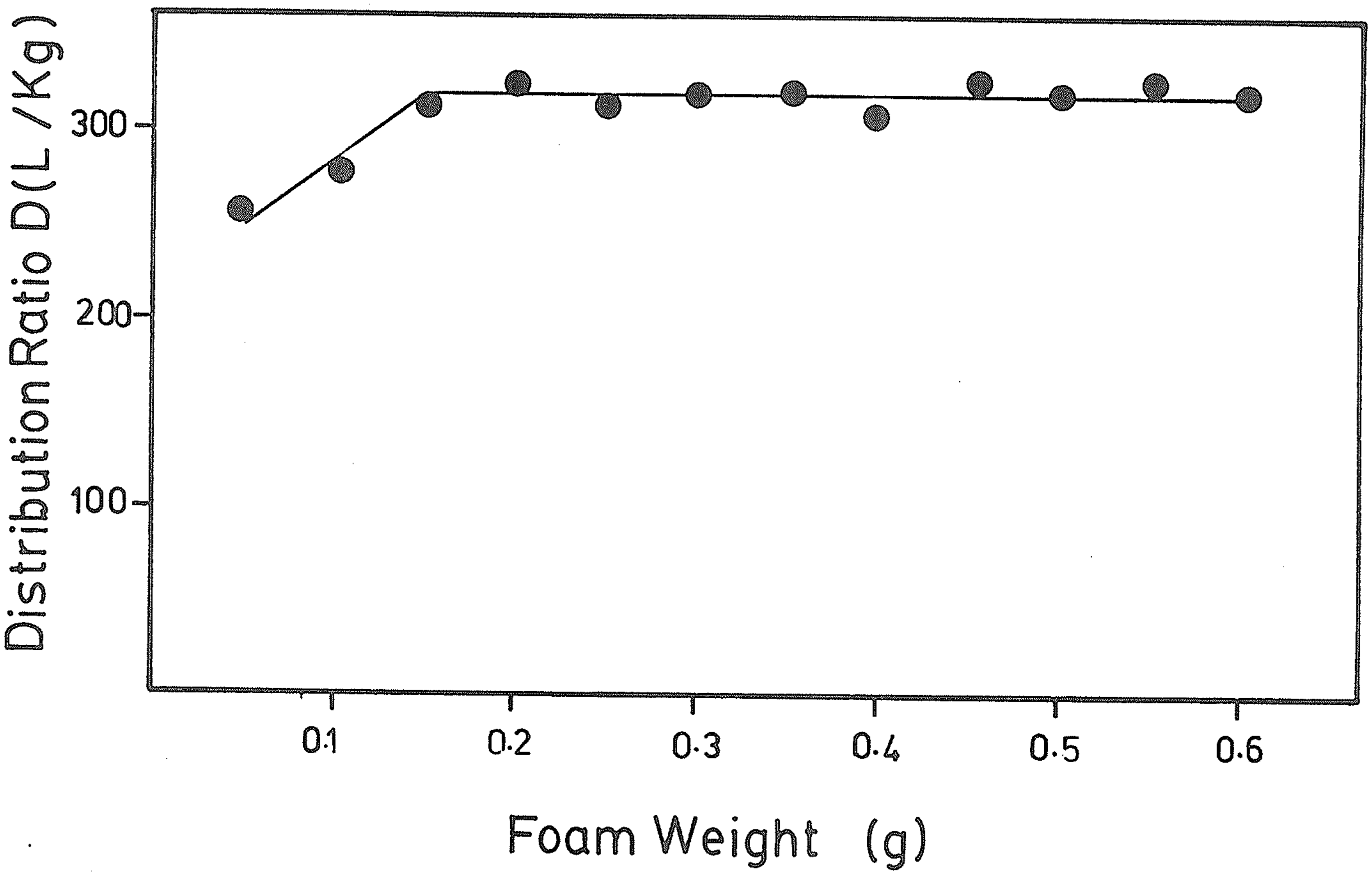

Distribution Ratio D(L /Kg)
300
200
100
0.1
0.2
0.3
0.4
0.5
0.6
Foam Weight (g)

TABLE 9 EXTRACTION OF LEAD PICRATE AS A FUNCTION OF FOAM WEIGHT

Foam Weight Gram	Distribution Coefficient (L Kg^{-1})	
	D(apparent)	D'(corrected)
0.0510	260	306
0.1001	282	308
0.1512	311	332
0.2017	320	339
0.2520	307	322
0.3011	315	328
0.3494	318	331
0.4017	308	320
0.4512	320	332
0.5008	316	327
0.5511	320	331
0.6015	315	326

Conditions: $[Pb^{2+}] = 1 \times 10^{-4}$ M, [Picric acid] = 2.5×10^{-2} M

1 milliequivalent/gram) it is most unlikely that the drop in "D" values indicates the saturation of the foam.

6. Extraction Equilibria

The following may be taken as a simplified representation of the divalent cation extraction from the aqueous solution of a bulky anion similar to that of monovalent cation system. Aggregation or dissociation of the extracted species in the foam has been neglected in this treatment.

When the aqueous phase containing a divalent metal ion (M^{2+}) and a counter anion A^-, is brought into contact with the polyether foam the equilibrium can be written as:

$$M^{2+} + 2A^- \overset{K_{ex}}{\rightleftharpoons} MA_{2f} \tag{19}$$

$$K_{ex} = [MA_2]_f/[M^{2+}][A^-]^2 \tag{20}$$

where MA_2 designates ion-pairs between the divalent metal ion (Pb^{2+}, Ba^{2+}, Hg^{2+}) and the counter anion (e.g. picrate); the subscript "f" indicate the foam phase and the absence of subscripts denote the aqueous phase; the molar concentrations are given in brackets. The constituent equilibria are:

i) Ion-pair formation

$$M^{2+} + A^- \overset{K_1}{\rightleftharpoons} MA^+ \tag{21}$$

$$K_1 = [MA^+]/[M^{2+}][A^-] \tag{22}$$

$$MA^+ + A^- \overset{K_2}{\rightleftharpoons} MA_2 \tag{23}$$

$$K_2 = [MA_2]/[MA^+][A^-] \tag{24}$$

ii) Distribution of the ion-pair between the two phases:

$$MA_2 \xrightarrow{K_{2ex}} MA_{2f} \tag{25}$$

$$K_{2ex} = [MA_2]_f/[MA_2] \tag{26}$$

according to equation 7 the distribution of metal is expressed as:

$$D = \frac{\text{Total metal ion on the foam per unit weight of foam}}{\text{Total metal ion in the aqueous phase per unit volume of solution}}$$

Using equations 21, 23 and 25

$$D = [MA_2]_f/[M^{2+}] + [MA^+] + [MA_2] \tag{27}$$

Substituting the values for $[MA_2]_f$, $[MA_2]$ and $[MA^+]$ from the equation 22, 24 and 27

$$D = K_1K_2K_{2ex}[M^{2+}][A^-]^2/[M^+] + K_1[M^{2+}][A^-] + K_1K_2[M^{2+}][A^-]^2 \tag{28}$$

$$D = K_1K_2K_{2ex}[A^-]^2/1 + K_1[A^-] + K_1K_2[A^-]^2 \tag{29}$$

$$D\ (1 + K_1[A^-] + K_1K_2[A^-]^2) = K_1K_2K_{2ex}[A^-]^2 \tag{30}$$

The values of K_1, K_2 and K_{2ex} have been estimated as follows:

a) at very high concentration of the anion one can assume that:

$$[MA_2] \quad >> [M^+] \text{ and } [MA^+]$$

equation 27 can be simplified to

$$D = [MA_2]_f/[MA_2] \tag{31}$$

$$\text{or} \quad D \simeq K_1K_2K_{2ex}[MA^{2+}][A^-]^2/K_1K_2[M^{2+}][A^-]^2 \tag{32}$$

$$D \simeq K_{2ex} \tag{33}$$

b) on the other hand, at low concentration of anion A^- it is reasonable to assume that $[M^{2+}] >> [MA^+]$ and $[MA_2]$ and thus equation 27 can be written as follows:

$$D \simeq [MA_2]_f/[M^{2+}] \tag{34}$$

$$D \simeq K_1K_2K_{2ex}[M^{2+}][A^-]^2/[M^{2+}] \tag{35}$$

$$D \simeq K_1K_2K_{2ex}[A^-]^2 \tag{36}$$

Thus the value of $K_1K_2(\beta)$ can be determined from the slope of a plot between "D" and $[A^-]^2$ for very low concentration of anion. Values of K_1K_2 and K_{2ex} have been estimated for Pb^{2+} and Ba^{2+} for the picrate system from the data presented in Table 10. Using the reported value of K_1 for Ba^{2+}/picrate system(141) and the "best fit" for Pb^{2+}/picrate the values of K_2 have also been estimated and are given in Table 11 along with the values of the other constants. Since in all experiments, $[A^-_T]$ is always $>> [M^{2+}_T]$, it is reasonable to assume that $[A^-_T] \simeq [A^-]$. Using the appropriate values of K_1, K_2 and $[A^-]$, the plots (Figure 50) of $\log D(1 + K_1[A^-] + K_1K_2[A^-]^2)$ vs $\log [A^-]$ yield straight lines with a slope of nearly two for both Pb^{2+} (1.86) and Ba^{2+} (1.90). Thus, it is reasonable to conclude that the distribution coefficient, for the extraction of a divalent metal cation into polyether foam from an aqueous solution of anion, can be adequately represented by the equation 27.

TABLE 10 EFFECT OF PICRATE CONCENTRATION ON THE EXTRACTION OF DIVALENT CATIONS BY POLYETHER FOAM

[Picric Acid] M	Distribution Coefficient (L Kg^{-1})	
	Ba^{2+}	Pb^{2+}
2.5×10^{-3}	18 ± 4	35 ± 5
3.75×10^{-3}	29 ± 3	60 ± 3
5.0×10^{-3}	37 ± 3	80 ± 4
6.25×10^{-3}	48 ± 4	102 ± 3
7.5×10^{-3}	60 ± 5	118 ± 5
8.75×10^{-3}	68 ± 5	-
1.0×10^{-2}	73 ± 3	162 ± 10
1.25×10^{-2}	84 ± 5	185 ± 10
1.5×10^{-2}	90 ± 4	220 ± 8
2.0×10^{-2}	98 ± 3	265 ± 12
2.5×10^{-2}	100 ± 5	320 ± 10
3.0×10^{-2}	98 ± 5	362 ± 15
3.5×10^{-2}	-	400 ± 18
4.0×10^{-2}	-	398 ± 15
4.5×10^{-2}	-	401 ± 16
5.0×10^{-2}	-	400 ± 12

Figure 50

Plots of log D $(1 + K_1[A] + K_1K_2 [A]^2)$ vs log [picrate acid] for divalent metal picrate systems.

Notes:

Pb^{2+} (■)
Ba^{2+} (●)

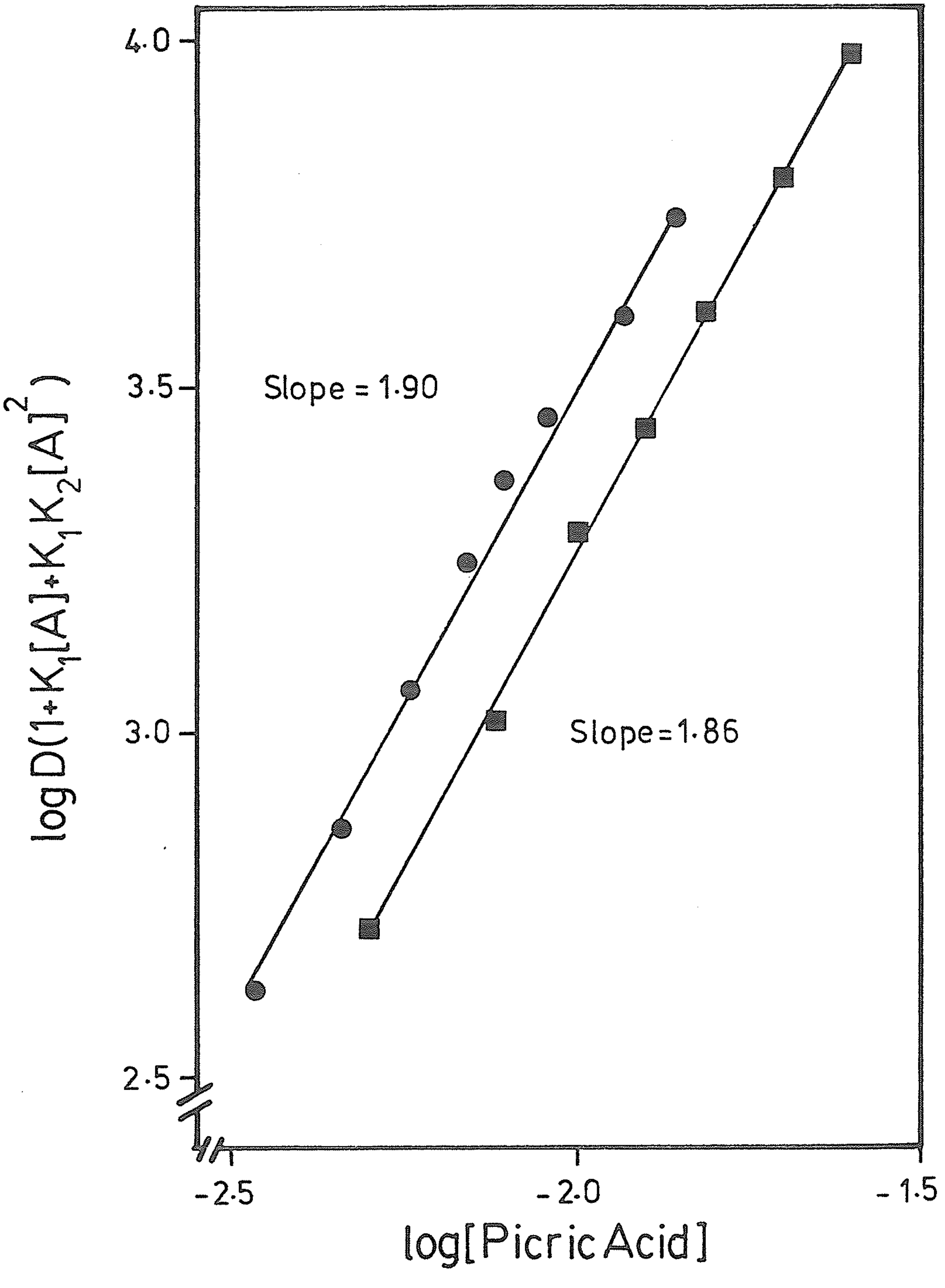

4.0
3.5
3.0
2.5
Slope = 1·90
Slope = 1·86
$\log D(1+K_1[A]+K_1K_2[A]^2)$
-2·5
-2·0
-1·5
log[Picric Acid]

TABLE 11 EQUILIBRIUM CONSTANTS K FOR LEAD, BARIUM-PICRATE ION-PAIR EXTRACTION INTO POLYETHER-BASED POLYURETHANE FOAM.

Cation	K_1(L/mol)	K_2(L/mol)	K_{2ex}(L/Kg^2)	K_{ex}(L^3/mol^{2}Kg)
Ba^{2+}	3980*	2.8	100	1.11×10^6
Pb^{2+}	1038.5	3.0	400	1.25×10^6

*Ref. No. 141

III. Extraction of Alkali Metal Cation by Polyether-Based Polyurethane Foam

As mentioned earlier, no detectable amount of alkali metals was extracted from the aqueous picrate solutions. It was thought that a higher extraction of these cations might result from a less solvating medium, and therefore, experiments were performed to study the extraction of sodium, potassium and cesium into polyether-based polyurethane foam from 80% aqueous methanol picrate solution. As expected, measurable amounts of alkali metal picrates were extracted by polyether foam. The order of extraction obtained from this study was $Na^+ < Cs^+ < K^+$. Attempts were also made to study the extraction of alkali metal ions from the aqueous solutions of some other anions e.g. ANS and tetraphenyl borate (TPB). The results of preliminary experiments indicated that only a small amount of potassium could be extracted from aqueous ANS solution by polyether foam ($D = 12 \pm 2$), whereas no detectable amount of lithium, sodium, rubidium, or cesium was extracted under similar experimental conditions. These results suggest a higher extraction of the intermediate sized potassium by polyether foam in contrast to the general principle of simple solvent-like ion pair.

The extraction of potassium and cesium was also carried out from aqueous tetraphenyl borate solutions. Polyether foam cubes each weighing about 0.10 g were squeezed for ten hours in a series of 100 mL solutions 5×10^{-5} M in potassium and containing varying amounts of sodium tetraphenyl borate ranging from 1.25×10^{-4} to 8.7×10^{-4} M. Samples were then removed and analyzed for potassium. The extraction behaviour of cesium was also studied under similar conditions except that the initial concentration of cesium was lower, (1.25 x 10^{-6} M), as the higher concentration resulted in the precipitation of $CsBPh_4$. The extraction behaviour of both potassium and cesium is shown in Figure 51. As expected, a higher extraction of both cations is obtained from the aqueous solutions of the bulkier and more hydrophobic anion (TPB).

Although different initial concentrations of potassium and cesium were used in these experiments, nevertheless, it is reasonable to compare the extraction behaviour of both cations since it is most likely that only mononuclear species are involved in the extraction of both cations. Comparing the extraction behaviour of these cations, it is clear from Figure 51, that a higher extraction of potassium than that of cesium was obtained under similar experimental conditions. A survey of the literature reveals that the extraction of alkali metals from aqueous tetraphenyl borate solution into organic solvents has been studied, and reported to increase with increasing cation size according to the principle of simple solvent-like ion-pair extraction(142). It is obvious (Figure 51) that the distribution of potassium and cesium tetraphenyl borates between aqueous phase and polyether foam does not follow the general rule of ion-pair extraction.

Figure 51:

Effect of varying the initial concentration of tetraphenyl borate on the distribution of alkali metal cations between polyether foam and aqueous solutions.

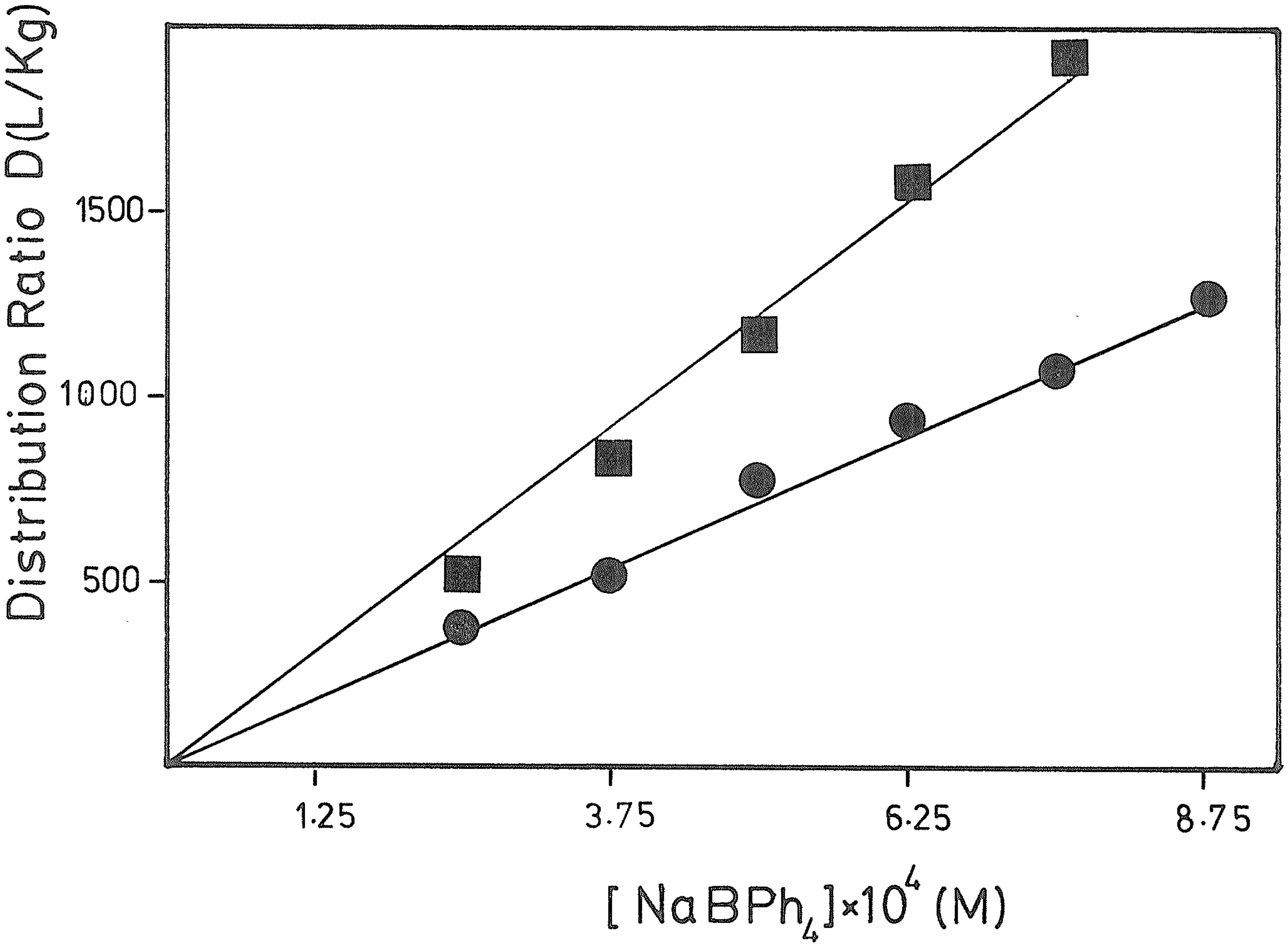
Initial solution conditions:

Solution volume	100 mL
Foam weight	0.10 ± 0.01 g
Temperature	25.00 ± 0.05°C

Notes:

(■) 5 x 10^{-5} M K^+

(●) 1.25 x 10^6 Cs^+


Distribution Ratio D(L/Kg)
500
1000
1500
1.25
3.75
6.25
8.75
[NaBPh$_4$]×10^4 (M)

D. INTERPRETATION

1. Possible Mechanism of Foam-Extraction

Based on the results presented so far, the following can be said regarding the extraction of these cations by polyether-based polyurethane foams from aqueous solutions of bulky anions such as picrate, ANS, and TPB:

i) The polarity of the organic phases does not play any significant role in the extraction of these ion-pairs.

ii) The "polyol portion" of polyurethane foam must be playing a dominant role in the extraction of ion-pairs since among the various types of polyurethane foam tested, only the polyether variety displayed special extracting ability.

iii) For a particular cation, the role of the accompanying anion is in complete accordance with the rules of simple solvent-like ion-pair extraction (i.e. bulkier and more hydrophobic anions yield higher extraction). On the other hand, in the presence of a particular anion, the sorption of both mono- and divalent cations exhibits an anomalous order of extraction, displaying a maximum for intermediate sized cations.

