THE UNIVERSITY OF MANITOBA

MECHANISMS OF
EXTRACTION BY
POLYURETHANE FOAM

By

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A thesis submitted to the Faculty of Gradute Studies in partial

fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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LIST OF ABBREVIATIONS

D   Distribution coefficient

DPA^- Dipicrylaminate

TPB^- Tetraphenylborate

WSEIP   Water structure-enforced ion-pairing

ABSTRACT

The extraction of a variety of compounds by polyurethane foam was studied to determine the extraction mechanism. Relatively hydrophilic compounds such as salicylic acid, 8-hydroxyquinoline, 1-amino-2-naphthol-4-sulfonic acid and cinnamic acid were extracted only in the neutral form by a simple solvent extraction mechanism. The mechanism was confirmed by use of the salting-out effect and pH studies.

Bulky and hydrophobic anions such as tetraphenylborate (TPB^-) and dipicrylaminate (DPA^-) were extractable in the presence of various alkylammonium and alkali metal ions from aqueous solution. The selectivity for the alkylammonium ions was affected by a combination of effects including hydrophobic interaction, steric and inductive effects. The extractability sequences of $NH_4^+ >$ t-butylammonium $>$ isopropylammonium $>$ ethylammonium $>$ methylammonium and $K^+ \approx Rb^+ > Cs^+ > Na^+ > Li^+$ for the extraction with polyether foam suggested that the cation chelation mechanism might be operative . However, the same order of $K^+ \approx Rb^+ > Cs^+ > Na^+ > Li^+$ was obtained for the extraction with 100% polypropylene oxide polyether foam which does not normally adopt a helical structure to form oxygen-rich cavities as easily or as effectively as polyethylene oxide to accomodate alkali metal ions. This result indicated that a hole-size / cation-diameter relationship was not required for the high extraction of K^+. The extraction of alkali metal DPAs and hydroxides from methanol demonstrated the importance of the solvent effect. It indicated that the water-structure enforced ion-pairing (WSEIP) was the driving force for extraction of the ion-pairs.

In light of these results, the extraction mechanism for ionic species can be described as an ion-pair extraction process. Two factors, ion-pair formation in water and interaction of the extracted ions with foam, play significant roles in the extraction of the ion-pairs. The

overall effect of these two factors appeared to determine the extractability of the ions of the extractable ion-pair. The high extractability of K^+ by polyether foam containing either a mixture of polyethylene oxide and polypropylene oxide or 100% polypropylene oxide can be explained by the strong interaction between K^+ and the foam, which provides an adequate number of ether oxygens but not necessarily with a helical structure, to compensate for the lower association of the potassium ion-pair relative to the rubidium and the cesium counterparts in water.

CHAPTER 1

GENERAL INTRODUCTION

1.1 Polyurethane Foam Synthesis

Rigid polyurethane foam was first prepared by Otto Bayer[1] in 1937. The preparation of flexible foam was first reported by Hochtlen[2] in 1952.

Polyurethanes are substituted amide esters of carbamic acid (R–NH–COOH) and are produced by the condensation-polymerization of polyesters or polyols with diisocyanates[3], equation (1).

$$\text{OCNRNCO} \; + \; \text{HOR'OH} \; \text{------>} \; \text{OCNR} \boxed{\text{NH–CO–O}} \text{R'OH} \qquad (1)$$
diisocyanate   polyol   urethane group
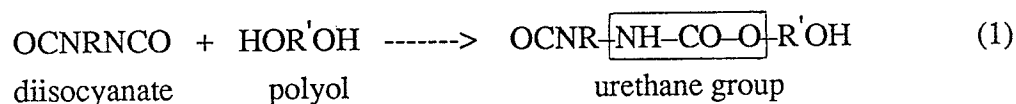
R is generally an aryl group because the electron-withdrawing effect of the aromatic rings makes the isocyanate carbon more positive and thus facilitates attack by the electron-donating hydroxyl group[3]. R' is typically an alkyl polyester or polyether chain.

The reaction of isocyanate with water is responsible for foam formation by carbon dioxide liberation as an in situ blowing agent.

$$\text{RNCO} \; + \; \text{H}_2\text{O} \; \text{------>} \; [\text{R–NH–CO–OH}] \; \text{------>} \; \text{R–NH}_2 \; + \; \text{CO}_2 \qquad (2)$$
carbamic acid
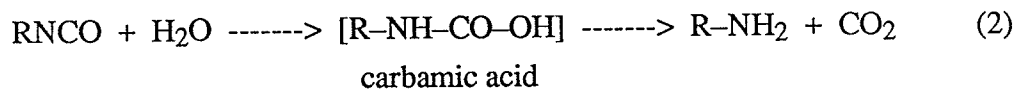
The reaction with water forms an unstable carbamic acid which decomposes to an amine and carbon dioxide.

The amine from equation(2) can react with an additional isocyanate to produce substituted urea-amine.

1

$$RNCO \ + \ RNH_2 \ \text{------>} \ R\text{---}\boxed{NH\text{---}CO\text{---}NH}\text{---}R \qquad (3)$$
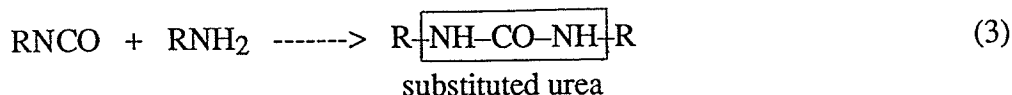
<div align="center">substituted urea</div>

On the other hand, carbamic acid may react with an isocyanate to form carbamic acid anhydride which decomposes to give carbon dioxide and substituted urea.

$$[R\text{---}NH\text{---}CO\text{---}OH] \ + \ RNCO \ \text{------>} \ R\text{---}NH\boxed{CO\text{---}O\text{---}CO}NH\text{---}R \ \text{------>}$$

<div align="center">anhydride</div>

$$\text{------>} \ R\text{---}NH\text{---}CO\text{---}NH\text{---}R \ + \ CO_2 \qquad (4)$$
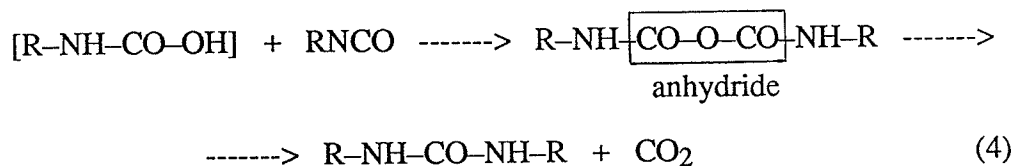
Reactions leading to branching and cross-linking are the isocyanate-urethane reaction producing allophanate (equation 5) and the isocyanate-urea reaction yielding biuret (equation 6).

$$R\text{---}N{=}C{=}O \ + \ R\text{---}NH\text{---}CO\text{---}OR' \ \text{------>} \ R\boxed{NH\text{---}CO\text{---}NR\text{---}CO\text{---}O}R' \qquad (5)$$