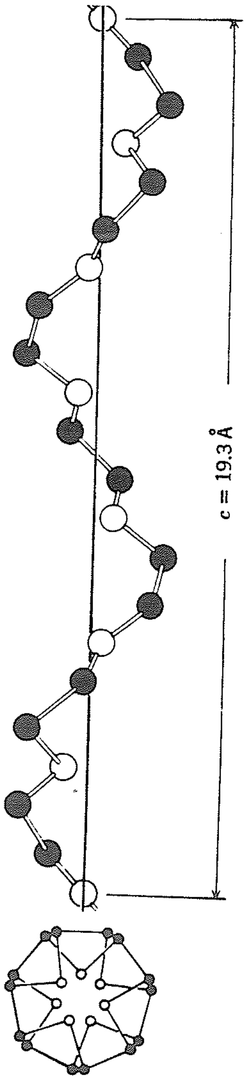
In general, no single theory can adequately describe all ion-pair extraction systems. Extraction has been variously related, for example, to the molecular weight(139), to the degree of branching on an aliphatic chain(134), and to the classical "Like Dissolves Like" theory advocated by Frieser(143). However, due to the polar nature of the ion-pairs, it is believed(138,139) that the polarity of the organic phase plays the most significant role in the extraction of ion-pairs. It has been suggested(134) that one could use the dielectric constant of the organic phase as a guide in choosing a suitable solvent for ion-pair extraction. In addition to these, the distribution of some ion-pairs has been analyzed in terms of specific solvation(144). It has also been suggested(145) that solvents containing nucleophilic sites (for example ethers) will be more effective for the solvation of ion-pairs in which the cation is smaller than the anion in size and thus has a relatively high charge density. Furthermore, it has been demonstrated that in some cases solvation of the extracted species is the dominant factor in affecting the degree of extraction.

Keeping in mind the conclusions drawn earlier regarding the extraction of ion-pairs into polyether foams, as well as the fact that the solvating ability of polyethers is now well established, it seems that the extraction of these metal cations from the aqueous solution of a bulky anion may be rationalized by the "Cation Chelation Mechanism" (CCM) proposed by Hamon(22) for the sorption of $Na_2Co(SCN)_4$ by polyether-based polyurethane foam. According to the CCM, the extraction of ion-pair ($M^{p+}X^{m-}$) in the polyether foam is due to the specific solvation or chelation of M^+ by the polyol segment of the foam.

Several reports regarding the effective solvation or chelation of the metal cations by polyethers have been mentioned earlier. In order to understand completely the solvating ability of polyether foams, however, it is necessary to consider the structural properties of poly (ethylene oxide)(PEO), the polyether polyol most commonly used in the manufacture of polyether-based polyurethane foam.

2. Complexing Ability of Poly(ethylene oxide) and its Derivatives

Numerous studies have been undertaken to determine the structure of poly(ethylene oxide) chains both in the crystalline form and in solution. From x-ray analysis(146) it has been determined that the poly(ethylene oxide) polymer chain in the crystalline state has a helical conformation, which has a unit cell containing seven structural units ($-CH_2-CH_2-O$) in two turns (as shown below):



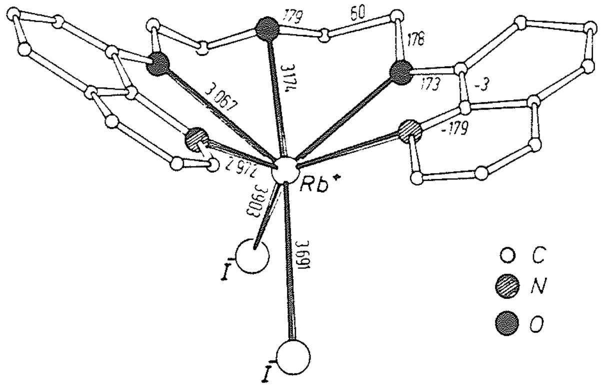
Skeletal model of Poly(ethylene oxide) incrystalline state(146). (○) oxygen atom, (●) methylene group.

I.R. and Raman(147) studies of non-aqueous solutions of poly(ethylene oxide) indicate that the polymer chains are randomly oriented in the trans and gauche conformations and thus represent a disordered structure. Other spectroscopic studies(148) have also established that the conformations of the O-C, C-C and C-O bonds are trans, gauche and trans respectively. On the other hand, the Raman spectra of the aqueous solutions show that only a very small structural change occurs upon dissolution in water(147), indicating the existance of some helical structure.

Several investigations have indicated that such an order arrangement of polyethers may be enhanced in the presence of some metal cations. Sharma and coworkers(113) have shown that K^+ and NH_4^+ cations behave as structure makers in aqueous polyether solution. The higher solubility of sodium salts in polyethers has also been ascribed(98,101) to the ability of polyethers to form a structurized solvation shell around the sodium ion. Furthermore, the complexation of polyethers with metal cations has also been attributed to the ability of the polyether chain to wrap around the cations in a spiral fashion(116). From these results, it seems that although the polyether chains may not initially exist in a spiral conformation, they can easily adopt this geometry in order to solvate the cations. The x-ray studies(117) performed on the cationic complexes of PEO and its derivatives have confirmed this idea.

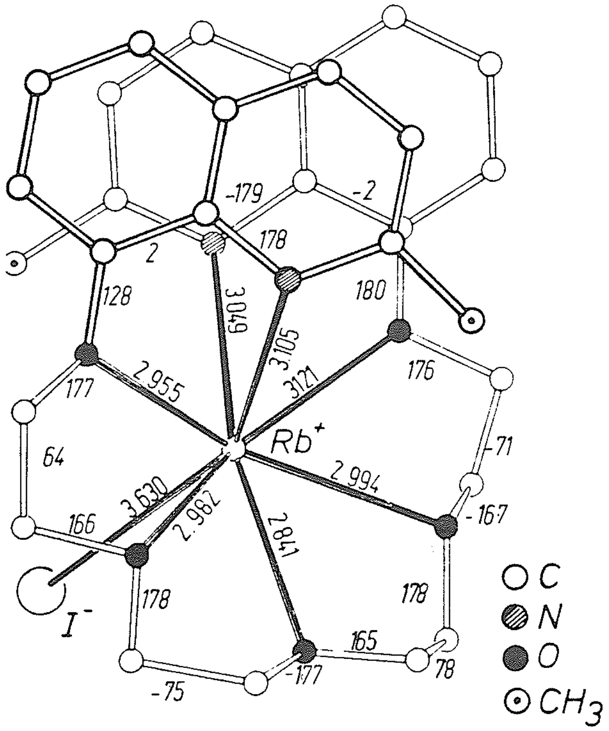
X-ray analysis(121a) of the 1:1 complex of tetraethylene glycol dimethyl ether ($CH_3O(CH_2-CH_2-O)_4-CH_3$) with $HgCl_2$ showed that the ligand is fixed in a circular geometry but does not form a closed circle. The five almost coplanar inwardly-directed oxygen atoms closely enclose the Hg^{2+} ion. Whereas, X-ray study(121c) of the mercuric complex of hexaethyl glycol diethyl ether ($C_2H_5(CH_2-CH_2-O)_6-C_2H_5$) shows that the ligand conformation is such that it utilizes seven oxygen atoms to bond two Hg^{2+} ions.

Recently W. Saenger and coworkers(117) have performed the x-ray analysis of cation complexes of arene-$(O-CH_2-CH_2)_n$-O-arene type ligands having different values of "n" in order to explore further the phenomenon of metal cation wrapping by linear polyethers. These authors have found different configurations of the ligand around the metal cation, depending upon the chain length of the polyether. The wrapping of a cation by short ligands containing five ligating atoms offers no steric problem and so ligands wrap in a circular fashion around the cation e.g. in the complex of RbI with 1,5-bis(8-quinolyloxy)-3-oxapentane (as shown below).



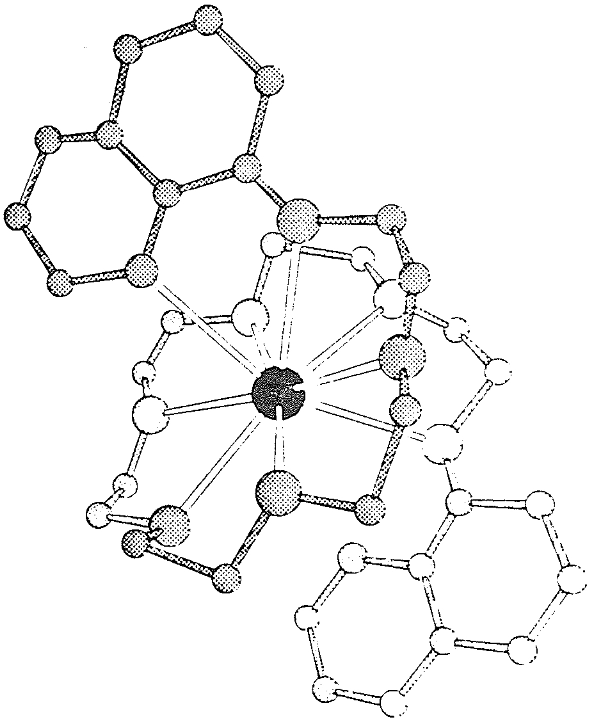
X-ray crystal structure of complex formed between RbI and 1,5-bis(8-quinolyloxy)-3-oxapentane(117).

If the ligand contains six to ten ligating atoms, it cannot wrap in a circular fashion around the cation and therefore has to adopt a helical structure. The x-ray analysis performed on the 1:1 complex of 1,11-bis(8-quinolyloxy)-3,6,9-trioxaun-decane with RbI provided the proof for a helical arrangement of the linear polyether around the cation (as shown below).


-179
-2
2
178
128
180
3.049
3.105
3.121
2.955
177
176
Rb⁺
64
71
2.994
-167
3.630
2.982
2.841
166
178
178
I⁻
165
78
-177
-75
○ C
▨ N
● O
⊙ CH₃

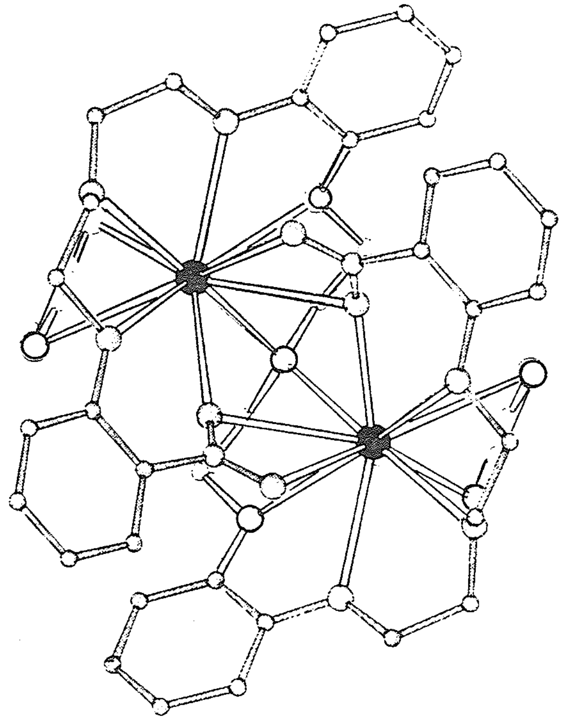
X-ray crystal structure of complex of 1,11-bis(8-quinolyloxy) -3,6,9-trioxaun-decane with RbI$^{(117)}$.

On the other hand, very long ligands containing more than ten ligating atoms, have been found to adopt two types of arrangements around the cation. For example, in the complex of Rb^{+} with 1,20-bis(8-quinolyoxy)-3,6,9,12,15,18 hexaoxaeicosane, the metal ion is spherically wrapped by the ligand with more than one turn and is thus completely shielded from the anion (see below).



X-ray structure of complex formed between Rb^+ and 1,20-bis(8-quinolyoxy)-3,6,9,12,15,18 hexaoxaeicosane$^{(117)}$.

In contrast to the spherical wrapping of the decadentate ligand around Rb^+, the ligand 1,5,-bis{2-[5-(2-nitrophenoxy)-3-oxapentyloxy]-phenoxy}-3-oxapentane is "S" shaped in the complex and binds a KSCN ion-pair in each "S" loop. The helical arrangement of the polyether chain holds only in a limited sense for this complex because, while the two K^+ cations are coordinated in circular complex-structures, these are not stacked on top of each other to form a helix but are side by side in an "S" like configuration (as shown below).



X-ray structure of complex formed between 2KSCN and 1,5,bis{2-[-(2-nitrophenoxy)-3-oxapentyloxy]-phenoxy} -3-oxapentane(117).

These studies have confirmed the ability of polyether chains to adopt a spiral type configuration in order to chelate metal cations.

The polyols most commonly used in the production of polyether-based polyurethane foam have approximately 10 to 40 (CH_2-CH_2-O) units per chain of prepolymer. Therefore, it is quite reasonable to assume that in polyurethane foam those polyether segments which are free to do so can also chelate a cation in a spiral wrap-around fashion. On the other hand, due to the limited flexibility of the ester bond, it is difficult for a polyester-based polyurethane foam to adopt a helical conformation. Furthermore, since the polyester polyols usually employed in manufacturing the foam contain large numbers (8 to 16) of carbon atoms in each monomer unit, the result is a decrease in the density of oxygen atoms and also an increase in the size of any possible cage formed. The possibility of a polyester chain effectively solvating the metal cation in a spiral wrap-around fashion i.e. chelating it seems remote, therefore based on this information, the effective sorption of a metal cation from an aqueous solution of bulky anions by polyether foam can be attributed to the ability of polyether polyol to adopt a special conformation which forms a solvation shell around the cation by completely or partially replacing the hydration shell. As far as the conformation of the cationic complex is concerned, we have no means to distinguish whether the polyether chain is spherically wrapped around the cation with more than one turn to form a helix (and thus completely shielding the cation from the anion) or if the polyether chain adopts an "S" like conformation in which the individual cations are not entirely shielded. In the latter case, the accompanying anions would most likely be closely associated with the cations to form a contact ion-pair in each loop.

After formulating the mechanism of ion-pair extraction by polyether type polyurethane foam, experiments were carried out to investigate further the cation complexing ability of polyether foam to acquire some experimental evidence in favour of the C.C.M. and also to explain the order of extractability displayed by polyether foam.

3. Experimental Tests of Cation Chelation Mechanism

a. Cation Selectivity Measurements

The extraction of a bulky and hydrophobic anion, such as picrate, in the presence of a large excess of metal ions has been used as the measure of complexing ability in the case of crown ethers by Pedersen(130) for macrotetralide actin antibiotics by Eisenman(131) and also for linear polyethers by several other workers(132). A similar procedure was adopted here in order to investigate further the effectiveness of the polyether-based polyurethane foam as a complexing agent for metal ions because it is a very rapid and simple method. Furthermore, although this is a semi-quantitative approach and the complexing efficiencies can only be ranked numerically, it is also a convenient way of comparing the relative complexing power of the polyether for different cations.

In the present experiments, a series of 90 mL aqueous solutions, 5×10^{-5} M in picric acid and 0.1 M in alkali metal chloride were equilibrated for twelve hours with polyether foam cubes each weighing 0.20 ± 0.01 g. Samples were then removed and analyzed for picrate spectrophotometrically. The results are summarized in Table 12, and show that the extraction of picrate increases, passes through a maximum at potassium, and then falls off as the size of the alkali metal cation increases. The extraction of picrate was also studied under varying picrate and cation concentrations in order to confirm the sequence of extraction. The results of these studies are also summarized in Table 12. It is clear from these results that under

TABLE 12 EFFECT OF COMMON SALTS ON THE SORPTION OF PICRATE BY POLYETHER-BASED POLYURETHANE FOAM

Experiment I:

Conditions:

[Picrate]	5×10^{-4} M
[Cation]	0.1 M
Solution volume	90 mL
Foam weight	0.20 ± 0.01 grams

Cation	Distribution Ratio (L Kg^{-1})
Li^+	495
Na^+	582
K^+	750
Rb^+	685
Cs^+	590
NH_4^+	745

TABLE 12

Experiment II:

Conditions:

[Picrate]	2.5×10^{-4} M
[Cation]	0.1 M
Solution volume	90 mL
Foam weight	0.15 ± 0.01 grams

Cation	Distribution Ratio (L Kg^{-1})
Li^+	147
Na^+	155
K^+	242
Rb^+	215
Cs^+	161
NH_4^+	220

TABLE 12

Experiment III

Conditions:

[Picrate]	2.5×10^{-4} M
[Cation]	0.2 M
Solution volume	90 mL
Foam Weight	0.25 ± 0.01 grams

Cation	Distribution Ratio
Li^+	215
Na^+	253
K^+	361
Rb^+	286
Cs^+	220

TABLE 12

Experiment IV:

Conditions:

[Picrate]	5 x 10^{-5} M
[Cation]	0.1 M
Solution volume	90 mL
Foam weight	0.3 ± 0.01 grams

Cation	Distribution Ratio (L Kg^{-1})
Li^+	350
Na^+	474
K^+	602
Rb^+	580
Cs^+	490
NH_4^+	655

different initial concentrations of picrate and alkali metal cation, polyether foam exhibits the same order of selectivity. The results of one such study are also shown in Figure 52a where the distribution coefficient is plotted against the cation size. For comparison, data reported by Pedersen(130) for 18-crown-6 is also presented in Figure 52b. It is interesting to note that both 18-crown-6 and polyether foam have the same sequence of selectivity (i.e. $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$).

Experiments were also carried out to study the effect of divalent cations on the extraction of picrate by polyether-based polyurethane foam. Foam cubes each weighing approximately 0.1 g were squeezed for twelve hours in a series of solutions each 2.5×10^{-4} M in picric acid and 0.1 M in divalent cation (added as a nitrate). Samples were then withdrawn and analyzed for picrate. The results in Figure 53 show that like the alkali metal series, the extraction of picrate by polyether-based polyurethane foam also displays a maximum for an intermediate-sized cation (Pb^{2+}) in this case.

The extraction of 8-anilino-1-naphthalene sulphonate (ANS) in the presence of various cations was also studied to further confirm the order of selectivity of polyether type polyurethane foam for mono- and divalent cations. A series of 90 mL solutions, 1×10^{-3} M in ANS and 2.5×10^{-2} M in metal cation, were equilibrated with 0.20 ± 0.02 g cubes of polyether foam. After twelve hours, samples were analyzed spectrophotometrically for ANS. It is clear that as with the picrate system, these results (shown in Figure 54) also exhibit the high specificity of polyether-based polyurethane foam for potassium among

Figure 52

a) Sorption of picrate from solutions containing various alkali metal cations by polyether foam.