<div align="center">allophanate</div>

$$R\text{---}N{=}C\text{---}O \ + \ R\text{---}NH\text{---}CO\text{---}NH\text{---}R \ \text{------>} \ R\boxed{NH\text{---}CO\text{---}NR\text{---}CO\text{---}NH}R \qquad (6)$$

<div align="center">biuret</div>
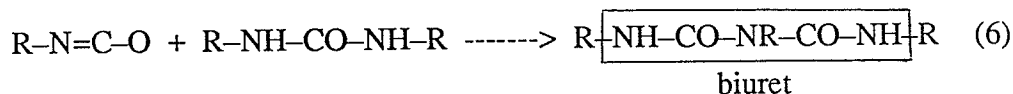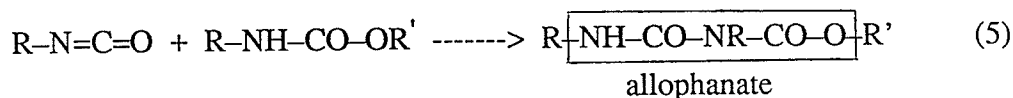
Polyols in the molecular weight range of 400 to 6000 are generally employed in polyurethane foam preparation. The most widely used isocyanate is toluene diisocyanate.

Catalysts are usually used to increase the reaction rate and to establish the balance between the chain extension and the foaming reaction. Organotin compounds such as tin octanoate, dibutyltin dioctanoate and dibutyltin acetate enhance the isocyanate-hydroxyl reaction and the tertiary amine catalysts; e.g., trimethylamine, *N-N'*-diethylpiperazine and tribenzylamine promote the isocyanate-water reaction.

1.2 Physical and Chemical Properties

The physical properties of polyurethane foams are dependent on the preparation process[3]. The cross-link density of the urethane polymer determines the flexibility or rigidity of the foam. Flexible foams are prepared from polyols of moderately high molecular weight and low degree of branching, while rigid foams are prepared from low molecular weight polyols and high degree of branching.

Bowen[4] examined the chemical properties of some commercial foams with different densities and found that they are quite stable and inert. They degrade when heated to between 180 and 220°C and slowly turn brown in UV light. Apart from swelling reversibly, they are unaltered 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 organic solvents such as light petroleum, benzene, carbon tetrachloride, chloroform, diethyl ether, diisopropyl ether, acetone, methyl isobutyl ketone, ethyl acetate, isopentyl acetate and alcohols. However, the foams can be dissolved in hot arsenic(III) chloride and concentrated sulphuric acid, and destroyed by concentrated nitric acid. They also reduce alkaline potassium permanganate.

Schollenberger and Stewart [5] reported that polyether foam is less susceptible to hydrolytic attack than is polyester foam. The decomposition reaction is acid catalyzed. Polyester foam containing polycarbodiimides was found to be more acid resistant because of the neutralization of carboxyl-terminated products by polycarbodiimides[6].

1.3 Polyurethane Foam as a Solid Sorbent

Although the extraction and separation of inorganic and organic substances by solvent extraction has long been known, the use of solid extractants has received much less

attention. Solid sorbents offer certain advantages over solvent extraction. There is no toxic vapor evolution which is a hazard commonly associated with organic solvents. Solid sorbents are usually not soluble in the solution from which the substances are extracted and the separation of the sorbent and the solution after extraction is simple.

The solid phase of polyurethane foams is distributed around many small gas bubbles (cells). If the gas bubbles occupy a volume smaller than 76%, they may be spherical. If they occupy a volume larger than 76%, they will be quasi-spherical polyhedra[7]. The polymer is distributed in the walls of the bubbles such that the foam is in a reticular membrane form. This distinctive membrane structure of polyurethane foams differentiates them from all other types of solid sorbents which are compact or porous solids. The diffusion rates of chemical species in membranes are considerably larger than those in bulky solids, and besides, the open pore structure of the foam allows high flow rate through the foam. This flow characteristic enables the foam to be used in the concentration of various trace components from large volumes of water or air in a relatively short time.

1.4   Extraction of Inorganic and Organic Species with Polyurethane Foam

Considerable progress has been made in recent years in the use of polyurethane foams for separation and preconcentration purposes. Several reviews[8-12] and monographs[13,14] have appeared.

In 1970 Bowen[4] pioneered the use of polyurethane foam for the extraction of several inorganic and organic substances from aqueous solution. Iodine, benzene, chloroform and phenol have been extracted from water. Mercury(II), gold(III), iron(III), antimony(V), thallium(III), molybdenum(VI) and rhenium(III) have been extracted from acidic chloride solution, and uranium(VI) has been extracted from saturated aluminum

nitrate solution. The high capacity of the foams (0.5-1.5 mol/kg) shows that the extraction process is absorption rather than adsorption. Bowen noted that the substances absorbed by the foam are also extractable from aqueous solution by diethyl ether. He also suggested that the foam may act as an anion exchanger by protonation of the nitrogen atoms in urea and urethane linkages or the ether oxygen atoms in acids.

Schiller and Cook[15] were able to separate gold(III) chloride from natural waters with polyurethane foams. Sukiman[16] reported the extraction of gold(III) chloride from acidic aqueous solution.

Gesser et al.[17] studied the extraction of gallium(III) from acidic chloride solutions. The high sorption capacity was related to the absorption of the gallium complex into the foam rather than adsorption on the foam surface. Later, Gesser and co-workers[18-20] investigated the diffusion of metal complexes, such as HMX_4 of gallium and iron across thin polyurethane films to determine the mechanism of extraction. It was suggested that the extraction is either through a simple solvent extraction mechanism or through a weak anion exchange mechanism by protonation of the ether sites in the foam. However, the results did not allow the authors to distinguish between the two proposed mechanisms. They concluded that the foam could be considered as a polymeric analogue of diethyl ether.

Lo and Chow[21,22] examined the extraction of tin(II) and tin(IV); and antimony(III) and antimony(V) from acidic chloride solutions with polyether and polyester foams. As previously suggested, the extraction process can be described as an "ether-like solvent extraction".

Koch[23] reported the extraction of platinum(II) in the form of chloro(trichlorostannato) platinum(II) anions in the presence of sufficient tin(II) chloride by foams from dilute hydrochloric acid. In a further study, Brackenbury and Koch[24] have shown that nickel, copper, iron, manganese, cobalt, tin, ruthenium, iridium, rhodium; and 0.1 M SO_4^{2-}, ClO_4^- and NO_3^- do not significantly interfere with the platinum extraction.

Foams were successfully used for the quantitative extraction and separation of rhodium from iridium in hydrochloric acid containing tin(II) chloride[25]. In a separate study[26], a partial separation of rhodium and iridium from solutions containing tin(II) chloride was achieved. Further work[27] on the extraction of platinum and rhodium under comparable conditions as described above[25] has been carried out which showed that platinum and rhodium can be separated from iridium and ruthenium.

The study on the extraction of uranium(VI) from aqueous nitrate solutions by Gesser *et al.*[28] gives further support for the earlier assumption that the foam acts as a solid solvent extractant with a moderate dielectric constant.

Numerous studies on the extraction of many metals from aqueous thiocyanate solutions have been reported. Braun and Farag[29,30] described the separation of cobalt(II) and iron(III) from acidic thiocyanate media. The high capacity of the foam for thiocyanate complexes was regarded as further evidence that the foam behaves as a solid polymeric extractant.