Initial solution conditions:

[Picric acid]	5×10^{-5} M
[Cation]	0.1 M
Solution volume	90 mL
Foam weight	0.20 ± 0.019

b) Extraction of 7×10^{-5} M picrate from aqueous solution by 7×10^{-5} dicyclohexyl 18-crown-6 in methylene chloride, 0.10 M cation and equal volume phases.

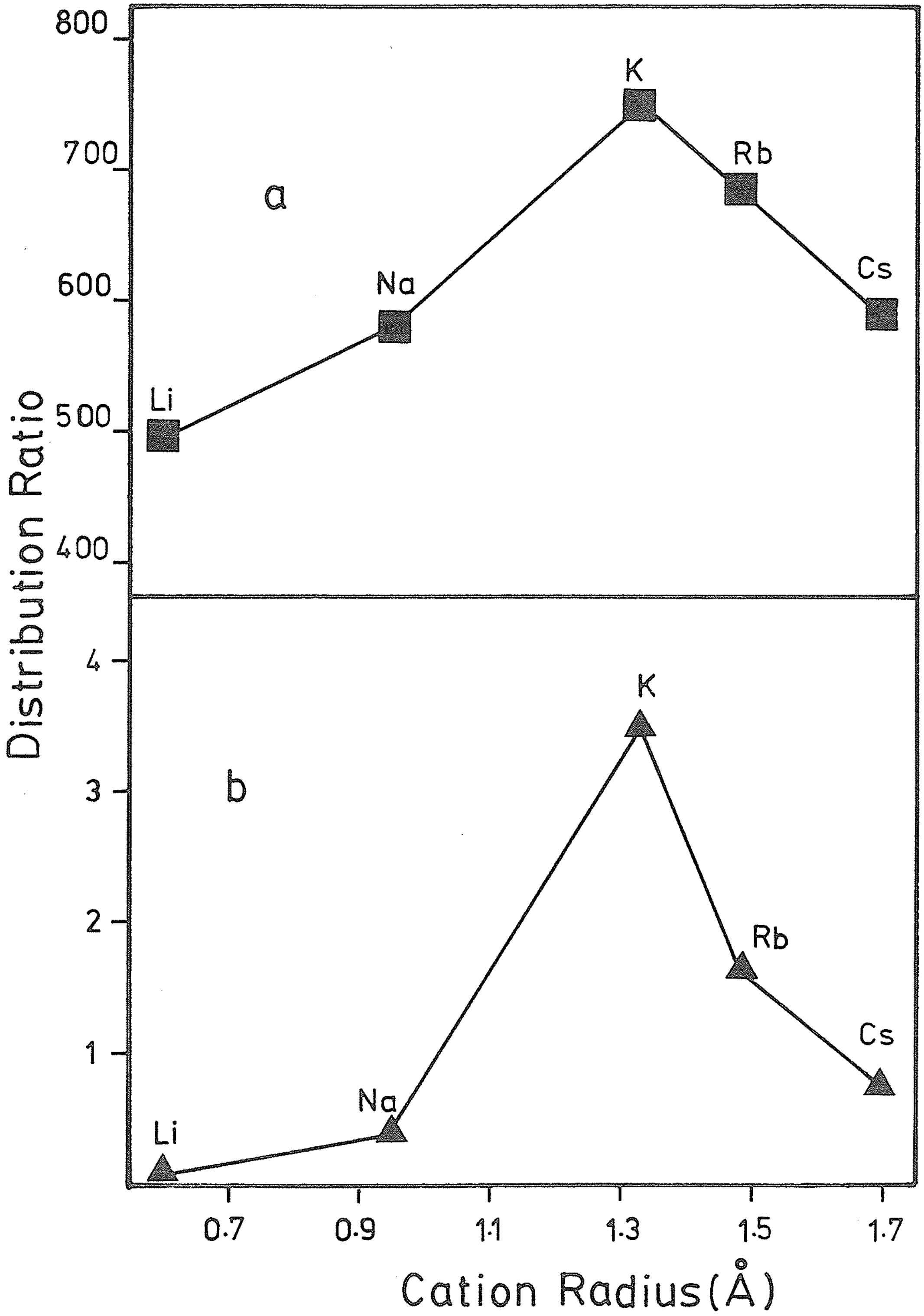

a
b
Li
Na
K
Rb
Cs
Li
Na
K
Rb
Cs
800
700
600
500
400
4
3
2
1
0.7
0.9
1.1
1.3
1.5
1.7
Distribution Ratio
Cation Radius(Å)

Figure 53

Extraction of picrate from aqueous solutions containing various divalent cations by polyether foam.

Initial solution conditions:

[Picric acid]	2.5×10^{-4} M
[Cation]	0.1 M
Solution volume	90 mL
Foam weight	0.10 ± 0.01 g

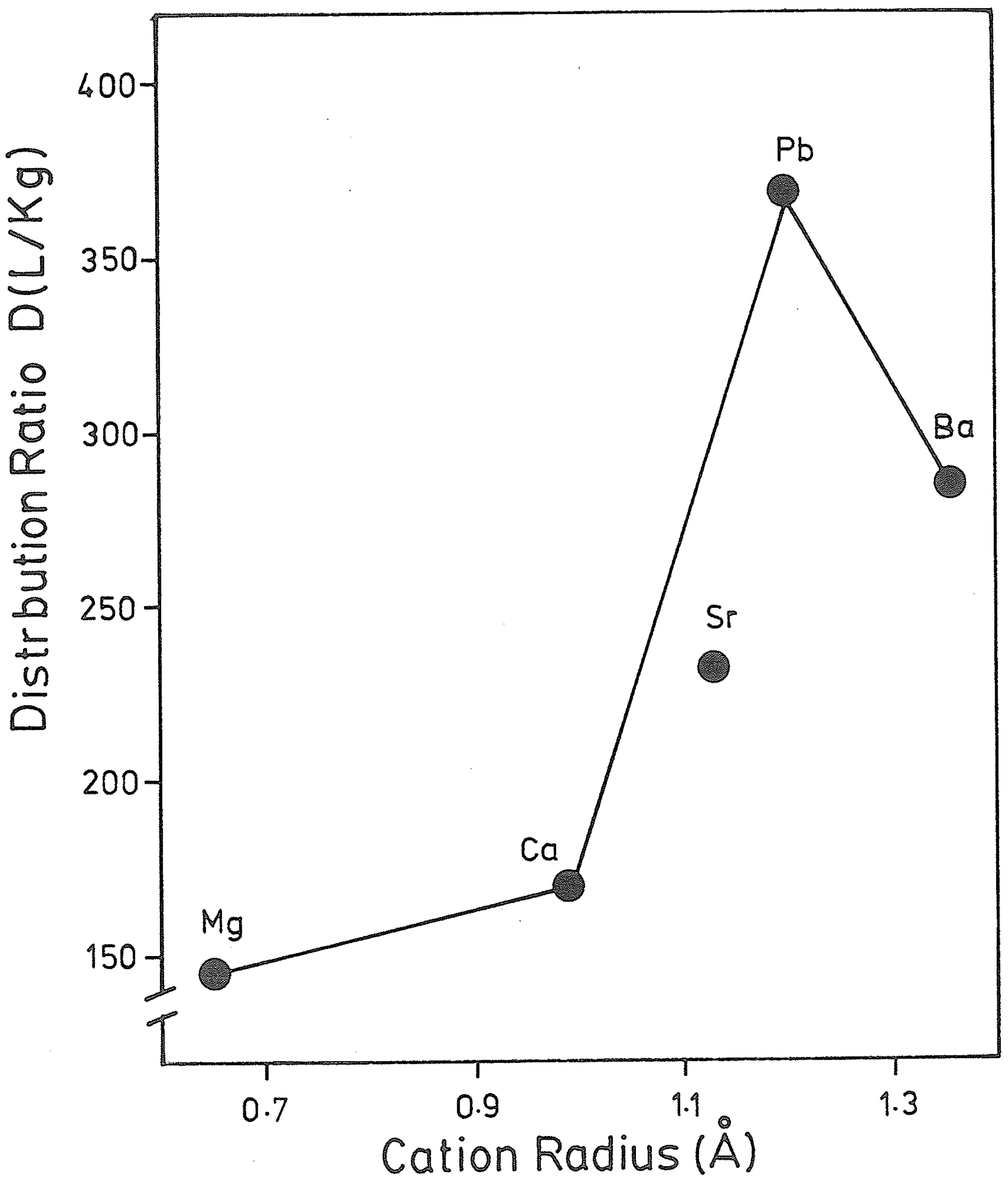
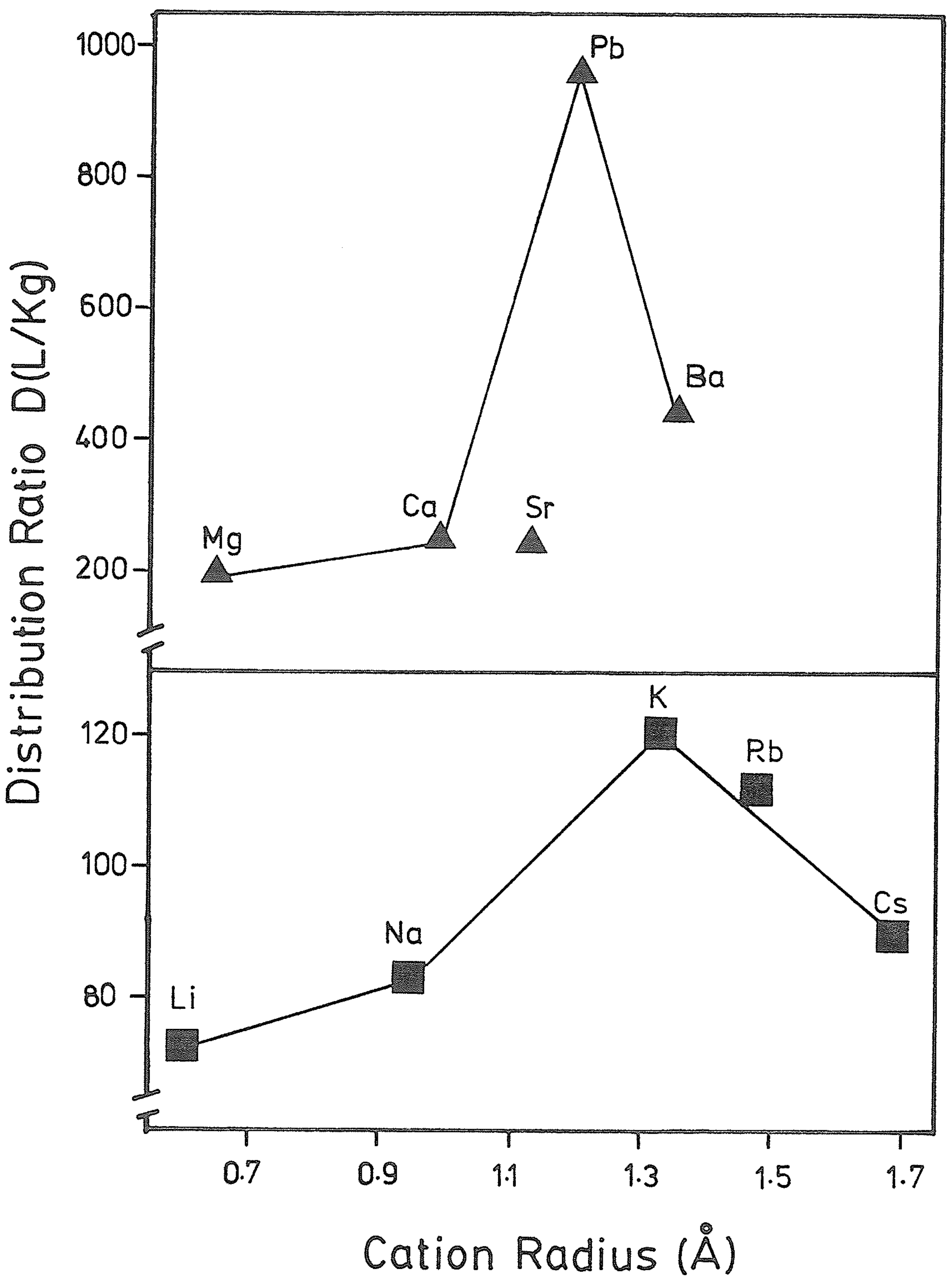

Distrbution Ratio D(L/Kg)
400
350
300
250
200
150
Pb
Ba
Sr
Ca
Mg
0·7
0·9
1·1
1·3
Cation Radius (Å)

Figure 54

Sorption of ANS from solutions containing various mono- and divalent-cations by polyether foam.

Initial solution conditions:

[ANS]	1×10^{-3} M
[Cations]	2.5×10^{-2} M
Foam weight	0.20 ± 0.02 g
Solution volume	90 mL


Distribution Ratio D(L/Kg)
1000
800
600
400
200
120
100
80
Pb
Ba
Ca
Sr
Mg
K
Rb
Cs
Na
Li
0.7
0.9
1.1
1.3
1.5
1.7
Cation Radius (Å)

alkali metal ions and for lead among the divalent metals studied.

In order to confirm that the order of selectivity exhibited by polyether foam for mono- and divalent cations is not limited to metal cations, the sorption of picrate in the presence of some different type of cations was also studied. Tetraalkyl ammonium ions were chosen for this purpose because the solvent extraction of picrate into chloroform in the presence of these ions has been reported in the literature(139).

A series of solutions, 5 x 10^{-5} M in picrate and 0.1 M in the specific cation, were extracted for twelve hours with 0.20 ± 0.01 g of polyether foam cubes. Samples were then analyzed for picrate. The results are summarized in Table 13. It is clear that picrate extraction does not follow a steady trend in going from NH_4^+ (the smallest cation) to Bu_4N^+ (the largest cation) as might be expected on the basis of simple ion-pair extraction into an organic solvent(139). In particular, the small cation (NH_4^+) produces higher picrate extraction than do larger (Me_4N^+, Et_4N^+) cations. Although it is most likely that simple ion-pair solvent-like extraction may be the predominant mechanism for the largest cation (Bu_4N^+), the higher extraction of picrate resulting in the presence of NH_4^+ is in complete agreement with the previously observed higher affinity of polyether foam for intermediate sized cations.

Based on the information obtained from several types of experiments, it appears that polyether-based polyurethane foam has the following order of selectivity for various cations: $Li^+ < Na^+ < Cs^+ < Rb^+ < K^+ < Ag^+ \sim Tl^+$ for monovalent cations and $Mg^{2+} < Ca^{2+} < Sr^{2+}$

TABLE 13 EFFECT OF SPECIFIC CATIONS ON THE SORPTION OF PICRATE BY POLYETHER-BASED POLYURETHANE FOAM

Cation	Distribution Ratio, D(L Kg^{-1}) Picrate
NH_4^+	800
Me_4N^+	245
Et_4N^+	630
Bu_4N^+	3300

Conditions: 0.1 M concentration of cations, 5×10^{-5} M picrate, and 0.1 g of foam.

$< Ba^{2+} < Hg^{2+} < Pb^{2+}$ for divalent cations. It is interesting to compare this with the order of stability constants reported by Christensen et al(47) for the "A" isomer of dicyclohexyl 18-crown-6: $Li^+ < Cs^+ < Na^+ < Rb^+ < K^+ < Ag^+ < Tl^+$ for monovalent cations and $Ca^{2+} < Hg^{2+} < Sr^{2+} < Ba^{2+} < Pb^{2+}$ for divalent cations. With a few minor exceptions, these two sequences of affinity are basicially the same, both showing distinct maxima for K^+ among the alkali metals and for lead among divalent cations. Yanagida et al(115) have also reported that there is no remarkable difference between the selectivity order for alkali and alkaline earth metal ions of non cyclic poly(ethylene oxide) derivatives and of 18-crown-6. Brierly et al(149) have also observed a sequence of extraction by Triton X-100 (a derivative of PEO) similar to that of 18-crown-6 for the alkali metal picrates. Furthermore, the complexing ability for mono- and divalent cations of another series of derivatives of PEO of the type $H_{3-n}(CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2)_n\text{-}NH_{3-n}$ n = 1 to 3 has also been studied(150). The following order of stability constants has been reported: $Ag^+ > Tl^+ > K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$ for monovalent cations and $Hg^{2+} > Pb^{2+} > Ba^{2+} > Sr^+ > Ca^{2+}$ for divalent cations.

The close similarity between the order of selectivity of 18-crown-6 and that of linear polyethers suggests that in spite of the very flexible nature of the polyether chain, it prefers to adopt a conformation which can mimic 18-crown-6. This idea is further supported by the fact that theoretical analysis also confirms that the most easily adopted conformation of poly(ethylene oxide) chains is that of 18-crown-6(151).

In view of these many facts, the order of cation selectivity displayed by polyether-based polyurethane foam can be attributed to its ability to behave as pseudo 18-crown-6. It is to be stressed here that differences between the linear and cyclic polyethers are quantitative only and both of them may be regarded as representatives of a single class of multidentate ligands binding the metal cation by the formation of a "solvate sheath".

b. Anion Selectivity

Having discussed the sequence of cation selectivity displayed by polyether-type polyurethane foam, we will now consider the order of affinity exhibited by foam for various anions. The results presented earlier clearly suggest that the efficient extraction of both mono- and divalent cations into polyurethane foam partly attributed to the presence of bulky anions, and increases in the following order:

$$NO_3^- < \text{2,4-dinitrophenolate}^- \sim \text{2,6-dinitrophenolate}^- < ClO_4^- < \text{picrate}^- < ANS^- < TPB^- .$$

It is interesting to note that A. Warshawsky and coworkers(152) have recently reported the synthesis and the complexation of polymeric pseudo crown ethers (PPCE) with salts of transition metal anion complexes such as MX_4^- or MX_4^{2-} ($M = Au^{3+}$, Fe^{3+} and Zn^{2+}, $X = Cl^-$, Br^- and I^-). These authors have concluded that the extent of complexation depends mainly upon the ability of the anion (and not the cation) to fit into the cavity of the PPCE. However, based on the universal law "Like charges repel each other" the solubilization of negatively charged anions (such as picrate, ANS, and TPB, etc) into the cavity formed by negatively charged inwardly directed oxygen atoms seems very remote. The observed order of extractability can be attributed more easily to differences in hydration of the anion in the aqueous phase (although differences in the solvation of these anions in the foam will also be of some importance). Furthermore, as we will observe later for phosphomolybdate ($PMo_{12}O_{40}^{3-}$), the charge on the anion also plays a very significant role in determining the mode of ion-pair extraction into polyether-based polyurethane foam.

Importance of the anions also has been reported for metal-crown ether systems. Pedersen(42, 130) noted right at the beginning of his studies that the extraction of cations is effective only in the presence of large and easily polarizable anions. Suzuki and co-workers(129) have also reported that the sorption of potassium by poly(styrene) bound PEO chains increases with increasing hydrophobicity of the counter anion. Recently, Marcus and Asher(55) have discussed many factors which are important to the extractability of anions in a metal-crown ether system. They concluded that the extent depends mainly on the free energy of hydration of the anion in the aqueous phase and also on the free energy of solvation in the corresponding organic solvent. Thus, it appears that the extraction of ion-pairs by polyurethane foam will depend on the effective sorption of both cation and anion and that their joint extractability will be limited by that of either individual ion.

c. Polymer Sorption Abilities

We have already noted that differences exist between the extraction behaviour of polyether-type foam and that of polyester-type foam, with the latter behaving more like simple solvent extractor. To substantiate this interpretation further, experiments were carried out to compare the extraction behaviour of polyester and polyether foams for the sorption of picrate and ANS in the presence of alkali metal cations.

A series of solutions, 5×10^{-5} M in picric acid and 0.1 M in alkali metal chloride, were equilibrated for twelve hours with polyester foam cubes, each weighing approximately 0.2 g. Samples were then withdrawn and analyzed spectrophotometrically for picrate. The results of this study are shown in Figure 55 where, for comparison, the results of a similar study using polyether foam are also included. As can be seen, for polyester foam the extraction of picrate increases slightly as the size of the accompanying cation increases from Li^+ to Cs^+. This extraction trend is in complete agreement with rules of simple solvent-like ion-pair extraction. Polyether foam, however, exhibits a distinct maximum for the intermediate-sized potassium ion. Similar behaviour was also observed for the extraction of ANS by polyester and by polyether foams in the presence of alkali metal cations (Figure 56). These results provide additional support to the idea of polyester foam behaving much like a simple solvent extractor. On the other hand, polyether foam, due to its ability to adopt a

Figure 55

Comparison of picrate extraction from solutions containing various alkali metal cations by polyether- and polyester-based polyurethane foam.

Initial solution conditions:

[Picric acid]	5×10^{-5} M
[Cation]	0.1 M
Solution	90 mL
Foam weight	0.20 ± 0.01 g

Notes:

Polyether foam (●)

Polyester foam (■)

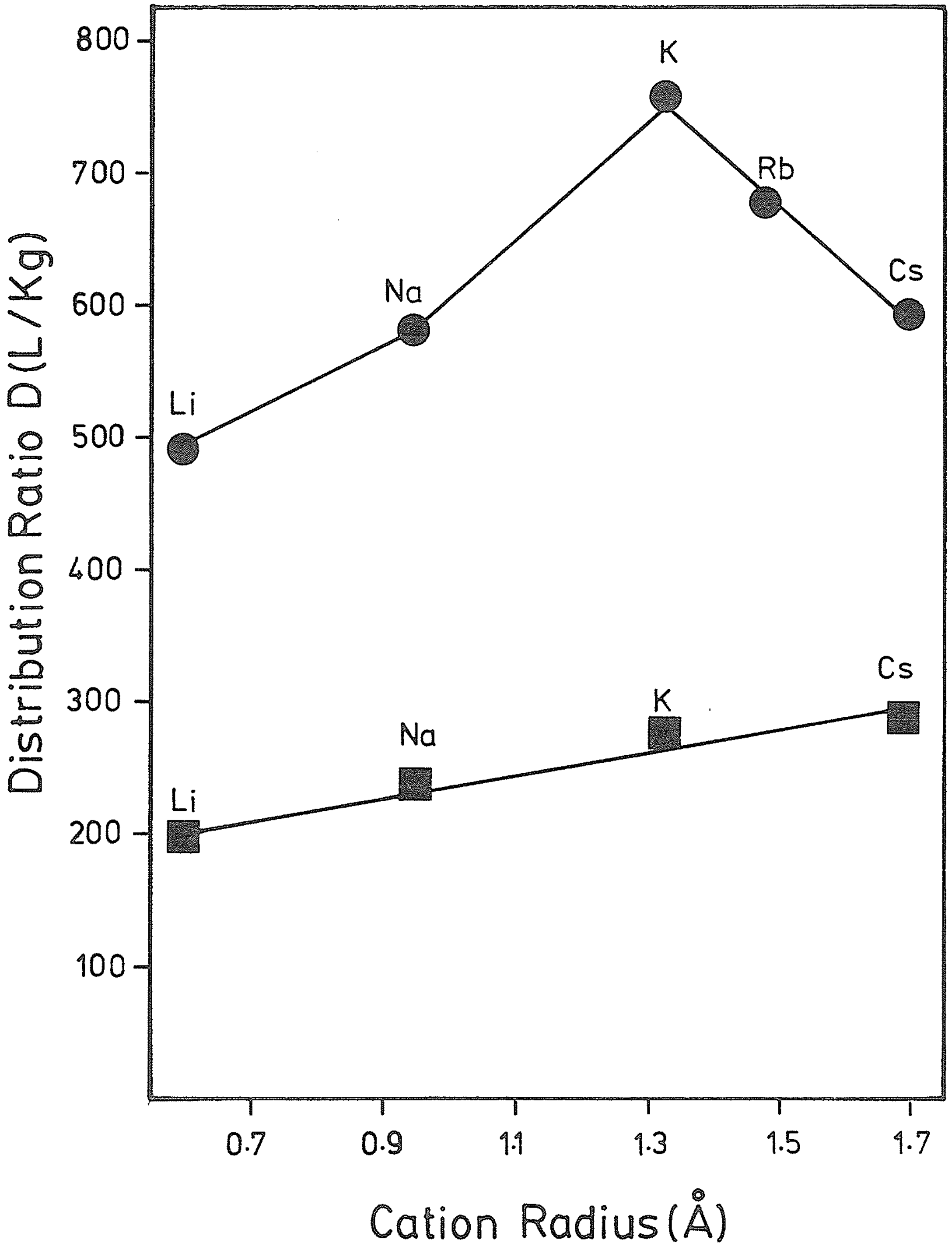

Distribution Ratio D(L/Kg)
800
700
600
500
400
300
200
100
K
Rb
Na
Cs
Li
Cs
K
Na
Li
0.7
0.9
1.1
1.3
1.5
1.7
Cation Radius(Å)

Figure 56

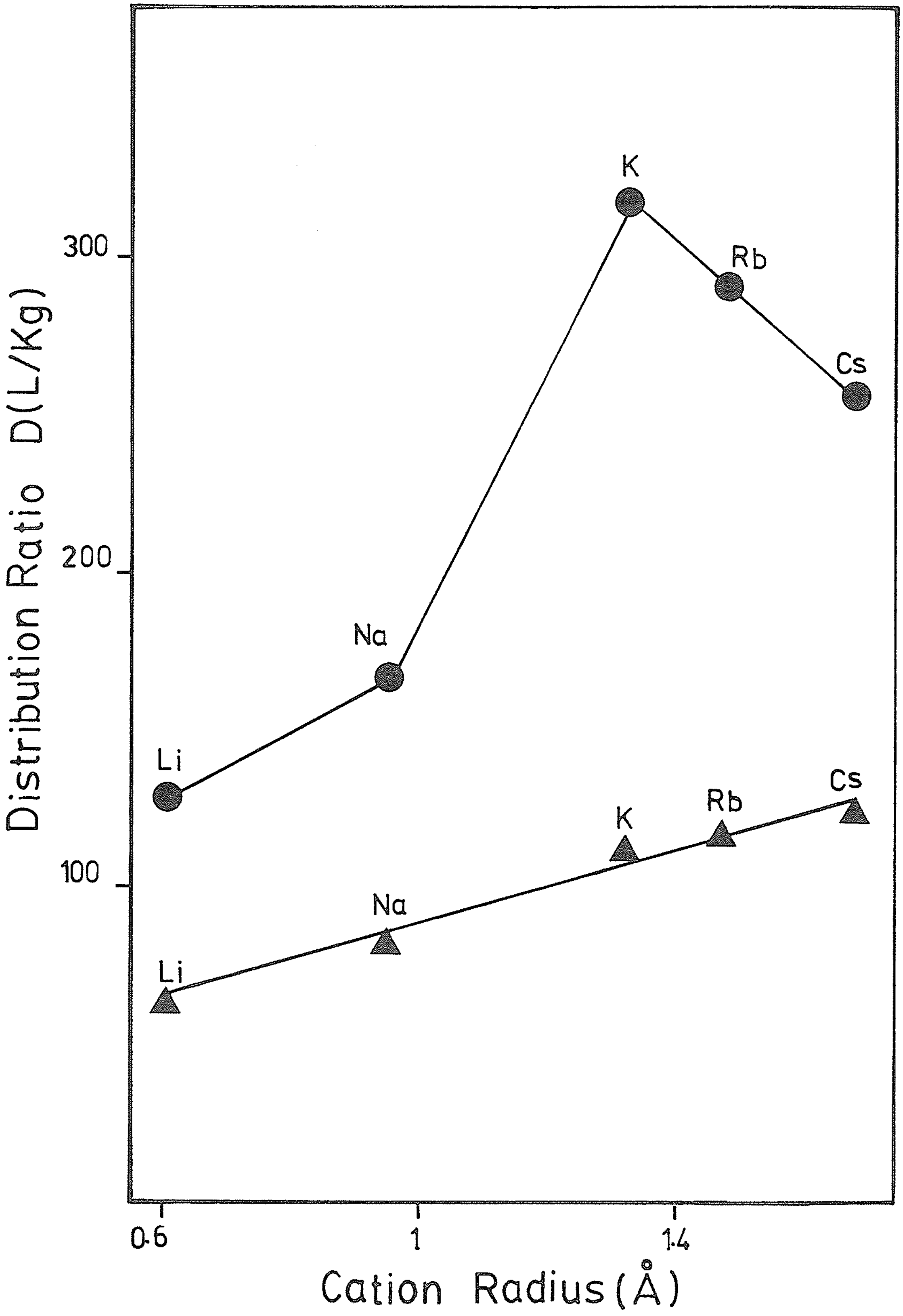
Comparison of ANS sorption from aqueous solutions containing various alkali metal cations by polyether- and polyester-based polyurethane foams.

Initial solution conditions:

[ANS]	1×10^{-3} M
[Cations]	0.1 M
Solution volume	90 mL
Foam weight	0.20 ± 0.01 g

Notes:

Polyether foam (●)
Polyester foam (▲)


Distribution Ratio D(L/Kg)
300
200
100
0.6
1
1.4
Cation Radius(Å)
K
Rb
Cs
Na
Li
Cs
Rb
K
Na
Li

spiral conformation around metal cations, behaves as a polymeric pseudo crown ether.

d. Additional Evidence in Support of CCM

Additional evidence in favour of the Cation Chelation Mechanism has been obtained by studying the extraction of anionic metal complexes by polyether foam in the presence of a large excess of chelatable cations. According to the CCM, in addition to other factors such as charge, size etc., the extraction of anions by polyether foam also depends upon the ability of the polyether chain to solvate the accompanied cation. Keeping in mind the order of selectivity exhibited by the polyether foam for alkali metal cations one would expect the highest extraction of a complex metal anion in the presence of potassium ions. Thus, experiments were performed to study the effect of alkali metal identity on the sorption of $M(SCN)_4^{2-}$ ($M = Co^{2+}$ or Zn^{2+}) by polyether foam.

A series of solutions, 1.7×10^{-5} M in Co^{2+}, 0.05 M in SCN^-, 0.01 M in HCl and 2.5 M in cation were equilibrated for twelve hours with polyether foam cubes each weighing approximately 50 mg. Samples were then taken and analyzed for cobalt. The results are summarized in Table 14, along with those similar studies using $Zn(SCN)_4^{2-}$. As can be seen, higher extraction of $M(SCN)_4^{2-}$ occurs from solutions containing K^+ or NH_4^+ ions. These results are in complete accordance with the CCM, which predicts that the degree of anion sorption depends largely upon the ability of polyether foam to solvate the accompanying cation. Al-Bazi(23) and Lo(16) of these laboratories have also observed the higher extraction of $Pd(SCN)_4^{2-}$ and $SnCl_6^{2-}$, respectively, by polyether foam in the presence of potassium ion. A similar effect

TABLE 14 EFFECT OF COMMON SALTS ON THE SORPTION OF COMPLEX METAL ANIONS BY POLYETHER-BASED POLYURETHANE FOAM

Cation	Distribution Ratio D (L Kg^{-1})	
	$Co(NCS)_4^{2-}$ [a]	$Zn(NCS)_4^{-}$ [b]
Li^+	540	550
Na^+	580	1020
K^+	1120	2510
NH_4^+	1920	2570

Conditions: a) 1.7×10^{-5} M Co(II), 0.05 M SCN^-, 0.01 M H^+, 2.5 M cation; 0.05 gram, Polyether foam.

b) 2×10^{-4} M Zn(II), 0.02 M SCN^-, 0.01 M H^+, 2 M cation; 0.050 gram Polyether foam.

of cations on the extraction of $Zn(SCN)_4^{2-}$ by several non-ionic surfactants (derivatives of PEO) has also been reported by Suzuki et al(153). These results further confirm the higher affinity of polyethers for intermediate-sized cations.

Further strong evidence which indicates the interaction of the polyether chain with metal cations is provided by an infrared study. It was expected that such interactions would bring about some changes in the infrared spectrum of the polyurethane foam. For this purpose, the polyurethane material was used in the form of thin films in order to obtain its spectrum since severe light scattering made the measurement of spectra directly on foam quite difficult.

The polyurethane film, prepared from polyurethane foam as described in the experimental section, was soaked for eighteen hours in 50 mL of solution containing 50 ppm of Co^{2+}, 0.1 M NaSCN and a large excess of sodium chloride (the solution was saturated with sodium chloride in order to prevent dissolution of the plate). The IR and UV-visible spectra of the film and sorbed species were then recorded directly and are shown in Figure 57 and 58. The C-O vibrational modes are observed at 1100 cm^{-1} for the blank polyurethane film (Figure 57b) and are shifted to nearly 1070 cm^{-1} for polyurethane film loaded with $Na_2Co(SCN)_4$ (Figure 57a). This downward shift indicates metal-ether interactions. The blue-green colour of the polyurethane film and the visible absorption spectrum shows a maximum at 615 nm and a shoulder at 580 nm, indicating the presence of cobalt in the polymer as the tetrahedral $Co(SCN)_4^{2-}$ ion. Thus, cobalt atoms do not seem to be directly involved in any interaction with ether links. The observed

Figure 57

Changes in the infrared spectrum of polyether-based polyurethane film accompanying sorption of $Na_2Co(NCS)_4$ from aqueous solution.

a) after sorption
b) before sorption

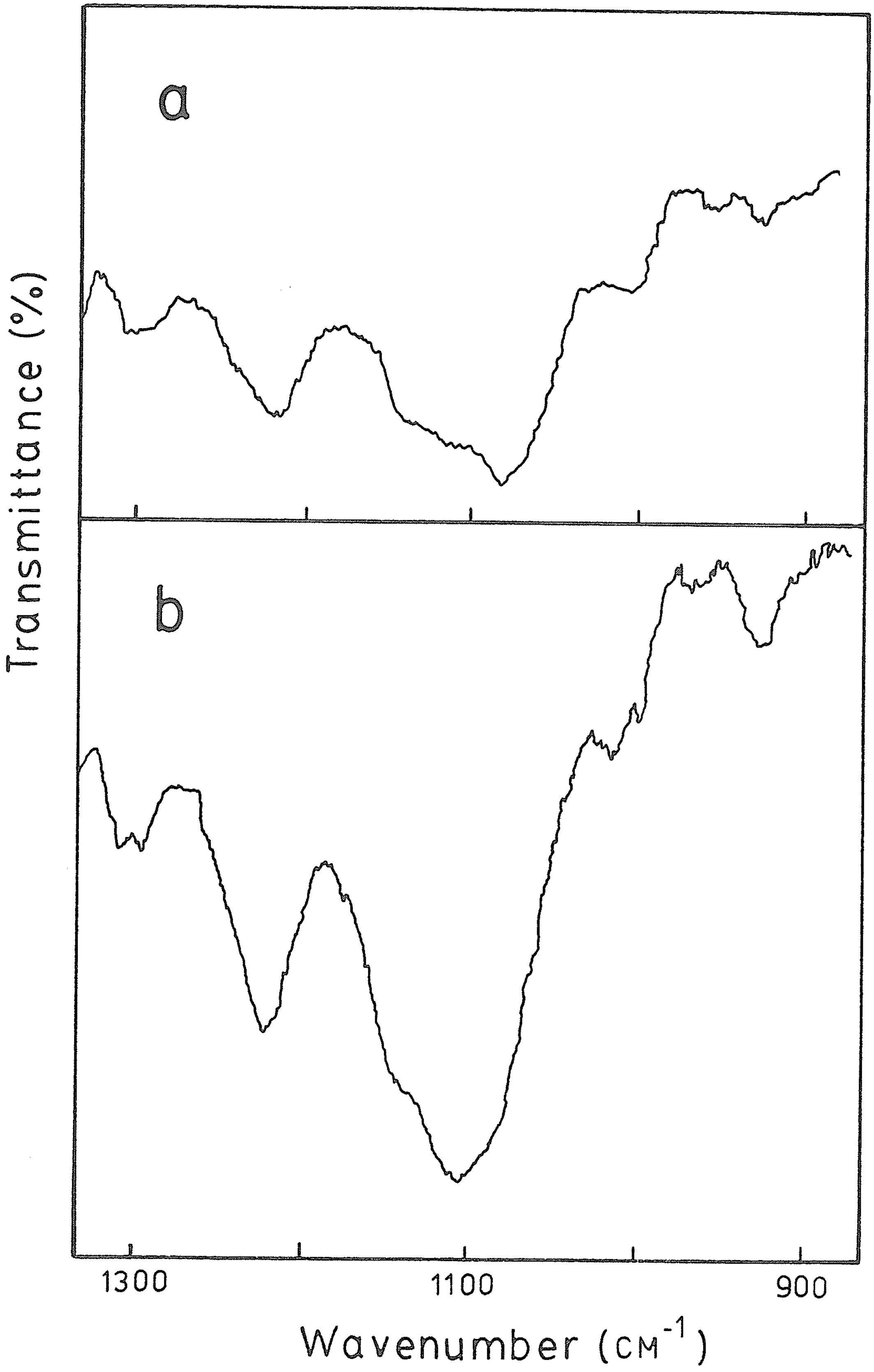
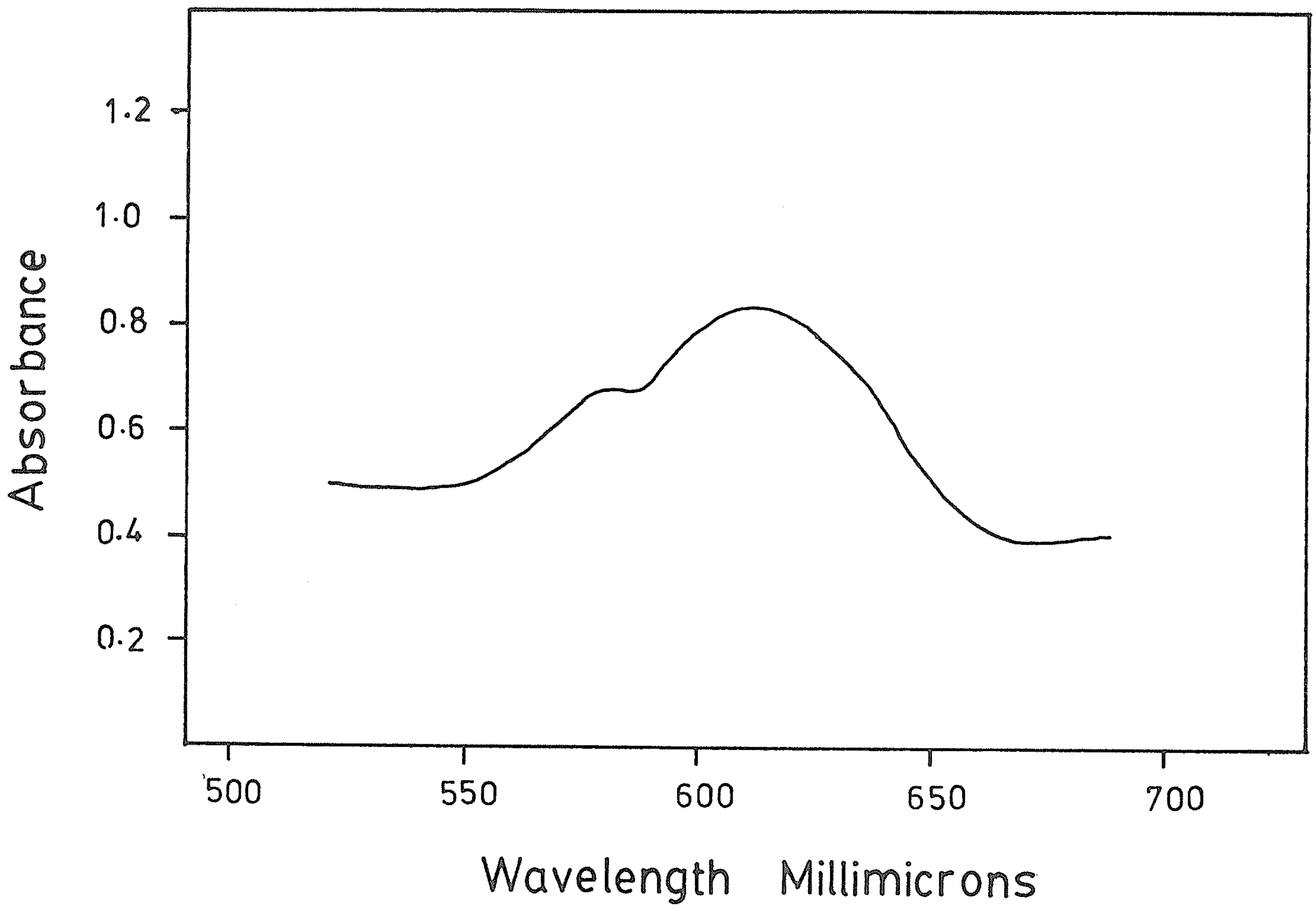

a
b
Transmittance (%)
1300
1100
900
Wavenumber (cm^{-1})

Figure 58

Electronic spectra of $Co(NCS)_4^{2-}$ sorbed on polyether-based polyurethane film.


1.2
1.0
0.8
0.6
0.4
0.2
Absorbance
500
550
600
650
700
Wavelength Millimicrons

shift in the infrared spectrum, therefore has to be attributed to sodium ion chelation by the polymer in sorbing $Na_2Co(SCN)_4$. Similar shifts in the infrared spectra have also been reported for several metal-crown ether complexes(154) and also for the complexes of polyethylene glycols and their derivatives with alkali and alkaline earth metals(155).