Hamon and Chow[31] were able to extract cobalt(II) from aqueous thiocyanate solutions with several foam types and foam pretreatments. The effect of various substances added to the solution has been examined.

Hamon *et al.*[32] have investigated the mechanism of metal ion sorption by polyurethane foam using the extraction of cobalt(II) thiocyanate complexes as the model. It was found that ether-like solvent extraction and some other proposed mechanisms fail to explain the extraction of cobalt thiocyanate complexes. A new proposal, termed the cation-chelation mechanism was suggested. It was observed that polyether-based foams demonstrate similar cation selectivity as 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6). The foam is viewed as an acyclic analogue of 18-crown-6 which can complex efficiently with cations in facilitating the extraction of anionic metal complexes.

Moody *et al.*[33] reported the extraction of Co^{2+}, Fe^{3+}, Zn^{2+}, Cd^{2+} and Mn^{2+} from potassium thiocyanate solution by polyether foam. The measured metal-to-thiocyanate and potassium-to-metal ratios associated with the foam are compared with the calculated stability constants for the participating complexes using the ECCLES computer program. The species involved are consistent with predications based on solution equilibria. The authors indicated that the thiocyanate complex can be extracted through the cation chelation mechanism.

Al-Bazi and Chow[34,35] examined the extraction of palladium as a thiocyanate complex from aqueous solution. The effect of alkali metal salts has been studied in order to evaluate the possible sorption mechanism. It was found that the extraction of $Pd(SCN)_4^{2-}$ at high pH increases in the order $Li^+ < Na^+ < Cs^+ < Rb^+ < K^+ \leq NH_4^+$ which is in good agreement with the cation chelation mechanism. In a further study[36], they showed that it is possible to separate palladium from a 20-fold excess of platinum under optimum conditions.

Ruthenium and osmium thiocyanate extractions have been reported by Al-Bazi and Chow[37,38]. Based on the result that, among other univalent cations, potassium chloride results in the greatest increase in the anionic metal complex extraction, it was considered that the extraction could be explained in terms of the cation chelation mechanism. By varying the conditions for complex formation, it is possible to separate ruthenium from rhodium and osmium.

Al-Bazi and Chow[39,40] studied the extraction of rhodium from acidic thiocyanate solutions. Conditions for the separation of rhodium from a 5-fold excess of iridium have been established. In contrast to $Pd(SCN)_4^{2-}$ and $Ru(SCN)_4^{2-}$, $Rh(SCN)_6^{3-}$ is extracted through a simple solvent-extraction mechanism rather than the cation chelation mechanism.

Liu and Chow[41] investigated the sorption of zirconium and hafnium thiocyanate by polyether foam. The foam is highly effective for the extraction from thiocyanate solutions

containing only hydrochloric acid and from those containing potassium chloride at pH 1.8. This extraction process can also be explained in terms of the cation chelation mechanism.

Caletka et al.[42] reported the extraction of molybdenum, tungsten and technetium by polyether-based foam and by a cyclic polyether from aqueous thiocyanate solutions. The same authors[43] also tested the extraction of 15 elements in the system containing polyurethane foam/HF-alkali metal fluoride and cyclic polyether/HF-alkali metal fluoride. Only tantalum, antimony, rhenium and technetium are well extracted with either the foam or cyclic polyether. They assumed that the extraction of these metal anions can be explained by the cation chelation mechanism. The extraction of many metals by polyurethane foam in HCl and HCl-KSCN media was examined[44]. Anionic thiocyanate or mixed hydroxo-thiocyanate complexes are favored and the results can be explained by the cation chelation mechanism.

Khan et al.[45,46] examined the extraction of alkali metal picrates (MA) in the presence of 18-crown-6 (Cr) into polyether and polyester foams. By treating the foam as an organic phase, theoretical equations were derived to describe the distribution coefficient as a function of picric acid, crown ether and metal ion concentrations. The results were found to be consistent with these equations. It was concluded that the extraction can be considered as the ion-pair extraction of MCrA by an organic solvent. Furthermore, the efficiency of the extraction into the more polar polyester foam is greater than into the less polar polyether foam.

Khan et al.[47] reported the sorption of silver(I), thallium(I), barium(II) and lead(II) ions from aqueous solutions containing picric acid. In the absence of picric acid, no detectable extraction was observed. However, in the presence of a bulkier anion, 8-anilino-1-naphthalene sulfonic acid, the sorption of thallium(I) is higher than that obtained from aqueous picric acid solution. Formation of an ion-pair complex between the metal ion

and the picrate ion was suggested. The authors concluded that the extraction cannot be explained by a simple ion-pair mechanism but rather by the cation chelation mechanism.

Khan and Chow[48] studied the extraction of phosphorus in the presence of molybdate from acidic aqueous solutions. The effect of alkali-metal chlorides on the sorption of phosphomolybdate was investigated. It was found that in the presence of sodium or potassium chloride the distribution ratio decreases rapidly initially, then slowly with increasing alkali metal concentration. Thus, the cation chelation mechanism cannot account for the extraction of phosphomolybdate by polyether foam. It was considered that the oxonium type anion exchange mechanism in which the ether oxygen of the foam is protonated is operative.

Braun and Farag[49] used polyether foam for the sorption and recovery of gold from ammoniacal cyanide media. It was shown that more than 95% of gold can be recovered from an industrial ammoniacal gold-cyanide waste solution directly by the foam with both the normal column and the column pumping methods.

The use of foam for the sorption of iridium(IV) and platinum(IV) from nonaqueous solvents has been investigated by Moore and Chow[50]. The sorption of iridium and platinum from ethyl acetate solution is higher than from acetone. The extraction behaviour of these complexes from ethyl actetate and acetone was said to be not explicable by a simple solvent extraction mechanism.

Polyurethane foams have been widely used for the extraction of various species, but very few methods have included a direct determination of the component on the foam. Some have used the foam as a preconcentration method before recovery for analysis. Others have determined the extractable species concentration in solution before and after extraction. Chow *et al.*[51] used the foam to extract cobalt thiocyanate and determined cobalt on the foam by X-ray fluorescence. A linear response was obtained for samples treated identically. Cobalt at levels as low as 0.05 ppm can be quantitatively extracted and cobalt

can be determined in the presence of several other metal ions such as nickel, lead, iron, zinc and copper.

Chow and Ginsberg[52] have examined the application of the above procedure[51] to the determination of other metals. Iron, cobalt and zinc as well as platinum and palladium were extracted individually and collectively from aqueous thiocyanate solutions. The metal extraction is more than 95% complete and the determination of one metal is not affected by the presence of the others. Thus, this method allows the simultaneous determination of several elements at low concentrations.

Khan and Chow[53] were able to determine arsenic on foam by X-ray fluorescence. Arsenic was extracted as arsenomolybdate by the foam. Arsenic concentrations as low as 36 μg/mL can be detected in 100 mL of aqueous solution. The same authors[54] described an indirect X-ray fluorescence method for phosphate based on the extraction of phosphomolybdate by foam. The molybdenum, which is associated in a fixed ratio with phosphorus, is determined directly on foam by X-ray fluorescence.

Other methods have also been employed to directly analyze the extracted species on foam. Radioactive iodine has been extracted from aqueous solution[55-57] and from milk[58] into polyurethane foams. The foams were analyzed directly for iodine-131 by gamma spectrometry. Schiller and Cook[15] measured gold on foam by neutron-activation. More recently, Farag et al.[59] determined trace amounts of phosphate in tap and natural waters using "foam thin-layer colorimetry". The determination is based on the measurement of the blue molybdoantimony phosphoric acid species in the presence of ascorbic acid sorbed in a foam thin layer.

Polyurethane foams have been successfully applied to concentrate various organic contaminants from water such as chlorinated organic compounds and aromatic hydrocarbons(PAH). In 1971, Gesser et al.[60] initiated the use of polyurethane foams for the concentration of organic compounds. Two foam plugs were packed in a column, then

aqueous solutions containing polychlorinated biphenyls (PCB) in the range of 2 to 20 μg/L were passed through the column at a flow rate of 250 mL/min. It was found that 95% of the PCB is retained by the first plug and a few percent by the second plug.

Foams were used as an alternative to activated carbon for the determination of trace organic contaminants in water by Gesser et al.[61]. The foam material was placed in a standard carbon adsorption metering apparatus and used to monitor organic matter in drinking water. It was found that the water treatment process does not significantly reduce the organic contaminants from the raw river water. The authors noted the superiority of foam over activated carbon since the recovered material is often different from the original form due to catalytic effects exhibited by activated carbon.

Musty and Nickless[62] studied the extraction of chlorinated insecticides by foam as a function of pH. Quantitative recoveries were obtained at pHs between 6 and 9. It was pointed out polyurethane foam is a better sorbent than activated carbon for the same reason as mentioned above[61].

Saxena et al.[63] reported the extraction of benzo(a)pyrene which is considered a major representative of carcinogenic PAHs in water by foam. It was found that the retention efficiency increases with increasing pH of the solution (pH 3 to 10). It was also observed that the retention efficiency increases with heating the water to 60°. This increase was ascribed to the desorption of BaP from suspended particles into water. Basu and Saxena[64] also investigated the sorption of a mixture of PAH containing benzo(a)pyrene, fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene and benzo(ghi)perylene by polyurethane foam. The retention efficiencies of the individual PAHs are generally not less than 88 and 72% from finished and raw waters respectively.

Afghan et al.[65] demonstrated that polyurethane foam is capable of concentrating PAH at the parts per trillion (ppt) level in natural waters and the method can be modified to analyze dissolved PAH from environmental samples. The concentrating ability of the

foams was found to be similar to other sorbents such as XAD-2 and C18-bonded phase packing. Significant amounts of PAH are retained by particulate matter in the samples. It was recommended that the use of foam for quantitative recovery of PAH requires initial filtering of the sample followed by extraction of the filtered particulate matter and the packing material.

Gough and Gesser[66] reported the retention and recovery of phthalate esters by polyurethane foam. Phthalates with side chains varying in length from one to ten carbons were extracted. It was found that phthalates with longer side chains are not significantly extracted by the foam. The observation was attributed to the probable slow sorption rates of these phthalates on the foam.

Schumack and Chow[67] studied the mechanism of the extraction of simple aromatic compounds by polyurethane foams. Comparison with identical extractions into diethyl ether and the salting-out effect observed suggest that the basic extraction mechanism is an ether-like solvent extraction mechanism. It was noted that compounds containing a phenolic or carboxylic group have larger distribution coefficients due to hydrogen bonding with the foam. The hydrogen bonding is prevented by the presence of a strong electron-donor group ortho to the hydrogen bonding group as in *o*-nitrophenol and salicylaldehyde where intra-molecular hydrogen bonding can take place. It was concluded that hydrogen bonding is stronger with polyether foam than with polyester foam.

Chow *et al.*[68] investigated the extraction of many organic dyes by polyurethane foam from aqueous and 50% aqueous methanol solutions. It was found that the extraction of neutral dyes can be explained by a simple solvent extraction mechanism. However, the extraction of anionic dyes is consistent with the cation chelation mechanism.

A comparative study was made by Gomez-Belinchon *et al.*[69] for the collection of aliphatic, aromatic, chlorinated hydrocarbons and fatty acids from sea water by Amberlite XAD-2 resin, liquid-liquid extraction and polyurethane foam. Significant differences in the

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extraction of the high molecular weight aliphatic and aromatic hydrocarbons were observed among these methods. Liquid-liquid extraction provides these compounds in higher relative amounts, while polyurethane foam gives intermediate yield and XAD yields the lowest proportion. It was concluded that liquid-liquid extraction is the method of choice. However, when field conditions prevent the use of liquid-liquid extraction, extraction on polyurethane foam is the better alternative method.

Recently, Farag et al.[70] used the foam for the extraction and recovery of some alkaloids from dilute aqueous solutions (0.01-0.1 ppm). Recovery of greater than 94% was obtained. Farag et al.[71] also reported the collection and recovery of some P- and S-containing insectides from aqueous solution by polyurethane foams. Ahmad et al.[72] applied polyurethane foam to extract carboxylic acids from water and aqueous solutions containing other compounds.

Various organic compounds such as PAH[73-76], organophosphorus pesticides[77-79] and chlorinated organic compounds[80-83] have been successfully concentrated from air by polyurethane foams. Recently, a comparative study[84] was carried out for the sorption of ambient organic vapors by polyurethane foam and Tenax-GC. The methods were adsorption/solvent extraction with polyurethane foam plugs (ASE/PUFP) and adsorption/thermal desorption with Tenax-GC cartridges (ATD/Tenax-GC). It was found that PUF cannot be used for the determination of compounds more volatile than acetanaphthylene. However, compounds less volatile than pyrene are not desorbed easily from the Tenax-GC cartridges. It was concluded that both ASE/PUFP and ATD/Tenax-GC are valid methods for the analysis of many ambient organic vapors at the ng/m^3 level. ASE/PUFP is well suited for the concentration of nonvolatile compounds using high sample flow rates.

Polyurethane foams loaded with various compounds, e.g., solvent extractants[85-87], hydrophobic chelating reagents[57,88-91], liquid ion exchangers[92-94] and other functional

groups[95], have been extensively used to extract inorganic and organic species from aqueous solutions.

Braun et al.[96] reported that 1-(2-pyridylazo-2-naphthol) (PAN)-loaded polyether foam can extract gold and mercury from thiocyanate solutions quantitatively. Diethylammonium diethyldithiocarbamate (DDC)-loaded polyester foam can recover indium and mercury thiocyanate quantitatively.

Palagyi[97–99] used polyether foam impregnated with a tri-alkylamine containing dissolved inactive iodine to extract radioactive iodine-131 from water and milk. 95% and 80% yield of the radioactive iodine can be obtained from water and milk respectively.

Korkish and Steffan[100] applied powdered foam impregnated with tri-n-octylphosphine oxide (TOPO) to extract uranium quantitatively from 1 M HCl containing ascorbic acid. The presence of several other cations does not interfere with the extraction and uranium can be desorbed by ethanol.