It should now be quite clear that like cyclic and linear polyethers, polyether-based polyurethane foam also possesses the unique ability to effectively (but certainly not equally) chelate many metal cations. The chelation of the cation M^+ is most likely a result of the ability of polyether chains to adopt a helical configuration in which 6 to 10 or so inwardly-directed oxygen atoms constitute a "solvent shell" around the cation. Based on this fact, the sorption from aqueous solution of ion-pairs including chelatable cations such as Na^+, K^+, NH_4^+, Rb^+, Cs^+, Ag^+, Tl^+, Ba^{2+}, Sr^{2+}, Pb^{2+}, Hg^{2+} etc. by polyether-based polyurethane foam can be attributed to the effective solvation of these cations by the polyol segment of the foam. The extent of ion-pair sorption depends not only on the complexing affinity for the cation of the polyether chain (which is mainly influenced by the size and charge of the cation) but also on the solubility of the counter anion.

E. Conclusion

The work presented in this section demonstrates the ability of polyurethane foam to extract certain mono- and divalent cations (e.g. Na^+, K^+, NH_4^+, Rb^+, Cs^+, Ag^+, Tl^+, Ba^{2+}, Hg^{2+} and Pb^{2+}) from the aqueous solutions of bulky anions such as picrate, ANS and TPB. General expressions are also obtained for the distribution of mono- and divalent cations between foam and aqueous anion solutions. Although extraction increases with increasing size and hydrophobicity of the counter anion, several results of this work indicate that the extraction of these metal picrates, sulphonates, and tetraphenyl borates cannot be explained solely by a simple solvent-like ion-pair extraction mechanism. Since the effective extraction of these ion-pairs is achieved only by polyether-based polyurethane foams, the polyol segment of the polymer apparently plays the most significant role in extraction and the Cation Chelation Mechanism (C.C.M.) has been put forward to account for the observed phenomenon. According to CCM, the extraction of an ion-pair (M^+X^-) is the result of effective solvation of the metal cation (M^+) by the polyol portion of the polyether-based polyurethane foam.

Experimental evidence has been presented to confirm the proposed mechanism. The results indicate that the solvation (chelation) of metal cations by polyether-based polyurethane foam is more responsible for the sorption of these ion-pairs than are other parameters such as the polarity of the polymer.

It is further noted that polyether foam exhibits an order of selectivity for particular metal cations. The following sequence of (e.g. picrate, ANS, $Co(SCN)_4^{2-}$, and $Zn(SCN)_4^{2-}$):

$$Li^+ < Na^+ < Cs^+ < Rb^+ < K^+ \sim NH_4^+ < Ag^+ \sim Tl^+ < Ba^{2+} < Hg^{2+} < Pb^{2+}$$

Based on the similarity between the order of preference exhibited by polyether foam and that of 18-crown-6 derivatives(47) and also of noncyclic polyether(149,150), it has been concluded that polyether-based polyurethane foam can be considered as a pseudo crown ether.

CHAPTER IV. EXTRACTION OF HETEROPOLY ANIONS BY POLYETHER-BASED POLYURETHANE FOAM

A. INTRODUCTION

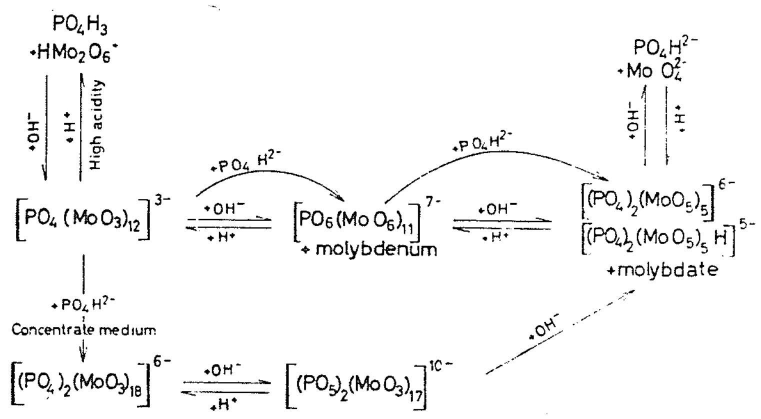
The first report on the behaviour of heteropoly anions towards organic solvents appeared in 1864, when Marignac(156) studied various physico-chemical properties of heteropoly acids including their solubilities in diethyl ether. Later, Scroggie(157) studied in detail the extraction of heteropoly acids by ether. He also tested several organic solvents for the extraction of heteropoly anions and observed that esters, ketones, aldehydes and ether, i.e. oxygen-containing organic solvents, are good extractants whereas carbon tetrachloride, chloroform, benzene and toluene are not suitable. Since then, a large number of reports have appeared in the literature regarding the extraction and separation of heteropoly anions into various oxygen-containing organic solvents. For example, Stoll(158) has reported the extraction of phosphomolybdate by ethyl acetate. Similarly, the selective extraction of phosphomolybdate has been achieved by using butyl acetate. Extraction of phosphomolybdate into 2-methyl-1-propanol has also been reported(160,161). Rainbow(162) investigated the use of 3-methyl-1-butanol, whereas Schaefer et al(163) have recommended 1-octanol for the extraction of phosphomolybdate. Recently, high molecular weight amines have also been introduced for the extraction of heteropoly anions(164). Since hydrocarbons and halo-hydrocarbons etc. do not extract heteropoly anions, it is generally believed that the extraction of heteropoly anions requires the presence of basic nitrogen or oxygen atoms in the organic solvents(156).

Phosphomolybdate is the most readily extractable among the heteropoly acids of molybdenum. The order of extractability reported(165) for the heteropoly acids of molybdenum is: phosphomolybdate > arsenomolybdate > silicomolybdate > germanomolybdate. The extraction behaviour of molybdenum and tungsten heteropoly acids, having the same central atom, is similar for all solvents studied(166). It is difficult to say anything definite about the extraction behaviour of the reduced heteropoly anions but judging from the available data, it appears that they are extracted slightly more than their unreduced analogues(167).

Most of the earlier studies of the extraction of these bulky anions have been of an applied nature and have reported only the optimum conditions for the extraction or separation of a given heteropoly anion. Recently, systematic studies have also been carried out to investigate the influence of various factors on the extraction, including the nature of the solvent, the acidity of the aqueous phase, the composition of the extracted compound etc. The results of several studies show that extraction is greatly influenced by the base strength and the dielectric constant of the solvent and also by its structure and miscibility with water. It is also noticed that the theoretical order of extractability based on a single factor, e.g. base strength or dielectric constant, does not agree with the experimental order. Murata and Kiba(168) have studied the corelation between the extracting power of a solvent, the solubility of the heteropoly anion in it, and the dielectric constant of the solvent. The relationship between solubility and extracting power has also been studied by others(169). In general, amongst the oxygen-containing solvents, alcohols are the most effective and ethers and ketones the most selective for the extraction of heteropoly anions(156).

The acidity of the aqueous phase plays the most dominant role both in the formation as well as in the extraction of the heteropoly anions. Several workers have reported the optimum range of acidity for phosphomolybdate. Drogomiretskay _et al_(170) did not notice any change in the absorption spectra of the solution containing molybdate and phosphate, when the pH was greater than 3. Mellon and coworkers(171) have reported that pH 0.9 to 1.25 with H_2SO_4 give maximum yellow colour development. The formation of several other heteropoly molybdate complexes has also been confirmed at other pH values as well(172).

Souchay(173) proposed the existence of the following complicated equilibria between various kinds of phosphomolybdates in aqueous solution.


PO_4H_3
$+HMo_2O_6^-$
$+OH^-$
$+H^+$
High acidity
$[PO_4(MoO_3)_{12}]^{3-}$
$+PO_4H^{2-}$
$+OH^-$
$+H^+$
$[PO_6(MoO_6)_{11}]^{7-}$
+ molybdenum
$+PO_4H^{2-}$
$+OH^-$
$+H^+$
PO_4H^{2-}
$+MoO_4^{2-}$
$+OH^-$
$+H^+$
$[(PO_4)_2(MoO_5)_5]^{6-}$
$[(PO_4)_2(MoO_5)_5H]^{5-}$
+molybdate
$+PO_4H^{2-}$
Concentrate medium
$+OH^-$
$[(PO_4)_2(MoO_3)_{18}]^{6-}$
$+OH^-$
$+H^+$
$[(PO_5)_2(MoO_3)_{17}]^{10-}$

The sorption studies show that the extraction increases with increasing acidity of the aqueous phase. Usually, the optimum activity range of extraction is wider than the optimum range of acidity for the stability of the heteropoly anion. The extraction range differs considerably for different solvents(174). Generally, the nature of acid employed has no significant influence on the extraction of heteropoly anions of phosphorus and arsenic but different ranges of acidity have been reported in the case of silicomolybdate(165).

In addition to the identical spectra of aqueous phosphomolybdate ($PMo_{12}O_{40}^{3-}$) and organic extracts(169), the results of several other studies(169,175) e.g. chemical analysis of the organic phase, also confirm that the stoichiometric composition of the organic extracts corresponds to a constant P:Mo ratio of 1:12 (even at high or low ratio of molybdate to phosphorus in aqueous phase). It is interesting to note that sodium is extracted into ethyl acetate together with phosphorus and molybdenum in the portions Na:P:Mo, 2.1:1:11.9 and 0.7:1:11.9 depending on the acidity of the solution(176). It is also reported that the extraction of phosphomolybdate ($PMo_{12}O_{40}^{3-}$) is more complete in the presence of lithium, sodium and potassium than in their absence(177). Furthermore, the quantitative extraction of cesium from heteropoly anion solution has also been reported(178). These data indicate that heteropoly anions in general and phosphomolybdate in particular enter into organic phase in the form of the phosphomolybdic acid or its salts.

Various mechanisms have been proposed for the extraction of heteropoly anions into oxygenated organic solvents. At present, two mechanisms have been discussed in literature most frequently, both of which are based on the assumption that a donor-acceptor interaction takes place between oxygen atom of the organic solvent and the heteropoly complex. However, according to one mechanism, the oxygen atom of the solvent interacts with the molybdenum of the heteropoly molybdate. The changes in the absorption spectra of the extracts of heteropoly complexes have been attributed to the increase in the coordination number of molybdenum atom(164,179). On the other hand, evidence has also been presented in favour of a different mechanism, commonly known as the hydrate-solvate mechanism, according to which the extraction is due to the interaction of the solvent with the cationic part of the heteropoly acid or salt(174,175,180). It is obvious that both mechanisms differ only in one respect, that is which part (cationic or anionic) of the extracting species interacts with the oxygen atom of the solvent.

The extraction of phosphomolybdate by polyether-based polyurethane foam was studied with the hope that the results of such study would facilitate the investigation of the mechanism of heteropoly anions extraction and furthermore, would also extend the analytical value of polyether foam for the extraction of phosphorus, arsenic, silicon and germanium etc.

B. EXPERIMENTAL

Apparatus and Reagents

Packard Tri-Carb Model 3320 Liquid Scintillation Spectrophotometer.

Varian Model 634 S UV-Visible Spectrophotometer.

Fisher Accumet Model 520 pH meter.

X-ray fluorescence unit used in the present study consisted of the following components:

i) Nuclear Semi-Conductor Model 558

ii) New England Nuclear XRF Source (Am^{241}, 0.5 Ci)

iii) Tracor Northern Model 1705 Pulse Height Analyzer

Extraction cells of ~200 mL capacities (Figure 27).

Thermostated Multiple Automatic Squeezer (Figure 28).

Liquid Scintillation Vials catalogue #NEF 923 (New England Nuclear).

Phosphorus-32 Half life 14.3 days, obtained from New England Nuclear of Canada (Catalogue #NEX-054).

Aqueous Counting Scintillant (ACS) was supplied by Amersham Co (USA).

All the following reagent grade chemicals were obtained from Fisher Scientific Co. unless otherwise indicated:

Sodium Molybdate

Sodium Dihydrogen Phosphate (Shawingan Chemical Co)

Lithium Chloride

Potassium Chloride

Hydrochloric Acid

Foam

Acid-resistant polyether type polyurethane foam. (Union Carbide type "A", a gift of Dr. C. G. Seefried of Union Carbide Corp., Chemical and Plastics, P. O. Box 8361, South Charleston, W. Virgina, USA).

GENERAL PROCEDURE

Washing of the Foam

Foam cubes each weighing 70 ± 5 mg were washed according to the procedure described earlier in Chapter 3.

Cleaning of the Glassware

All glassware was soaked in 5% aqueous solution of Extran "300" (a phosphate-free cleaning agent supplied by B.D.H) for about six to eight hours, then cleaned thoroughly with water, rinsed with distilled water and dried in an oven at 70°C.

Preparation of Stock and Sample Solutions

Stock solutions of molybdate and phosphate were prepared from sodium molybdate and sodium dihydrogen phosphate respectively. These stock solutions were stored in polythylene bottles to prevent contamination from glass.

Sample solutions were made up by diluting the stock solutions to give the required concentration.

Extraction Procedure

The 100 mL of sample solution and a foam cube were placed in the extraction cell, and brought to equilibrium using thermostated automatic squeezing apparatus as described in Chapter 3.

Measurement of Extraction Efficiency

The tracer technique was used for measurement of the percentage extraction. P-32 tracer was used and diluted prior to use. The sample solutions containing the required amount of phosphate and other reagents were spiked with sufficient amount of ^{32}P tracer (approximately 25 μ L) to yield count rate of at least 10,000 counts per minute per 2 mL of sample mixed with 10 mL of ACS.

Counting Technique

A 2 mL aliquot of the sample was mixed in a clean scintillation vial with 10 mL of the ACS scintillation cocktail. The vial containing the sample solution was then placed in a Packard Tri-carb liquid scintillatorion counter and counted for two or five minutes. The activity of each sample was determined from the average of 8 counts of two minutes duration or 5 counts of five minutes duration. The average activity was then corrected for background which was determined from the average of ten measurements.

Determination of Percentage Extraction by Tracer Technique

The percentage extraction was determined by counting the radioactivity of a 2 mL aliquot of sample, mixed with 10 mL of ACS scintillation cocktail, before and after equilibration with foam.

$$\%\ \text{Extraction by Foam} = \frac{\text{Activity}_{\text{before}} - \text{Activity}_{\text{after}}}{\text{Activity}_{\text{before}}} \times 100$$

The distribution coefficient was calculated, using the percentage extraction according to equation 12 (Chapter 2).

X-Ray Analysis

The X-Ray studies were performed on a Nuclear Semi-Conductor system model 588, with a Si (Li) detector. The signals were passed through an amplifier into a TN 1705, multichannel analyzer. Foam disc was supported on a Mylar film stretched across an X-Ray source holder. The disc was placed in the center of the Mylar film as reproducibly as possible. An Am-241 source was used for the excitation of the characteristic X-ray lines of the samples. Spectra were accumulated for 100 seconds. The area under the peak of interest (i.e. Mo K_α) was obtained by integration with TN 1705 Unit.

C. RESULTS AND DISCUSSION

1. Preliminary Studies

The results of preliminary studies showed that heteropoly molybdates of phosphorus, arsenic and silicon, both in the reduced and non-reduced forms, are effectively extracted by the polyurethane foam. It was also noticed that foam does not extract any detectable amount of hetero atom (e.g. P, Si and As) in the absence of molybdate. The sorption behaviour of yellow phosphomolybdate into polyurethane foam was studied in detail because the analytical literature contains a large number of papers describing the most appropriate conditions for the formation and extraction of yellow phosphomolybdate into various organic solvents.

Experiments were performed to determine the effect of squeezing time for the phosphate extraction. A series of 150 mL solutions, 4×10^{-5} M in phosphate and 2×10^{-3} M in molybdate at pH 2.0 ± 0.1 were equilibrated with foam cubes (each weighing 70 ± 5 mg) for different time periods ranging from thirty minutes to twenty-four hours. It was observed that the extraction increases rapidly in the first three hours then starts to level off. The extraction efficiency remains practically constant after six hours of squeezing. In further studies, the foam cubes were squeezed in the sample solutions for nearly twelve hours to ensure the accomplishment of the equilibrium.

In order to establish the optimum conditions for the extraction of phosphorus as phosphomolybdate by polyurethane foam, the influence of various parameters was studied.

2. Effect of Acid Concentration on the Extraction of Phosphomolybdate

A yellow colour develops when acid is added to a solution containing phosphate and an excess of molybdate. The colour has been attributed to the formation of phosphomolybdate. It has been reported(168,181) that the formation of phosphomolybdate is maximum between pH 1 to 2.0. Due to the complex solution chemistry of the phosphomolybdate, it seemed necessary to confirm the optimum pH range for its formation. In order to do so, the absorbance of the solutions was measured at 420 nm. The results shown in Figure 59 are in complete accordance with the previous studies and further confirm that phosphomolybdate is most stable only between pH 1 and 2.

It has been reported that the acidity range for the extraction of heteropoly anion is mainly dependent upon the nature of the solvent(168,174) and for most of the solvents, is wider than the optimum range of acidity for the formation of a given heteropoly anion. Thus, experiments were performed in order to determine the optimum pH range for the extraction of phosphomolybdate into polyether foam.

A series of 150 mL solutions, 4×10^{-5} M in phosphate, 1×10^{-3} M in molybdate, containing sufficient amounts of lithium chloride to give 0.5 M ionic strength and at different pH values (the required pH values were adjusted using HCl or LiOH) were equilibrated with foam cubes for twelve hours. The samples were then withdrawn and analyzed for phosphorus. The results are shown in Figure 60. As can be seen, the distribution ratio of phosphomolybdate increases with increasing acidity of the aqueous phase (the value, 3.1, of the resulting slope suggest the extraction of $H_3PMo_{12}O_{40}$). The distribution

Figure 59

Influence of acidity on the formation of phosphomolybdate.