Caletka and Krivan[101] studied the separation of niobium and tantalum by foams treated with diantipyrylmethane (DAM), tri-n-butyl phosphate (TBP) and methyl isobutyl ketone (MIBK) in HF and HF/H_2SO_4 media. Generally, tantalum is strongly retained while niobium is readily eluted. Quantitative separation for the metal was achieved for all the loaded foams investigated.

It should be noted that the papers mentioned above regarding the application of loaded polyurethane foams for extraction purposes and the application of polyurethane foams for the extraction of organic vapors from air are illustrative and not exhaustive since the interest of this work is the application of unloaded polyurethane foams for the extraction of compounds from aqueous solutions. A detailed account of the work on loaded foams and concentration of vapors from air by polyurethane foams can be found in the reviews by Braun et al.[12,14].

1.5 Possible Mechanisms of Polyurethane Foam Extraction

There are several possible mechanisms by which metal ions are extracted from aqueous solution by polyether-type polyurethane foam. The predominant one is dependent on the conditions of extraction and the nature of the extractable species. The following is an outline of the possible mechanisms.

1.5.1 Surface Adsorption

Bowen[4] rejected the surface adsorption mechanism because of the relative high capacity measurement (0.5–1.8 mol/kg) for extracted species on the foam. The ability of several metal species such as $GaCl_4^-$ [18,19], $Co(SCN)_4^{2-}$ [102] and $FeCl_4^-$ [19] to diffuse through polyurethane membranes gives further support for the true absorption into the bulk of the foam.

1.5.2 Solvent Extraction

Bowen[4] noted that the compounds extractable by the foam are also extractable by diethyl ether and suggested the concept of an ether-like solvent extraction. Gesser *et al.*[17,20] later extended this idea to describe the foam as a polymeric analogue of diethyl ether. The solvent extraction mechanism is based on the assumption that neutral metal complexes are first formed in the aqueous solution and then extracted into the foam. The extraction process can be represented by:

$$mM^{p+} + pMeX_n^{m-} \rightleftharpoons (M^{p+})_m \cdot (MeX_n^{m-})_p \qquad (7)$$

$$(M^{p+})_m \cdot (MeX_n^{m-})_p \rightleftharpoons [(M^{p+})_m \cdot (MeX_n^{m-})_p]_f \qquad (8)$$
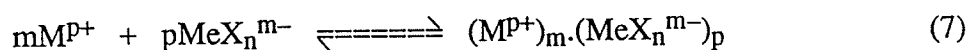
where M is the cation accompanying the extraction,

Me is the metal,

X is the anion,

f is the foam phase,

m, n and p are integers.

This mechanism has been widely accepted by many workers to describe the extraction of various species, e.g., $GaCl_4^-$ [17], $FeCl_4^-$ [20], $SnCl_5^-$ [21], $SbCl_4^-$ [22] and $Rh(SCN)_6^{3-}$ [39,40].

1.5.3 Ligand Addition or Exchange

Lone pair-containing atoms such as nitrogen and oxygen from the urethane, urea, ether or ester linkages are present in the foam. These donor atoms may act as ligands(L) to interact with the extracted species(MeX_n) through ligand exchange or addition reactions:

$$MeX_n \ + \ y(:L) \ \rightleftharpoons \ MeX_{n-y}L_y \ + \ yX \qquad (9)$$

$$MeX_n \ + \ y(:L) \ \rightleftharpoons \ MeX_nL_y \qquad (10)$$
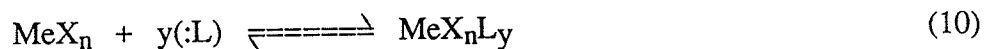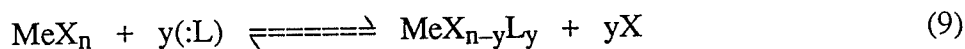
No report in the literature could be found to show the occurrence of these reactions, however.

1.5.4 Weak or Strong Anion-Exchange

Bowen[4] suggested that weak anion-exchange sites present in the foam are possible on the basis that nitrogen atoms in urea and urethane groups, as well as the ether groups could be protonated. The exchange of anionic metal complexes MeX_n^{m-} can occur as follows:

$$H^+ + A^- + (site)_f \rightleftharpoons [(H.site)^+]_f + (A^-)_f \qquad (11)$$

$$(mA^-)_f + MeX_n^{m-} \rightleftharpoons mA^- + (MeX_n^{m-})_f \qquad (12)$$
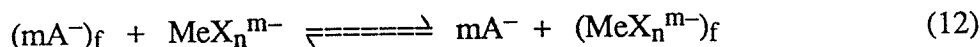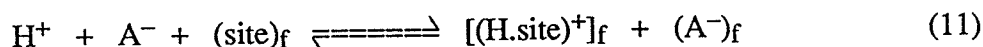
Obviously, this mechanism could work only in the presence of high concentrations of strong acids. It should be noted that the result of extraction of an ion-pair $mH.MeX_n^{m-}$ by solvent extraction followed by the association of the hydrogen ions with basic sites on the foam is similar to that resulting from an anion-exchange mechanism as described above. Gesser et al.[18,19] were unable to distinguish whether the solvent extraction or the anion-exchange mechanism occurred on the extraction of $HGaCl_4$ and $HFeCl_3$.

1.5.5 Cation Chelation Mechanism (CCM)

Hamon et al.[32,102] proposed the cation chelation mechanism to account for some anionic metal complexes extractions. Protonation of polyurethane foam sites is not required but it is closely similar to the weak base anion exchange concept. According to this mechanism, many cations M^{p+} are able to be effectively solvated by a certain portion of the polyether foam as a result of chelation as shown in equation (13).

$$(M^{p+})_f + (site)_f \rightleftharpoons [(M.site)^{p+}]_f \qquad (13)$$
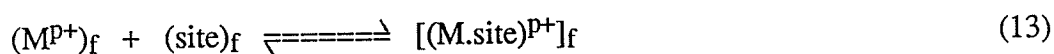
The extraction of ion-pairs including chelatable cations such as Na^+, K^+, NH_4^+, Rb^+, Ag^+, Tl^+, Ba^{2+}, Sr^{2+} and Pb^{2+}, etc., by the foam is due to the stability of the chelated cation. Moreover, the degree of the extraction is also dependent on the hydrophobicity and the nature of the anionic metal complex.

If MeX_n^{m-} is the only extractable anionic metal complex, the extraction may be regarded as a solvent extraction mechanism in which the cation is more strongly solvated than usual as described in equation (14).

$$mM^{p+} + pMeX_n^{m-} + m(site)_f \rightleftharpoons m[(M.site)^{p+}]_f + p(MeX_n^{m-})_f \qquad (14)$$
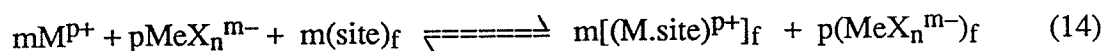
However, if the extraction of another anion A^- occurs either prior to or simultaneously with the extraction of MeX_n^{m-}, then the sorption may be regarded as an anion exchange mechanism as given in equations (15) and (16).

$$M^{p+} + pA^- + (site)_f \rightleftharpoons [(M.site)^{p+}]_f + p(A^-)_f \qquad (15)$$

$$MeX_n^{m-} + m(A^-)_f \rightleftharpoons (MeX_n^{m-})_f + mA^- \qquad (16)$$
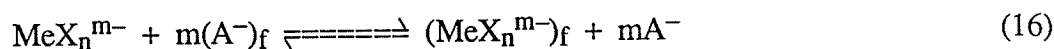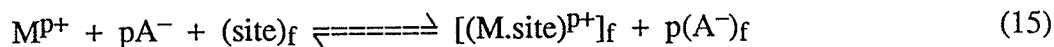
Thus, the cation chelation mechanism is closely related to both solvent extraction and anion exchange.

The ability of polyether foams to adopt a helical structure (Figure 1) with inwardly directed oxygen atoms is considered to be responsible for the specific interaction between the chelatable cation and the foam. Hamon[32] confirmed this mechanism by comparing the results obtained for the extraction of $Co(SCN)_4^{2-}$ with polyether foam and those reported with crown ethers. It was noted that the sorption of $Co(SCN)_4^{2-}$ by polyether foam increases with foams containing increasing proportions of polyethylene oxide (PEO) relative to polypropylene oxide (PPO). The difference of the extraction is attributed to the inability of PPO to assume the helical structure. Since then, many extraction systems have been reported[34,35,37,38,42,48] which have been able to be explained by this mechanism.

1.6 Objectives of the Present Work

From the above survey, it is apparent that polyurethane foams are useful to extract and separate a wide variety of inorganic and organic substances. With respect to the extraction mechanism, many extraction systems can be explained by the cation chelation

Figure 1   Proposed helical structure of polyether-type polyurethane foam by Hamon et al.[102] in the cation chelation mechanism for the extraction of $M_2Co(NCS)_4$ complex.
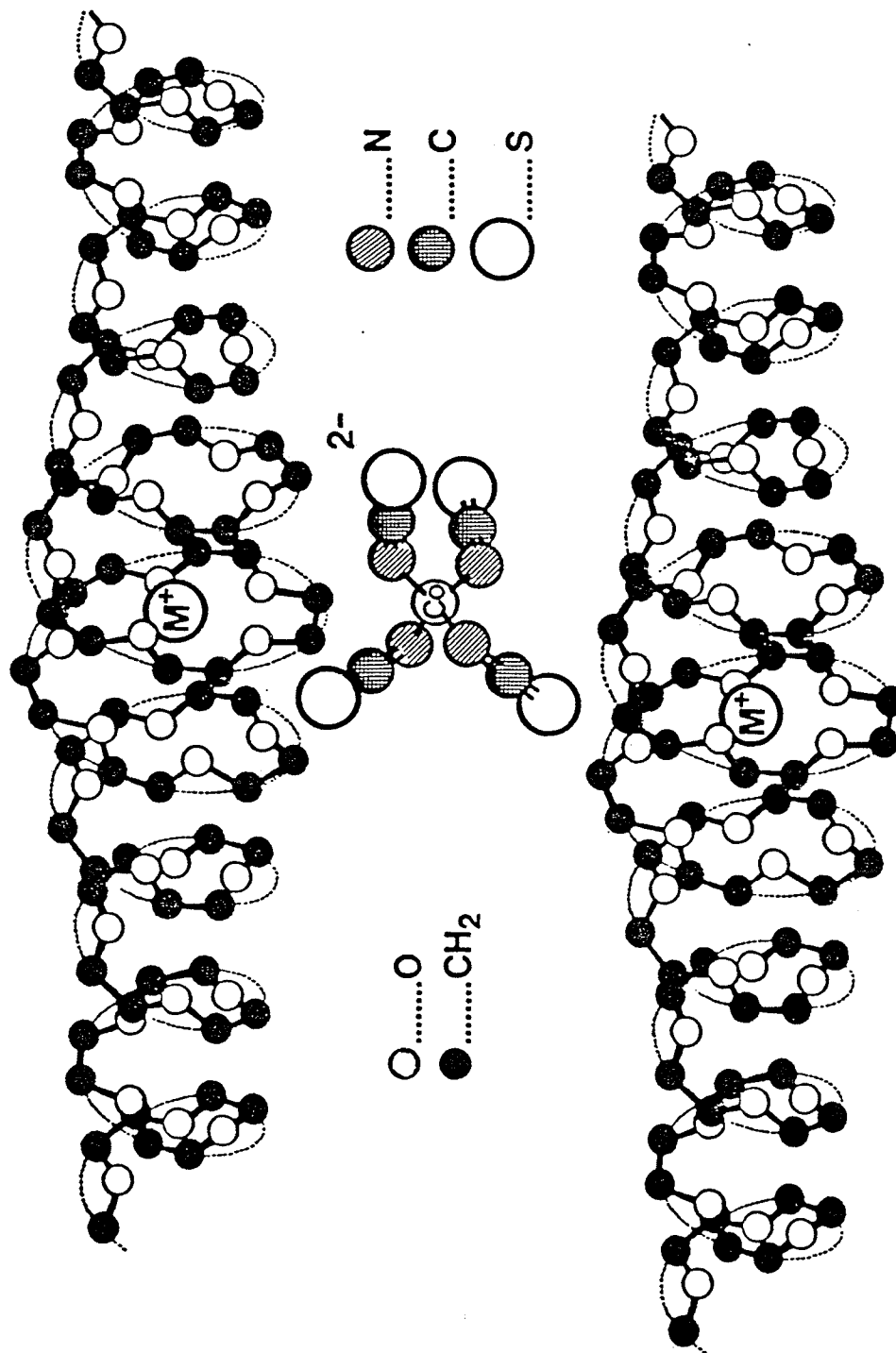
mechanism. Much of this work, however, has been concerned with the extraction of anionic metal complexes. In the present work, it was intended to study the extraction of organic anions in the presence of some chelatable cations proposed in order to determine whether the cation chelation mechanism is taking place in such an extraction system.

CHAPTER 2

EXTRACTION OF ORGANIC COMPOUNDS

2.1 Introduction

Although high molecular-weight polyethylene glycols have been known to form complexes with mercuric chloride[103,104] and with alkaline earth metal salts[105], the interaction of open-chain polyethylene oxide (PEO) derivatives with metal ions has attracted special interest only after Pedersen's discovery of macrocyclic polyethers[106]. These acyclic polyethers have the advantage of facile and inexpensive synthesis.