Conditions:

$[PO_4^{3-}]$	4×10^{-4} M
$[MoO_4^{2-}]$	1×10^{-2} M
Path length	1 cm
λ	420 nm

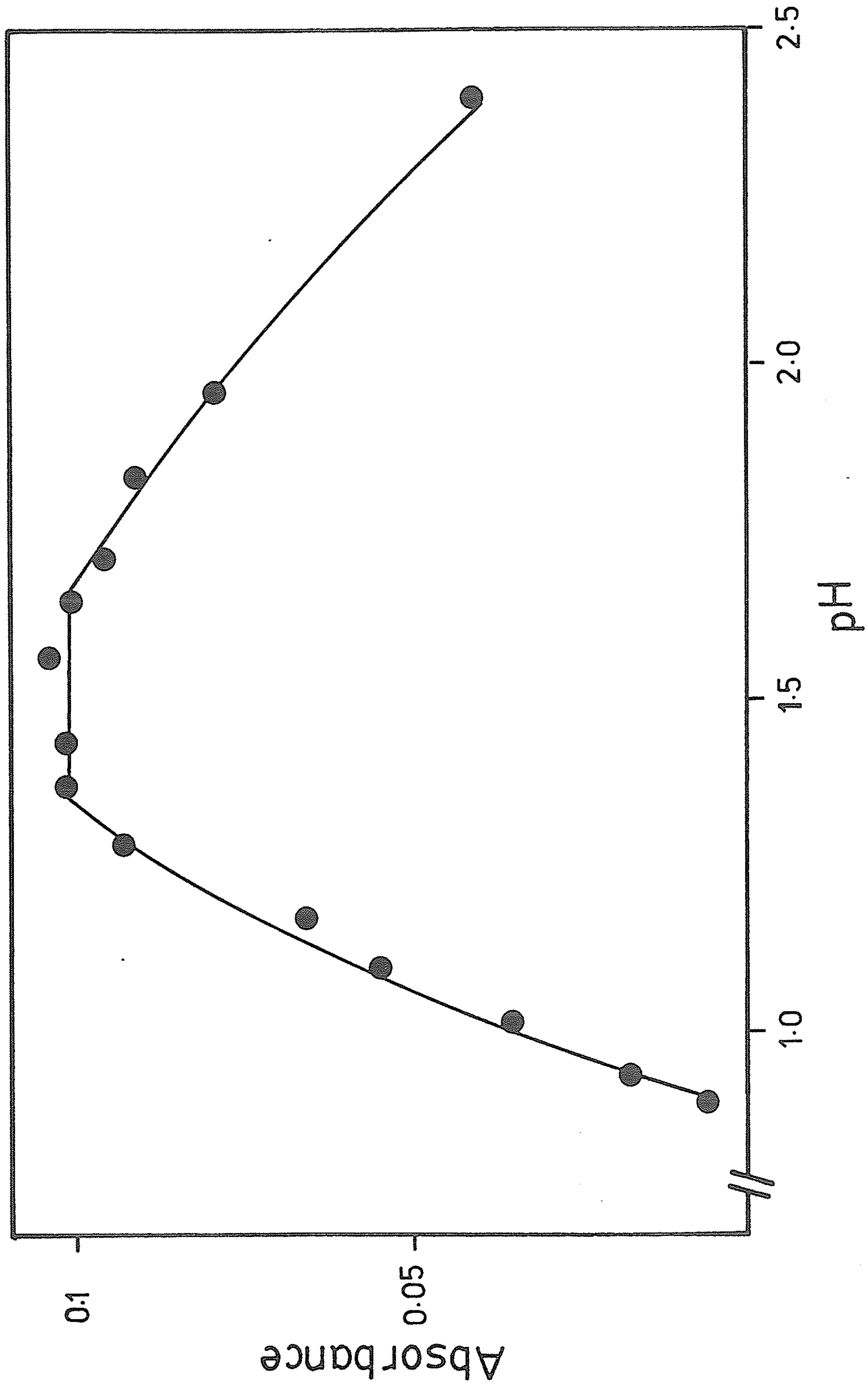
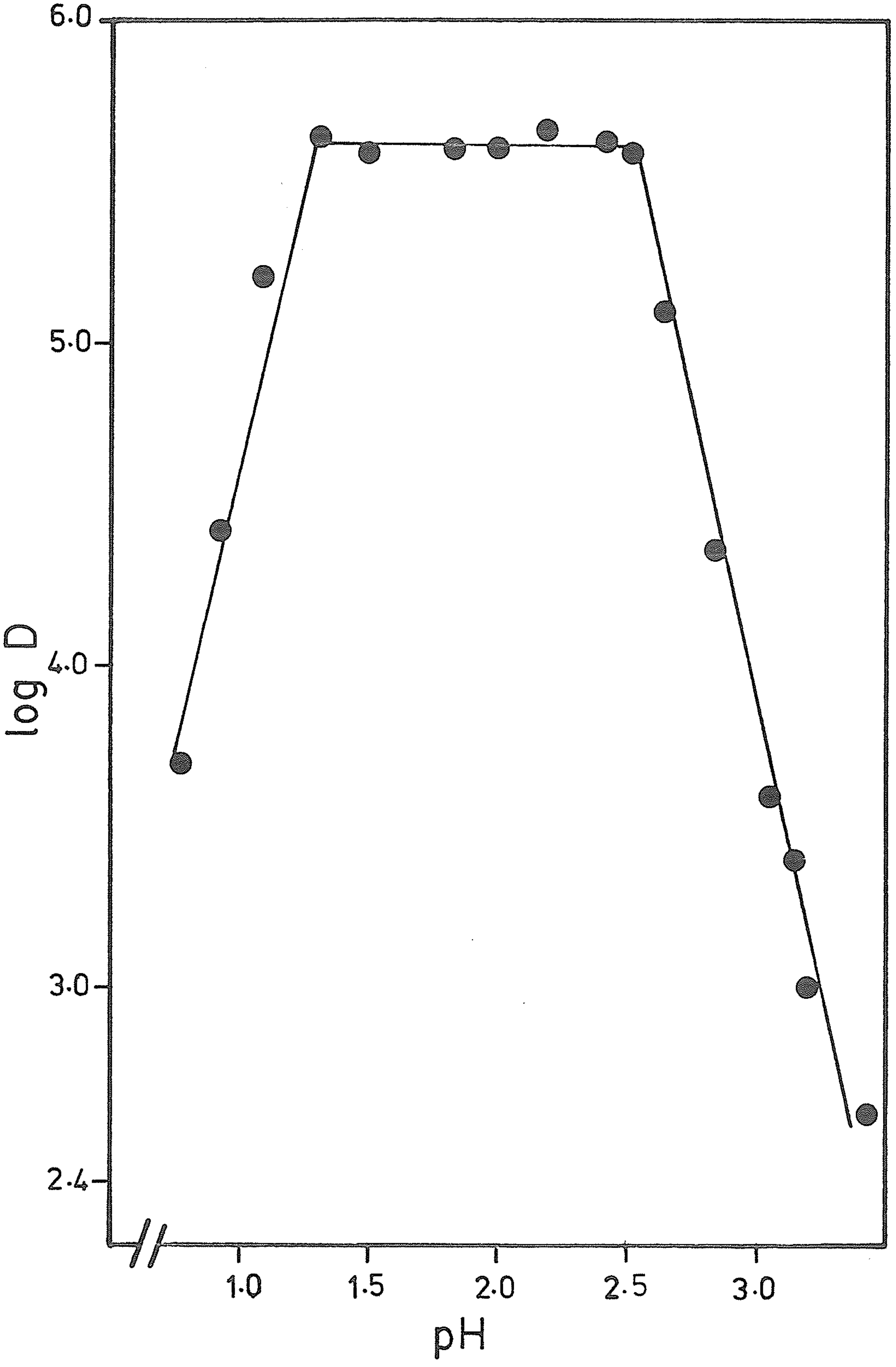

Absorbance
0.1
0.05
pH
1.0
1.5
2.0
2.5

Figure 60

Effect of pH on the extraction of phosphomolybdate by polyether foam.

Initial solution conditions:

$[PO_4^{3-}]$	4×10^{-5} M
$[MoO_4^{2-}]$	1×10^{-3} M
Foam weight	70 ± 5 mg
Solution volume	150 mL
Temperature	25.00 ± 0.05°C
Total ionic strength	0.5 M (maintained by LiCl)


6.0
5.0
4.0
3.0
2.4
log D
1.0
1.5
2.0
2.5
3.0
pH

ratio reaches a maximum at about 2.5 pH and remains constant up to pH 1.1. Further increase in the hydrogen ion concentration results in a sharp decline in the distribution coefficient. It is quite reasonable to assume that at higher acid concentration the sharp decrease in the extraction of phosphate results from the decomposition of the only extractable species i.e. $PMo_{12}0_{40}$, according to the equilibrium proposed by Souchy(173). The drop in the extraction of phosphomolybdate below pH 1 has also been reported by other workers(168,174). Since phosphomolybdate is stable only between pH 1 to 2, it is quite reasonable to assume that the upper limit of the acidity range for extraction is dictated by the stability of the heteropoly acid. It is also evident from the results that, like various solvent-extraction systems, the optimum acidity range for extraction of phosphomolybdate into polyurethane foam is wider than the acidity range of formation.

3. Effect of Molybdate Concentration on the Extraction of Phosphomolybdate

It has been reported(182) that a relatively large excess of molybdate is required to ensure the complete formation of phosphomolybdate. Thus an excess of molybdate is usually recommended for the extraction and subsequent determination of phosphate as phosphomolybdate by most workers(183,184). However, not much has been reported about the effect of a large excess of molybdate on the extraction of phosphomolybdate. It was desired therefore to study the extraction behaviour of phosphomolybdate into polyether foam as a function of molybdate concentration. Experiments were carried out to determine the minimum amount of molybdate which would yield the maximum phosphate extraction.

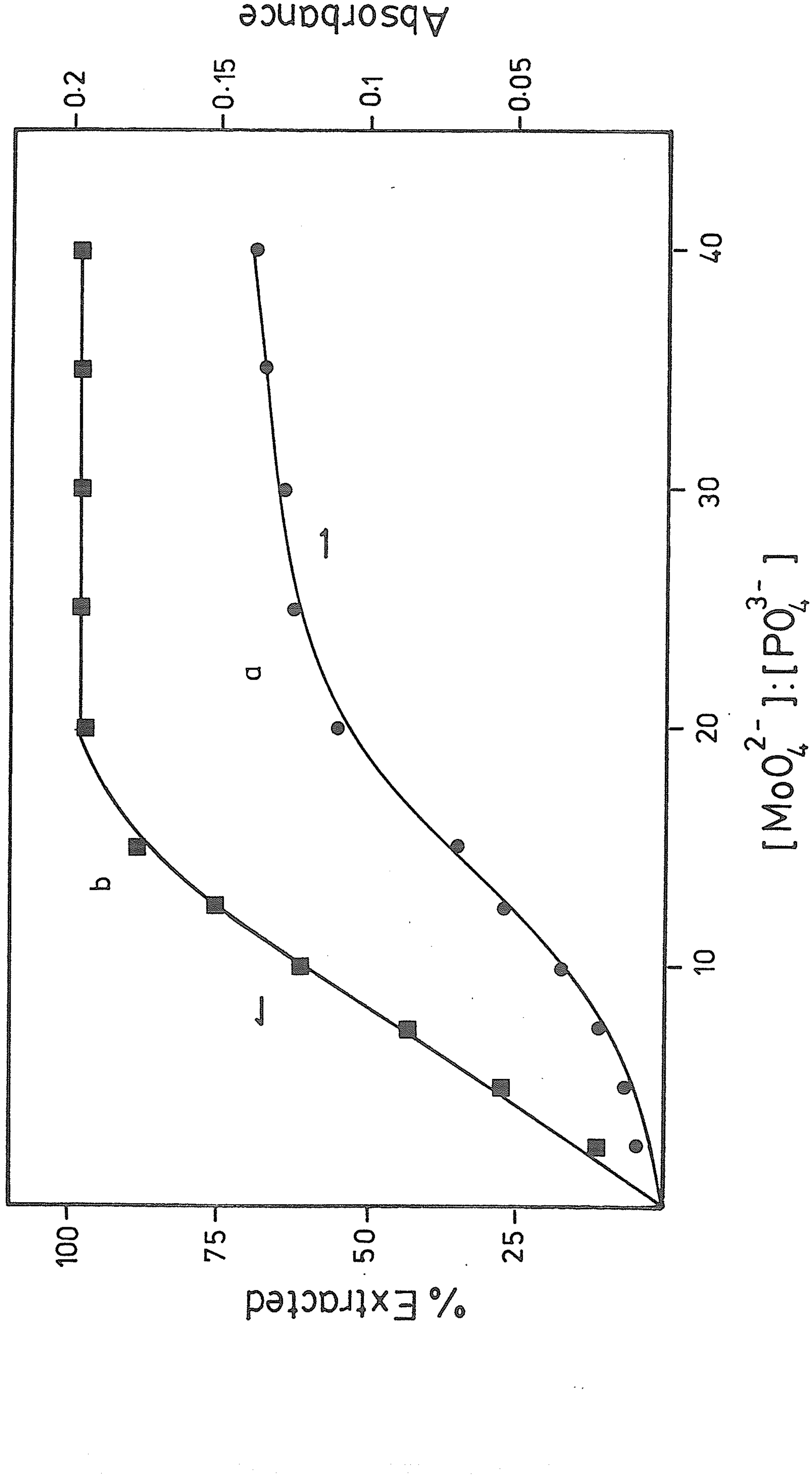
Foam cubes (each weighing 70 ± 5 mg) were squeezed for fifteen hours in a series of 150 mL solutions which contained 4×10^{-5} M phosphate, various amounts of sodium molybdate ranging from 1×10^{-4} to 1.4×10^{-3} M and sufficient lithium chloride to attain the total ionic strength of 0.5 M, at pH value of 2.0 ± 0.1 (adjusted by HCl or LiOH). The results of this study are shown in Figure 61. Curve a, displays the absorbance of aqueous solution as a function of molybdate to phosphate ratios; the "S" shape of the curve indicates that the formation of yellow 12-phosphomolybdate is not proportional to the amount of molybdate added. Similar results have been reported by Murata _et al_(168) who have suggested that a small amount of molybdate preferentially produces the colourless intermediate phosphomolybdate complexes which on further addition of molybdate are converted into

Figure 61

Effect of molybdate on the formation and sorption of phosphomolybdate.

Conditions:

a)	$[PO_4^{3-}]$	4×10^{-5} M
	pH	2.0 ± 0.1
	Path length	1 cm
	λ	420 nm
b)	$[PO_4^{3-}]$	4×10^{-5} M
	pH	2.0 ± 0.1
	Solution volume	150 mL
	Foam weight	70 ± 5 mg
	Temperature	25.00 ± 0.05°C
	Ionic strength	0.5 M (maintained by adding LiCl)


% Extracted
100
75
50
25
Absorbance
0.2
0.15
0.1
0.05
$[MoO_4^{2-}]:[PO_4^{3-}]$
10
20
30
40
a
b
1
1

the yellow 12-phosphomolybdate. Based on these studies, they have proposed the following equilibria for the formation of 12-phosphomolybdate:

$$\mathrm{PO_4^{3-}} + \mathrm{MoO_4^{2-}} \xrightleftharpoons[\mathrm{OH^-}]{\mathrm{H^+}} \underset{\substack{\text{complex}\\ \text{colourless}}}{\text{(Intermediate)}} \xrightleftharpoons[\mathrm{OH^-}]{\mathrm{H^+ + MoO_4^{2-}}} \underset{\text{yellow}}{\mathrm{PMo_{12}O_{40}^{3-}}}$$

It can be seen from Figure 61 that the absorbance does not reach the maximum even at 40 fold excess of molybdate. This confirms the early reports that a large excess of molybdate is required to ensure the complete formation of 12-phosphomolybdate.

Curve b in Figure 61 represents the percentage of extraction of phosphate as a function of molybdate. As expected, the extraction increases with increasing molybdate concentration and then reaches a maximum at 1 x 10^{-3} M molybdate. The striking feature of this curve is, that extraction reaches a maximum at about 25-fold excess of molybdate. The results of other experiments done using different amounts of phosphate and 25-fold excess of molybdate further confirm that a 25-fold excess of molybdate is sufficient to extract more than 99% of phosphate as phosphomolybdate into foam.

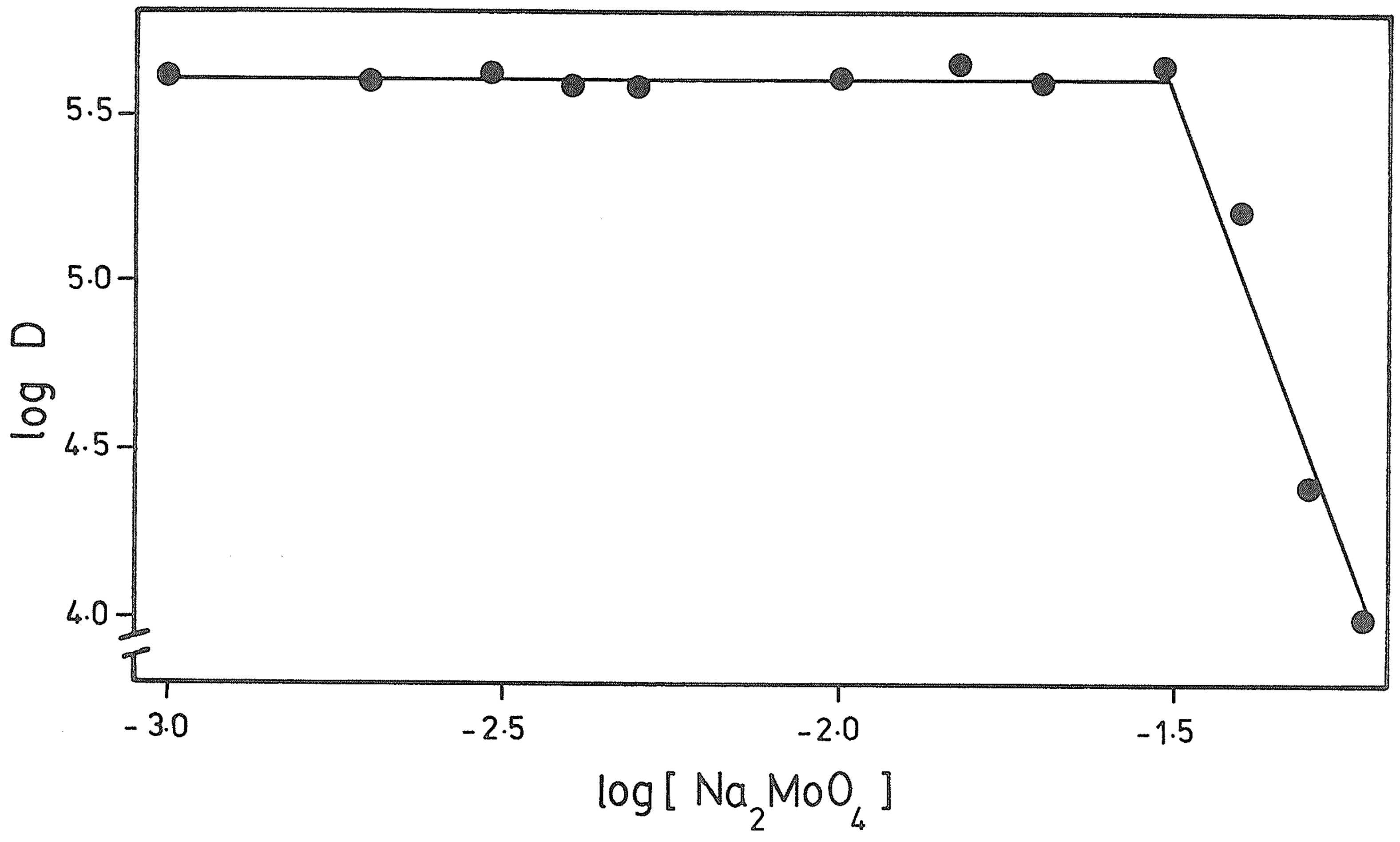
In another study, the extraction of phosphate was carried out from a series of solutions containing initial concentrations of molybdate ranging from 5 x 10^{-3} to 8 x 10^{-2} M. The results are shown in Figure 62 where log D is plotted against log of initial concentration of molybdate. As can be seen, the extraction of phosphomolybdate remains practically constant up to 3 x 10^{-2} M of initial molybdate concentration (i.e. up to 750 fold excess of molybdate) beyond which

Figure 62

Effect of varying the initial concentration of sodium molybdate on the extraction of phosphomolybdate.

Initial solution conditions:

$[PO_4^{3-}]$	4×10^{-5} M
pH	2.0 ± 0.1
Solution volume	150 mL
Foam weight	70 ± 5 mg
Temperature	25.00 ± 0.05°C
Ionic Strength	0.5 M (maintained by adding LiCl)


log D
5·5
5·0
4·5
4·0
- 3·0
- 2·5
- 2·0
- 1·5
log [Na$_2$MoO$_4$]

the distribution ratio steadily decreases with increasing molybdate concentration. The decrease in the distribution ratio is most likely caused by the increase in the simultaneous extraction of molybdate into the polyether foam. The sorption of molybdate into polyether-foam in the absence of phosphate was confirmed by XRF analysis of the foam. A decline in the extraction of phosphomolybdate into organic solvents at higher molybdate concentration has also been reported by other workers(167,185).

4. Effect of Phosphate Concentration on the Extraction of Phosphomolybdate

As mentioned earlier, the formation of phosphomolybdate in solution is influenced by a number of factors, in particular, the concentration of acid, molybdate and phosphate. After studying the effects of acid and molybdate concentration, it was of interest to investigate the influence of phosphate concentration on the extraction of phosphomolybdate into polyether foam.

A series of 150 mL solutions containing 6×10^{-3} M sodium molybdate, having pH values of 2.0 ± 0.1, different amounts of phosphate and sufficient amounts of lithium chloride to adjust the ionic strength at 0.5 M, were equilibrated with foam cubes each weighing 70 ± 5 mg. The samples of the solution were removed after twelve hours of squeezing and analyzed for phosphate. The results are shown in Figure 63, where log D is plotted as a function of log of initial concentration of phosphate. As can be seen, the "D" values are practically independent of phosphate concentration up to 1.2×10^{-4} M phosphate, however the distribution ratio drops above this concentration. In Figure 63, the results of two similar studies using higher initial concentrations of molybdate are also shown. All distribution curves are similar except that the break in the curve is shifted toward lower phosphate concentration with increasing molybdate concentration. The decrease in the extraction of phosphomolybdate with increasing initial concentration of phosphate might be attributed to one of, or combination of, the following possibilities:

i) It is quite reasonable to assume that the decrease in phospho-

Figure 63

Effect of varying initial concentration of phosphate on the extraction of phosphomolybdate.