Smid *et al.*[107] reported that dimethyl ethers or glymes (G) of the general formula $CH_3O(CH_2CH_2O)_xCH_3$ ($1 \leq x \leq 6$) form complexes with lithium, sodium and potassium fluorenyl carbanion salts (M^+,Fl^-) in low dielectric constant solvents such as THF and dioxane. The resulting complex can be either a glymated contact ion-pair (Fl^-,K^+,G) or a glyme-separated ion-pair (Fl^-,G,K^+). It was found that one glyme molecule with $x = 4-6$, coordinates with sodium to form a glyme-separated ion-pair, but 2 glyme molecules are required with $x = 2$ and 3. With potassium salt, a molecule of glyme ($x = 5, 6$) gives a glyme-separated ion-pair; but glyme ($x = 3, 4$) yields a glymated contact ion-pair with a single molecule of glyme and two molecules of glyme ($x = 3, 4$) are needed to form the separated ion-pair. It was concluded that the formation of glyme-separated ion-pairs is dependent on the radius of the cation and the chain length of the glyme. The complexation constants for Li^+, Na^+ and K^+ complexes have been determined. These constants increase rapidly with increasing number of oxygen atoms in the glyme chain, but level off above a certain value of x, depending on the size of the cation. Smid and Takaki[108] also came to the conclusion that the structure of the ion-pair in the complexation of barium difluorenyl

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(BaFl$_2$) with various glymes depends on the chain length of the glyme. With glyme-7 and glyme-9 (x = 6 and 8 respectively), the complex is of mixed tight-loose ion-pairs of the form (Fl$^-$, Ba^{2+}, glyme, Fl$^-$). This mixed tight-loose ion-pair represents a combination of a glyme-separated (Ba^{2+},glyme,Fl$^-$) and a glyme-complexed tight ion-pair (Fl$^-$,Ba^{2+},glyme). However, with glyme-23 (x = 22) which can envelope a barium ion to form a completed solvation shell, the complex is a fully separated ion-pair.

Miyazaki *et al.*[109] studied the association of alkaline earth metals with dicarboxylic acids containing ether linkages of the general formula HOOCCH$_2$O – (CH$_2$CH$_2$O)$_n$CH$_2$COOH (n = 0–3) in aqueous solution. The stability constants of these complexes are as follows: Complexes I and II (n = 0 and 1), calcium > strontium > barium > magnesium; Complex III (n = 2), calcium > strontium = barium > magnesium; Complex IV (n = 3), strontium = barium > calcium > magnesium. It was thought that the interaction between the oxygen atom of the ether linkage and the alkaline earth metal ions is responsible for the higher stability of the complexes with the ether groups present.

Chaput *et al.*[110] determined the complexation constants for monovalent cations (Na$^+$, K$^+$, Cs$^+$ and Tl$^+$) with some polyethylene glycol ethers and their derivatives in methanol. It was found that the 1:1 complex forms only when the number of repeating units of ethylene oxide in the glycol ether is greater than five and smaller than eight. It was also noted that replacement of the two methoxyl terminal groups in the chain by primary amide or ester groups lowers the complexing ability of the glycol ethers.

Rais *et al.*[111,112] studied the distribution of alkaline earth metal dipicrylaminates, tetraphenylborates and dicarbolides [(π-(3)-1,2-B$_9$C$_2$H$_{11}$)$_2$Co]$^-$ into nitrobenzene from aqueous solution. The distribution ratios increase by about 1,000 times in the presence of polyethylene glycols 400 (PEG 400).

Yanagida *et al.*[113] studied the complexation of alkali and alkaline earth metal ions with polyethylene glycols by means of the solvent extraction of their thiocyanates or

iodides into dichloromethane. Polyethers with more than 23 oxyethylene units have extracting power comparable to that of 18-crown-6, and the power increases with increasing number of oxyethylene units in them. However, polypropylene glycols have low extracting power since the extracting power for a series of block copolymers of propylene oxide and ethylene oxide increases with increasing number of oxyethylene units. It was noted that more than seven oxyethylene units are required in the polyether to bind and extract potassium ion from water. This finding indicates that the repeating oxyethylene is a governing factor for the extraction. Moreover, it was noticed that there is no remarkable difference in the selectivity for alkali metal ions between 18-crown-6 and the polyethylene glycol derivatives. They proposed that acyclic polyethylene glycols may take a helical structure in which the oxygen atoms of the oxyethylene units can interact with the cation. This structure can be used to explain the higher extracting power of polyethylene glycols relative to polypropylene glycols as polypropylene glycols are unable to adopt this structure owing to the steric effect of the methyl groups.

The same authors[114] also investigated the complexation in methanol by NMR. The splitting and the downfield shift of ethylene proton signals were used as a measure of the complexation of polyglycols and glymes with metal cations. Li^+ and Mg^{2+} do not cause any change of the spectra. It seems that there is an optimum number of oxyethylene units in the glycols for a given cation in the complexation. They concluded that sodium and calcium ions require six oxyethylene units; the potassium, rubidium, cesium and strontium ions need seven oxyethylene units. They also mentioned that the terminal hydroxyl groups play an important role in the complexation of the cations with either crown ethers (15-crown-5 and 18-crown-6) or glycols. In a later publication[115], by using NMR they found that four is the optimum number of oxyethylene units in the glycols for complexing magnesium in acetonitrile.

Suzuki *et al.*[116] studied the extraction behaviour of zinc(II) from HCl solution of several alkali and alkaline earth metal thiocyanates with acyclic polyethers into polar organic solvents. The extraction of zinc(II) with $C_8H_{17}C_6H_4O(CH_2CH_2O)_{10}H$ (Trition X-100) into dichloromethane in the presence of salts follows the order: LiSCN < NaSCN < NH_4SCN < KSCN and $Mg(SCN)_2$ < $Ca(SCN)_2$ << $Ba(SCN)_2$. It was observed that the distribution ratio increases with an increase in the number of ethylene oxide groups of the acyclic polyethers.

Bartsch *et al.*[117] examined the extraction of alkaline earth metal cations from aqueous solution into chloroform by acyclic polyether dicarboxylic acids. **(1)** (see Figure 2) has a high selectivity for Ba^{2+}. **(2)**, with one more ethylene oxide group than **(1)**, produces a marked decrease of Ba^{2+} selectivity. **(3)** and **(4)** having the same number of ether oxygens as **(1)** but with a different spatial arrangement show a pronounced decrease of Ba^{2+} selectivity. These results suggest that both the number of ether oxygens and the positioning of oxygens in the polyether chain are important for cation selectivity.

The effect of chain length and ether oxygen on cation selectivity is further demonstrated in a later study[118]. The high selectivity for Ba^{2+} shown by **(5)** with four ether oxygens decreases as ether oxygens are varied to three and five for **(6)** and **(7)** respectively. Compound **(8)** with two ether oxygens changes cation selectivity to Ca^{2+} >> Sr^{2+}, Ba^{2+}. Similar effect of chain length on cation selectivity was observed in compounds **(9)**, **(10)** and **(11)**. Cation selectivities are as follows: Ca^{2+} > Ba^{2+} > Sr^{2+} for **(9)** with two ether oxygens, Ba^{2+} >> Sr^{2+} $\approx$ Ca^{2+} for **(10)** with four ether oxygens, Ba^{2+} > Ca^{2+} > Sr^{2+} > Mg^{2+} for **(11)** with five ether oxygens.