Initial solution conditions:

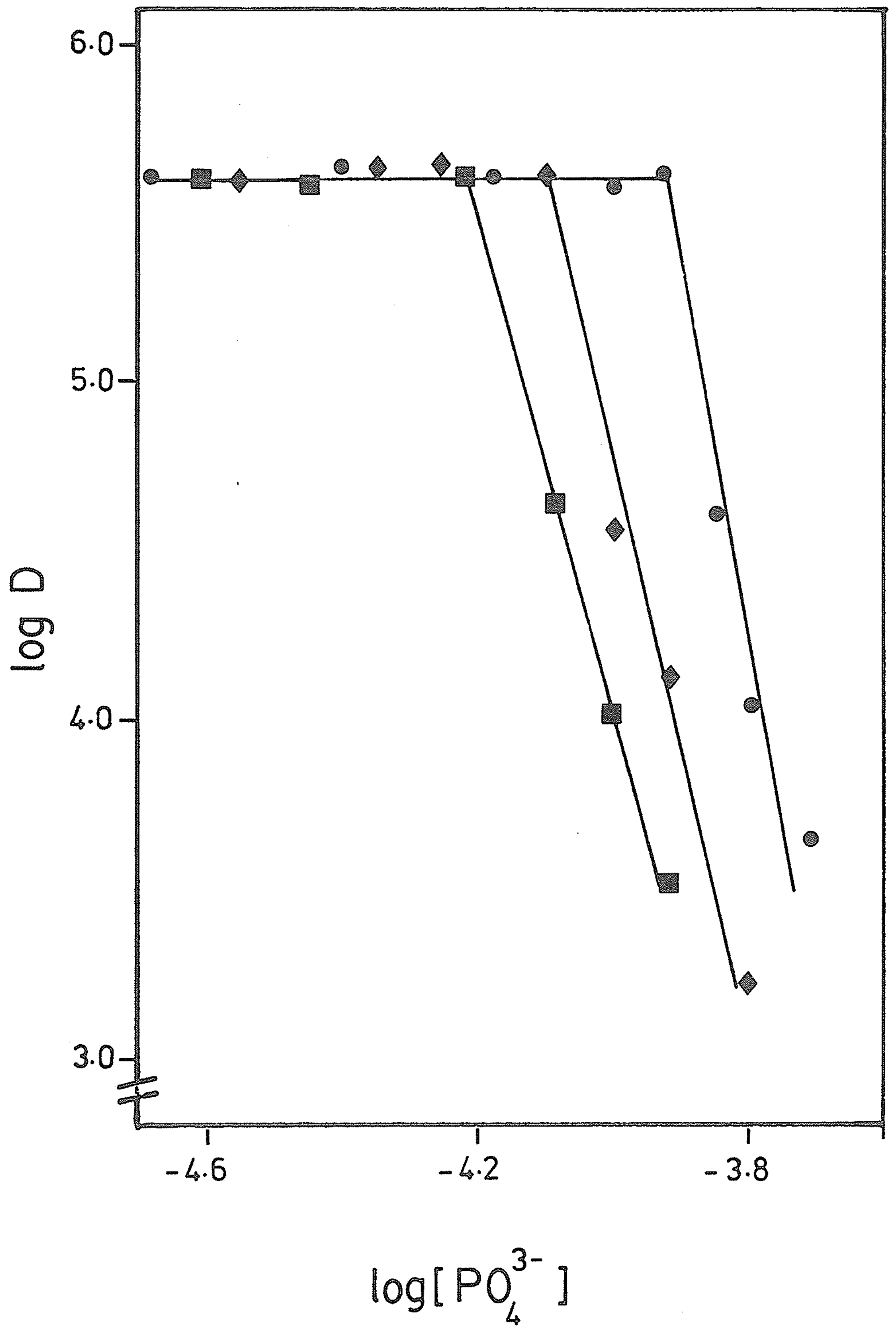
pH	2.0 ± 0.1
Solution volume	150 mL
Foam weight	70 ± 5 mg
Ionic strength	0.5 M (maintained by adding LiCl)
Temperature	25.00 ± 0.05°C

Notes:

(■) 2×10^{-2} M MoO_4^{2-}

(◆) 1×10^{-2} M MoO_6^{2-}

(●) 6×10^{-3} M MoO_4^{2-}


6.0
5.0
4.0
3.0
log D
-4.6
-4.2
-3.8
log[PO_4^{3-}]

molybdate extraction beyond certain concentration of phosphate is most likely due to dissociation of the extracting species ($H_3PMo_{12}O_{40}$) in the polyether foam. A similar extraction behaviour has been reported by Gesser and coworkers(15) for the extraction of Fe(III) from acidic chloride media into polyether foam. A drop in the distribution ratio has also been reported for Mo(VI)(186), In(III)(187) and Fe(III)(168) in liquid-liquid extraction systems and has always been attributed to the dissociation of the extracting species in the organic phase.

ii) On the other hand, a similar decrease in the extraction of heteropoly acids with increasing concentration of heteropoly acid has been observed earlier and has been attributed to the polymerization of heteropoly acid(165). Considering the very complex solution chemistry of phosphomolybdates, it is quite possible that addition of phosphate may result in the formation of nonextractable higher phosphomolybdates e.g. $P_2Mo_{18}O_{62}^{6-}$.

iii) In addition, it is equally reasonable to assume that the drop in "D" values, caused by the increase in the phosphate concentration indicates the capacity of foam. The value of capacity calculated from curve a (Figure 63) is 0.76 milliequivalent per gram of foam. This value of capacity is slightly lower than what has been reported for other systems i.e. ~ 1 millequivalent per gram of foam(122,189). The lower foam capacity for phosphomolybdate is most likely due to the simultaneous extraction of molybdate. is further confirmed by the results in Figure 63 where a steady decrease in the foam capacity per $H_3PMo_{12}O_{40}$ with the gradual increase in the initial concentration of molybdate can be seen.

5. Effect of Alkali Metal Chlorides on the Extraction of Phosphomolybdate

There are numerous reports regarding the solvent extraction of phosphomolybdate but the influence of added neutral salts has not been studied systematically. As we have seen earlier, for systems where the Cation Chelation Mechanism is at work, the nature and concentration of cations play an important role for the extraction of anions into polyether foam. The influence of neutral salts on the extraction of phosphomolybdate was studied with the hope that it might help us in understanding the mechanism of extraction.

Foam cubes weighing 70 ± 5 mg each were squeezed for twelve hours in 150 mL solutions which were 4×10^{-5} M in NaH_2PO_4, 1×10^{-3} in Na_2MoO_4 with pH values of 2.0 ± 0.1 and also containing various amounts of lithium chloride. The results of this study are shown in Figure 64 and are also summarized in Table 15. As can be seen, the extraction of phosphomolybdate remains constant up to 0.6 M LiCl, beyond which the distribution ratio decreases with increasing lithium chloride concentration. A similar decrease in the extraction of phosphomolybdate into butanol with increasing sodium chloride concentration has been reported by Anderson(185) without any explanation. The decrease in the extraction of phosphomolybdate in the presence of 0.3 M or more Na^+ concentration has also been reported by Russian workers(177) and has been attributed to the low stability of 12-phosphomolybdate under these conditions.

In order to understand the unexpected phenomenon, the influence of lithium chloride was studied at different initial molybdate concen-

Figure 64

Effect of varying the lithium chloride concentration on the sorption of phosphomolybdate.

Initial solution conditions:

$[PO_4^{3-}]$	4 x 10^{-5} M
pH	2.0 ± 0.1
Solution volume	150 mL
Foam weight	70 ± 5 mg
Temperature	25.00 ± 0.05°C

Notes:

(●) 1 x 10^{-3} M $[MoO_4^{2-}]$
(▲) 5 x 10^{-3} M $[MoO_4^{2-}]$
(◆) 1 x 10^{-2} M $[MoO_4^{2-}]$
(■) 3 x 10^{-2} M $[MoO_4^{2-}]$

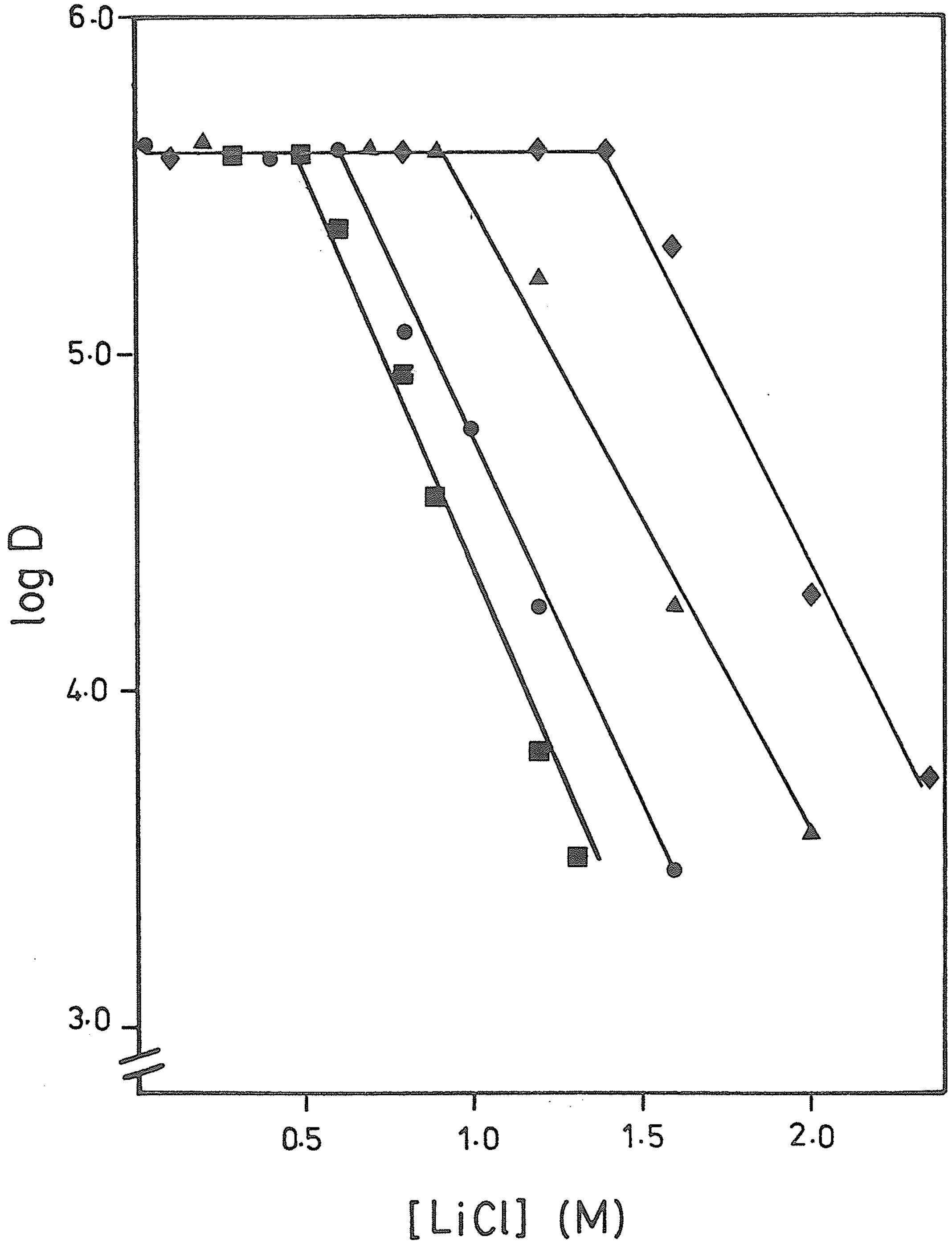

6·0
5·0
4·0
3·0
log D
0·5
1·0
1·5
2·0
[LiCl] (M)

TABLE 15 EFFECT OF LITHIUM CHLORIDE ON THE EXTRACTION OF PHOSPHOMOLYBDATE

Lithium Chloride (M)	Log Distribution Ratio (L/Kg) at Different Concentrations of Na_2MoO_4			
	1×10^{-3}M	5×10^{-3}M	1×10^{-2}M	3×10^{-2}M
0.0	5.62	5.6	-	-
0.1	5.60	-	5.60	-
0.2	5.62	5.64	5.61	-
0.3	-	-	-	5.61
0.4	5.60	-	5.63	-
0.5	-	-	-	5.61
0.6	5.61	-	5.62	5.37
0.7	-	5.62	-	-
0.8	5.08	5.61	5.61	4.95
0.9	-	5.61	-	4.52
1.0	4.78	5.4	-	-
1.2	4.25	5.22	5.61	3.81
1.3	-	-	-	3.50
1.4	-	-	5.61	-
1.6	3.46	4.25	5.32	-
2.0	-	3.58	4.29	-
2.3	-	-	3.76	-

Condition: $[PO_4^{3-}]$ = 4×10^{-5} M

pH 2.0 ± 0.1

Foam weight 70 ± 5 mg

Temperature 25.00 ± 0.05°C

trations. The results of these studies are displayed in Figure 64 and are also summarized in Table 15. It is clear from these results that for a given initial concentration of molybdate, the distribution ratio remains constant up to a certain concentration of lithium chloride, beyond which the extraction of phosphomolybdate deteriorates. On the other hand, for a given initial concentration of lithium chloride, (e.g. 0.8 M), the extraction increases with increasing molybdate concentration and reaches a maximum value, beyond which it also declines. Due to the very complex chemistry of phosphomolybdate, it is very difficult to give any definite reason for the extraordinary influence of lithium chloride on the extraction of phosphomolybdate, however, the drop in "D" values with the increasing LiCl concentration tends to suggest that CCM cannot account for the extraction of phosphomolybdate. This is further substantiated by the fact that phosphomolybdate is also extracted well by polyester-based polyurethane foam. The failure of polyether foam to extract $PMo_{12}O_{40}^{3-}$ anion through CCM may be attributed to the fact that according to the CCM the extraction of $PMo_{12}O_{40}^{3-}$, a triply-charged anion, would require the arrangement of three cation-containing helices of polyether chains around the phosphomolybdate. The possibility of such an arrangement is less frequent in the polymer. Al-Bazi(24) has also observed that, the extraction of triply-charged $Rh(SCN)_6^{3-}$ complex anion cannot be explained on the basis of the CCM, although the extraction of several doubly charged metal thiocyanato complex anions $[M(SCN)_4^{2-}]$ has been confirmed to take place through this mechanism.

The oxonium type mechanism might be considered to account for the sorption of phosphomolybdate into polyether foam. According to this mechanism, the protonation of etheral oxygen atoms of the polymer in acidic medium results in the formation of oxonium type salt, which thus can extract heteropoly anion ($PMo_{12}O_{40}^{3-}$) by an anion exchange mechanism. Based on this, polyether foam may be regarded as a weak base anion exchanger. The high values of distribution ratio (4×10^5) and of foam capacity (0.76 miliequivalent per gram) observed for the present system further support this idea. The possibility of polyether foam behaving as a weak base anion exchanger has also been mentioned by several other workers(4,15). In addition, the sorption of neutral acido species, $H_3PMo_{12}O_{40}$, may be very competitive, or perhaps the interaction of etheral oxygen atoms with molybdate, as suggested in solvent extraction systems, may be responsible for the observed extraction.

Assuming that phosphomolybdate is extracting into polyether foam by any mechanism other than CCM, the decline in phosphomolybdate extraction with the increase in LiCl concentration may be attributed to the simultaneous extraction of Li^+, along with MoO_4^{2-} or any other suitable anion, into polyether foam through CCM. Since according to this mechanism, the extraction of Li^+ will be accomplished by the formation of a helical pattern of inwardly directed oxygen atoms of polyether chains around the cation, the adoption of such a geometry by polyether chains to encage the cation will certainly limit the availability of ethereal oxygens for the extraction of phosphomolybdate i.e. would lower the extraction. The decrease in the extraction at high molybdate concentration can also be explained by using the same argument. Since sodium molybdate has been used as the source of molybdate, the addition of Na_2MoO_4 not only increases the formation and thus the extraction of phosphomolybdate, it also enhances the formation of helical structure in the polymer due to the extraction of sodium molybdate and thus decreases the number of "free" ethereal oxygen atoms to interact with phosphomolybdate.

In order to test this reasoning, the sorption of phosphomolybdate from sodium and potassium chloride solutions was studied. Since according to CCM polyether foam has the following order of extractability for alkali metal cations: $Li \ll Na^+ < Cs^+ < Rb^+ < K^+$, one would expect a greater interference in the presence of more extractable cation based on the above explanation. The formation of precipitate did not permit the study of the effect of rubidium and cesium. The effect of potassium was studied but over a small range of concentration again due to precipitation. However, the extraction of phosphomolybdate was studied over a wide range of NaCl concentration. The results of this study are shown in Figure 65, where the results of a similar study using lithium chloride are also included for comparison. As expected, the extraction of phosphomolybdate in the presence of equal amounts of alkali metal cations decrease in the following order: $Li \ll Na^+ < K^+$. These results tend to suggest that the presence of a chelatable cation enhances the formation of helical structure in the polymer and thus interferes with the sorption of species such as phosphomolybdate, which are not extracting through CCM.

Figure 65

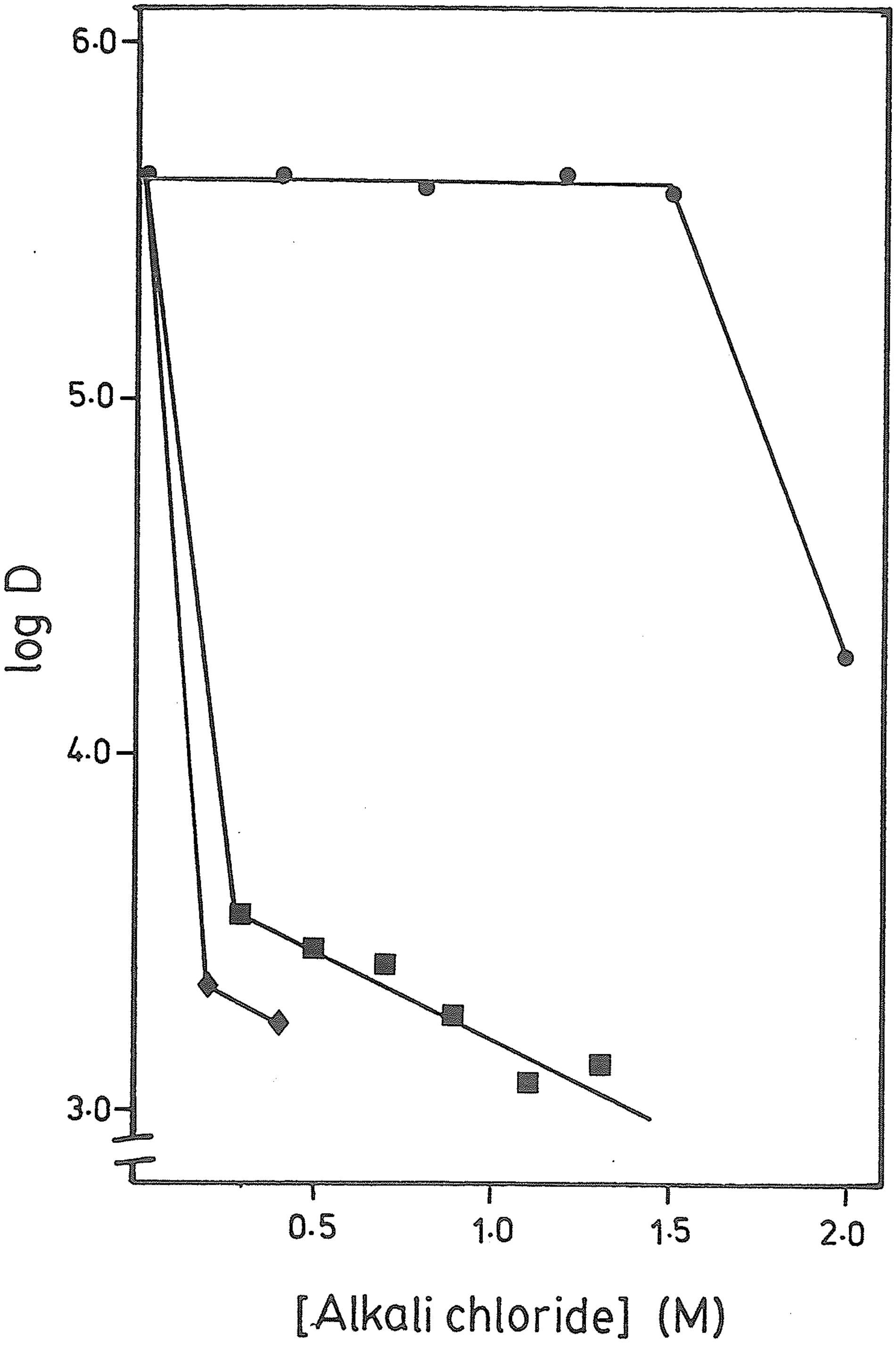
Effect of varying initial concentration of alkali metal chlorides on the extraction of phosphomolybdate.

Initial solution conditions:

$[PO_4^{3-}]$	4×10^{-5} M
$[MoO_4]$	6×10^{-3} M
pH	2.0 ± 0.1
Solution volume	150 mL
Foam weight	70 ± 5 mg
Temperature	25.00 ± 0.05°C

Notes:

LiCl(●)
NaCl(■)
KCl (◆)


6.0
5.0
4.0
3.0
log D
0.5
1.0
1.5
2.0
[Alkali chloride] (M)

6. The X-ray Fluorescence Determination of Phosphorus on Polyurethane Foam

Heteropoly anions have long been used for the determination of the hetero atoms. These anions can be determined by means of the absorbance of their aqueous solutions or their extracts in organic solvents. The extraction-photometric method has been used to determine phosphorus, silicon, arsenic, vanadium, germanium(183) etc. both in the reduced and the unreduced forms. The chief advantages of the extraction method over other methods are the high sensitivity and selectivity. Although, several other oxygenated organic solvents have been employed, butanol has been used most frequently for the extraction of phosphorus as phosphomolybdate with the subsequent reduction and photometric determination of the latter in the organic phase. Phosphorus has been determined in biological materials(190,191), natural waters(192,193), sea water(194), and steels(195) etc. by this method.

In addition to the traditional extraction and photometric method, in the last ten years several indirect methods have been developed. Phosphorus has been estimated by extracting the phosphomolybdate into a suitable organic solvent and the amount of phosphorus determined after analyzing the extract for molybednum by atomic absorption spectrophotometry(196). The stoichiometric ratio of phosphorus to molybdenum makes this method extremely promising for low concentration phosphorus.

Recently, the use of X-ray fluorescence (XRF) has been reported for the determination of cobalt directly on the foam(197). Thus, it was thought that an XRF method could also be combined with foam extraction for the indirect determination of phosphorus. Experiments were performed to study the feasibility of the procedure.

Foam discs(3.5 cm in diameter and weighing 0.10 ± 0.01 g) were squeezed for six hours in a series of 50 mL solutions, 5 x 10^{-3} M in Na_2MoO_4, having pHvalues of 2.0 ± 0.1 and containing different amount of phosphate ranging from 0 to 6.4 ppm. After extraction foam discs were washed with water, 0.1 M HCl and then water and finally air dried. Dried foam discs were placed on Mylar film over the detector for X-ray analysis. Spectra were accumulated for 100 seconds(a typical spectra is shown in Figure 66)and the integrated counts for MoK_α line were obtained. Each sample was integrated at least six times. The data corrected for average background was used to plot Figure 67. As can be seen a linear relationship exists between the counts for MoK_α lines and the initial phosphate concentration, suggesting the feasibility of XRF analysis combined with foam extraction for the determination of phosphorus.

In order to determine the lower detection limit, foam discs (3.5 cm in diameter and 0.1 ± 0.1 g in weight) were squeezed for six hours in 50 mL solutions of 0 to 3.0 ppm phosphate containing 2.5 x 10^{-3} M Na_2MoO_4 and sufficient HCl to maintain the pH value of 2.0 ± 0.1. The analysis of the aqueous phase after equilibration showed more than 99% extraction of phosphate. As can be seen in Figure 68, a plot of the counts of MoK_α lines versus initial phosphate concentration is a straight line passing throught the origin, indicating that 0.20 ppm of phosphate can easily be determined by this method. The detection limit can be further lowered by using superior

Figure 66

X-ray fluorescence spectrum of phosphomolybdate sorbed on polyurethane foam.

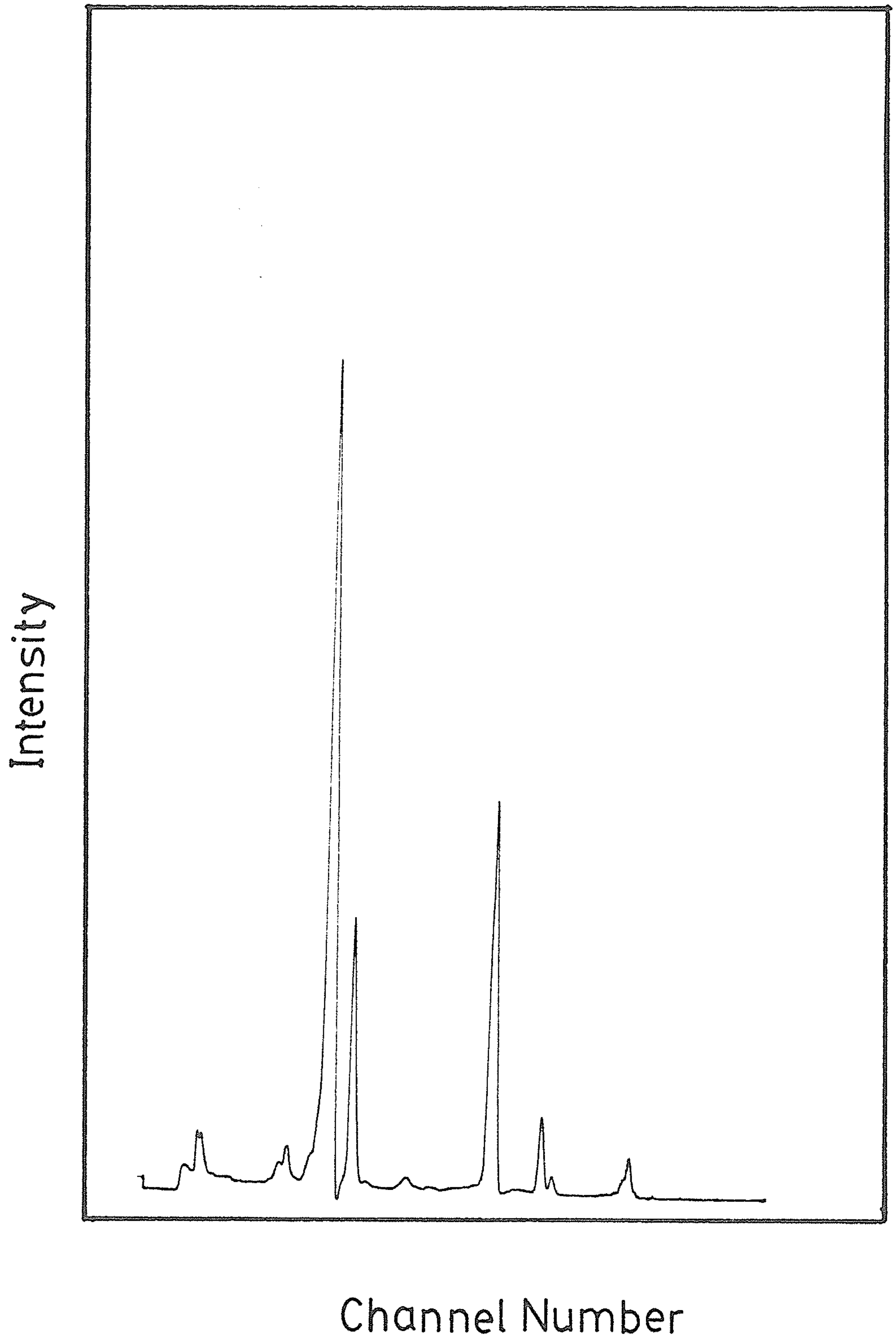

Intensity
Channel Number

Figure 67

Relation between intensity of MoK_{α} and the phosphate concentration in solutions.

Initial solution conditions:

$[\mathrm{MoO}_4^{2-}]$	5×10^{-3}
pH	2.0 ± 0.1
Solution volume	50 mL
Foam weight	0.10 ± 0.01 g

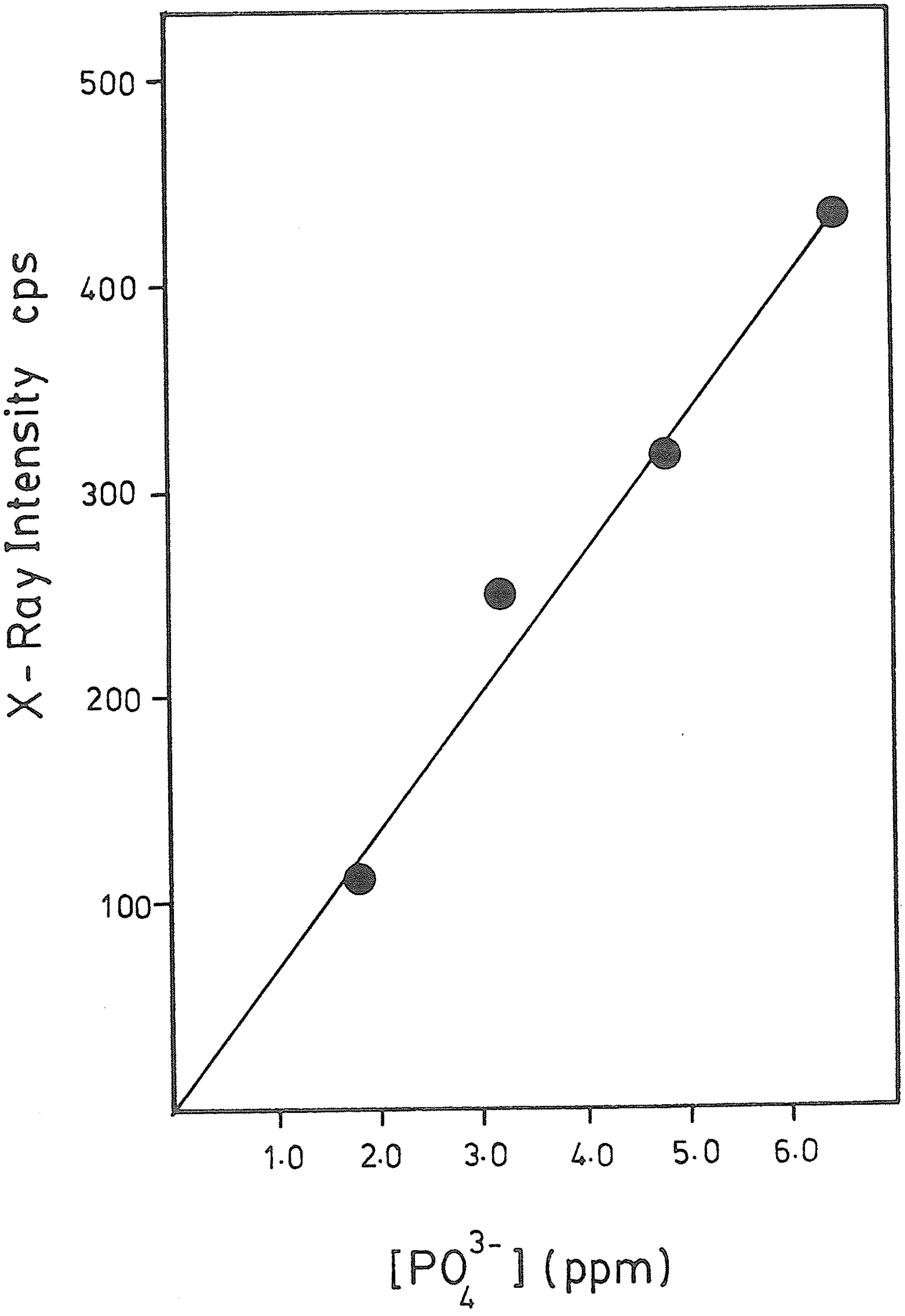
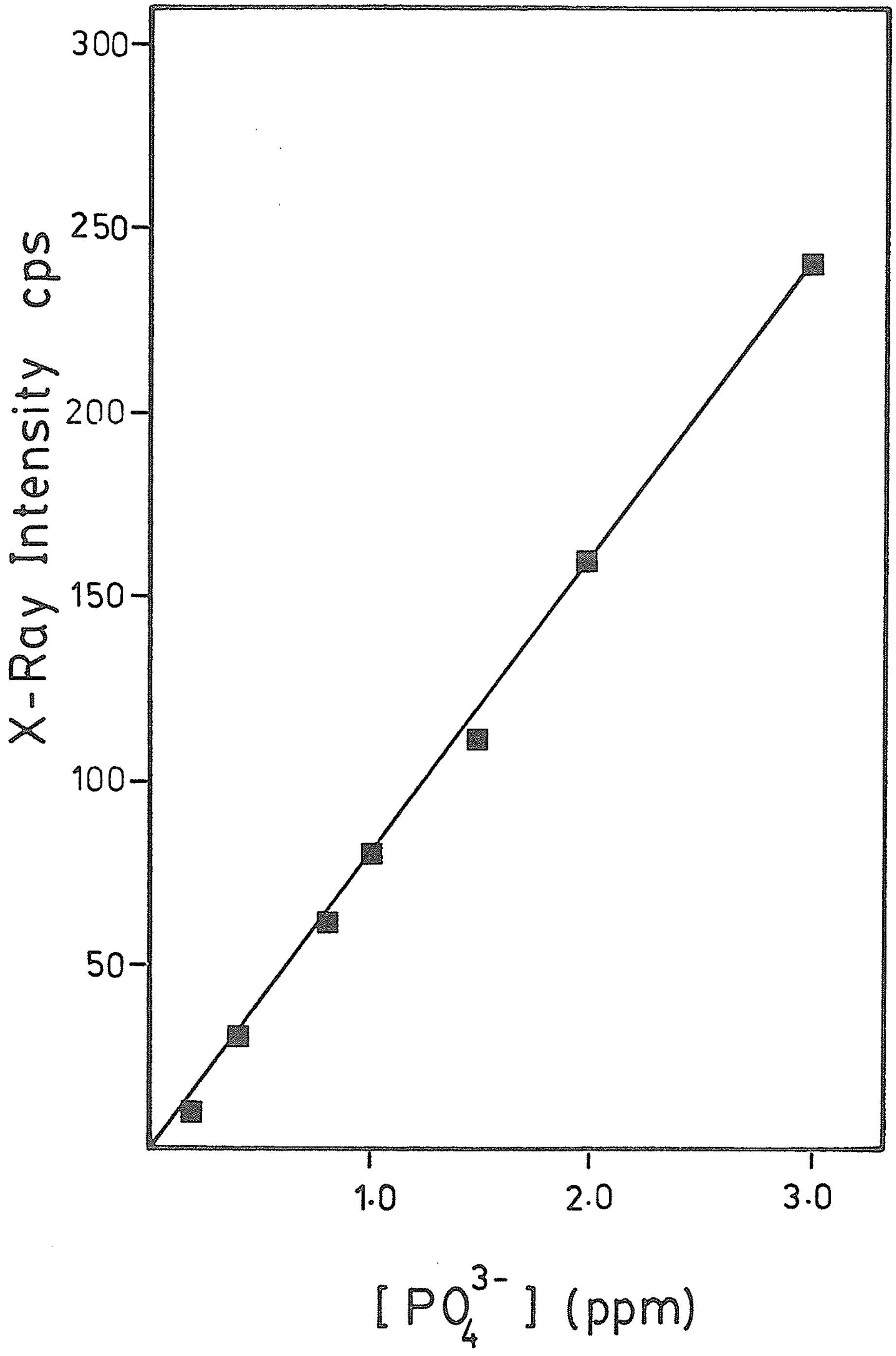

X - Ray Intensity cps
500
400
300
200
100
1.0
2.0
3.0
4.0
5.0
6.0
$[PO_4^{3-}]$ (ppm)

Figure 68

Plot of initial phosphate concentrations vs intensity of MoK_{α} line.

Initial solution conditions:

$[MoO_4^{2-}]$	2.5×10^{-3} M
pH	2.0 ± 0.1
Foam weight	0.10 ± 0.01 g
Solution volume	50 mL


X-Ray Intensity cps
300
250
200
150
100
50
1·0
2·0
3·0
[PO_4^{3-}] (ppm)

instruments and also by optimizing the various other factors e.g. weight and size of the foam discs.

D. CONCLUSION

The results of this study demonstrate that phosphate can be extracted very efficiently from acidic molybdate solutions by polyurethane foam. The distribution ratio of the foam extraction of phosphate as 12-phosphomolybdate is fairly high, of the order of 4×10^5 LKg^{-1}. The phosphate sorption capacity of the polyurethane foam (type A) is approximately 0.76 milliequivalent per gram of foam. The high values of distribution ratio and capacity suggest that polyurethane foam is a very good medium for the preconcentration of phosphate as phosphomolybdate.

The efficient extraction of phosphate is obtained under the following solution conditions:

a) In contrast to the necessity of the large excess of molybdate as reported for the solvent extraction systems(182), 25 fold excess of molybdate is found to be sufficient for efficient extraction of phosphate by polyurethane foam, whereas a large excess of molybdate is found to result in the decrease of phosphate extraction;

b) Similar to solvent extraction, there is an optimum range of pH, 1.0 to pH 2.5, for the efficient extraction of phosphomolybdate by polyurethane foam.

c) The results of this work also indicate that the addition of alkali salts (added to maintain the ionic strength) cause a decrease in phosphate sorption.

In addition, an X-ray fluroescence method has been developed for the determination of phosphorus as phosphomolybdate directly on the foam. The method described has been used for the determination of phosphate down to 0.2 ppm in solution. The detection can be further lowered by optimizing the various other parameters e.g. weight and size of the foam discs.

CHAPTER V. SUMMARY AND POTENTIAL APPLICATIONS

The work presented in this thesis has been divided into three sections.

The first section describes the use of both polyether- and polyester-based polyurethane foams for the extraction of alkali metal cations from the aqueous solutions of bulky anions using dicyclohexyl 18-crown-6 as a complexing agent. The results of this study clearly show that polyester foam is a better extractor of these ion-pairs (MCr^+A^-) than is the polyether foam. Analysis of the results of this study indicate that, although the extraction behaviour of polyester foam is in complete accord with simple solvent-like ion-pair extraction systems, the polyether foam behaves quite differently. The results of some experiments suggest that polyether-based polyurethane foam is capable of extracting metal cations from aqueous solutions of bulky anions even in the absence of crown ether.

Studies made in the second section demonstrate the ability of polyether-based polyurethane foam to extract some mono-and divalent cations, such as Na^+, K^+, Rb^+, Cs^+, NH_4^+, Ag^+, Tl^+ Ba^{2+} and Pb^{2+}, from aqeuous solutions of bulky anions. The results of this study also suggest that sorption of theseion-pairs cannot be explained by a simple solvent-like ion-pair extraction mechanism. The Cation Chelation Mechanism is proposed to account for the observed phenomenon.

The results of several types of measurements have confirmed the existence of a strong interaction between polyether and various cations. The following order of affinity of the polyether chain for particular cations is also noted; $Li^+ < Na^+ < Cs^+ < Rb^+ < K^+ \sim NH^+ < Ag^+ \sim Tl^+$ for monovalent cations and $Ca^{2+} < Sr^{2+} < Ba^{2+} < Hg^{2+} < Pb^{2+}$ for divalent species.

Based on the close similarity between the sequence of affinity displayed by polyether and that of 18-crown-6 derivatives(47), it has been concluded that polyether-based polyurethane foam can be regarded as pseudo 18-crown-6. Thus, the extraction of ion-pairs including chelatable cations can be attributed to effective solvation of the accompanying cation by the polyol portion of the polmyer.

On the basis of this special ability of the polyetherbased polyurethane foam to mimic 18-crown-6, it has considerable potential in several areas of chemistry:

i) It may be used for the extraction of essentially all of the metal cations which are known to form stable complexes with 18-crown-6 and its derivatives(47). Thus, the use of polyether foam can be extended to the sorption of Sr^{2+}, Cr^{3+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, UO_2^{2+}, Ce^{3+} and La^{3+} etc.

ii) Since 18-crown-6 forms a stable complex with Tl^+ but not with Tl^{3+}, it seems possible that polyether foam, a pseudo 18-crown-6, may be applied to the selective extraction of Tl^+ from a mixture of Tl^+ and Tl^{3+}. Similarly, the separation of Hg^{2+} and Hg^+ should also be possible.

iii) According to the theory of hard and soft acids and bases(198,199) Ag^+, Tl^+ and Hg^{2+} interact strongly with the sulphur atom. Therefore, if a polythioether foam is synthesized, it may be expected to have a greater extractability and a higher selectivity for these cations. The polythioether could thus find application in such areas as the recovery of silver from the effluents of the film processing industry and also for the clean-up of mercury contaminated rivers and lakes.

iv) Many organic reactions make use of alkali and alkaline earth salts as reagents but their efficiency is often impaired by the low solubility of these salts in organic solvents. Both cyclic(199) and noncyclic polyethers(200) have been used to solubilize many salts in apolar solvents. By complexing the cation, polyether foam might also enhance the reactivity of the counter ion and may thus find application in the area of catalysis.

In the last section, it has been observed that the polyether foam can be employed effectively for the sorption of phosphate as phosphomolybdate from acidic molybdate solutions. The results of this study also show that XRF analysis can be combined with the foam-extraction for the indirect determination of phosphate. It is also suggested that the use of polyurethane foam can be extended for the extraction-XRF determination of arsenic, silicon, germanium etc. Species once sorbed on the foam can also be analyzed by other methods (e.g. by neutron activation or even by visual examination in case of coloured species).

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