Yanagida *et al.*[119] synthesized resin beads with insolubilized acyclic poly(oxyethylene) derivatives (POE). The POE beads with more than five oxyethylene units are highly selective for K^+ in 10% w/w H_2O-acetone and methanol. The separation

24

Figure 2   Structural formulae of the various acyclic polyethers.
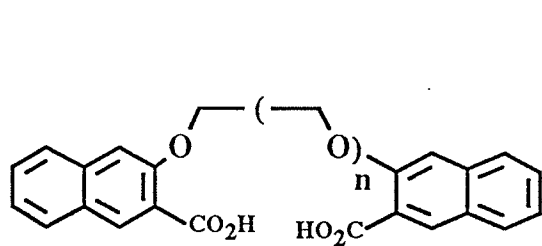
(1) n = 3
(2) n = 4
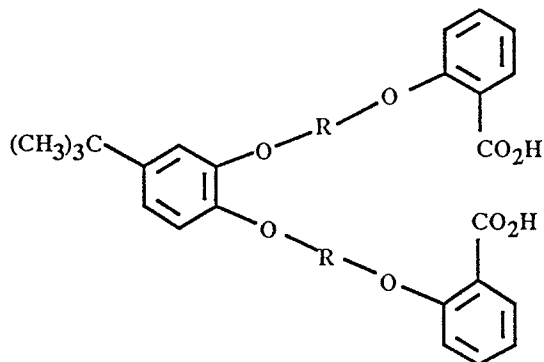
(3)
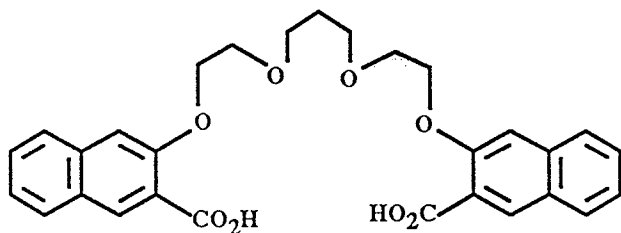
(4)
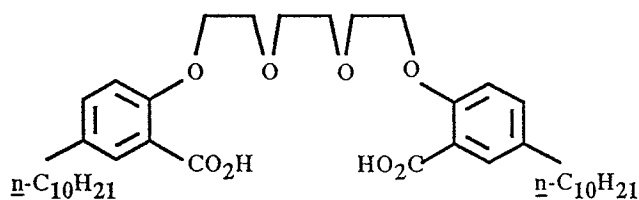
(5)
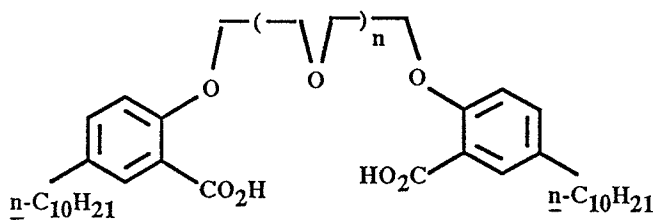
(6) n = 3
(7) n = 5
(8) n = 0

(9) n = 0
(10) n = 2
(11) n = 3

25
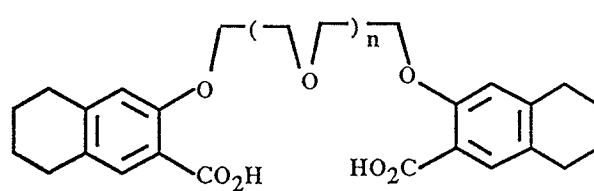
of LiSCN, NaSCN and KSCN was achieved by an HPLC technique using POE beads with seven or ten oxyethylene units.

Buschmann[120,121] determined the stability constants and thermodynamic values of complex formation of alkali and alkaline earth metal cations with acyclic polyethers by calorimetric titration in methanol. Polyethylene glycols with the general formula $RO(CH_2CH_2O)_nCH_2CH_2OH$ (n = 3–39) were studied. It was found that the reaction enthalpy which favours complex formation increases with increasing number of ether oxygens. However, the reaction entropy becomes more negative with chain length. As a result the stability constants for all the complexes with the cations are about the same. In other words, there is no selectivity for cations. It was deduced that the acyclic polyethers are flexible enough to get optimal interactions with the different cations. Values of reaction enthalpy obtained with some acyclic polyethers were higher than with 18-crown-6. The higher stability constants for crown complexes were attributed to the more favourable entropic contribution because crown ethers are more rigid. The same author[122] investigated the complexation between H^+ and glymes with the general formula $CH_3OCH_2CH_2O(CH_2CH_2O)_nCH_2CH_2OCH_3$ (n = 1–4). The same pattern of the increase of enthalpy with increasing chain length was obtained but there was no change of stability constant for the complexes. Thus the macrocyclic effect observed in the complexation with crown ethers was ascribed to the favourable entropic factor.

The determination of the crystal structure of complexes between acyclic polyethers and various cations by X-ray diffraction has been reported. Iwamoto[123,124,125] found that the 1:1 molecular complex of tetraethylene glycol dimethyl ether $CH_3O(CH_2CH_2O)_4CH_3$ (TGM) with mercuric chloride is circular but not closed. The five oxygen atoms are almost coplanar and positioned at the inner side of the circular molecule enclosing one $HgCl_2$ molecule with interatomic distances 2.78–2.96Å between the oxygen and mercury atoms. This structure suggests that electrostatic interaction between the positively charged metal

ion and the negatively charged oxygen atoms is important in the complex formation. The complex of tetraethylene glycol diethyl ether $CH_3CH_2O(CH_2CH_2O)_4CH_2CH_3$ (TGE) with $HgCl_2$ has also been studied. The unit cells are monoclinic and cubic for TGM-$HgCl_2$ and TGE-$HgCl_2$ complexes respectively. However, TGE has the same conformation as TGM with the exception of the diethyl terminal groups distorted to prevent steric interferences. The interaction between hexaethylene glycol diethyl ether $CH_3CH_2O(CH_2CH_2O)_6-CH_2CH_3$ (HGE) with $HgCl_2$ causes a drastic change of the conformation with the formation of a 1:2 complex. The conformation of the complexed chain is less stable than that of an uncomplexed simple chain. This conformation, however, allows stronger interactions between the oxygen and mrecury atoms in the complex.

Fenton et al.[126] reported the synthesis of crystalline complexes of sodium or potassium iodide and poly(ethylene oxide) in the proportion of 1 mol of salt to 4 mol of ethylene oxide repeating units. The X-ray and IR spectra of the complex differ markedly from those of pure poly(ethylene oxide). The solid complex can also be prepared from thiocyanate salt but not from chloride and bromide salts.

Vogtle et al.[127] prepared several crystalline complexes of alkali metal ions with various acyclic polyethers having different terminal groups. They introduced the terminal group concept in which hetero atoms located in terminal fixed groups can serve as donors. It was found that the geometric arrangement of the donor atoms is important because some ligands with an adequate number but improper arrangement of donor atoms do not form crystalline complexes.

Hughes et al.[128,129] reported the X-ray crystal structure of potassium with 2,2'di-o-carboxymethoxyphenoxydiethyl ether. The complex is a dimer with each potassium ion having irregular eight-fold coordination. The eight coordinating oxygen atoms form a shallow helix around each potassium ion with K–O distances 2.729–2.903Å. It was noted that there is no intramolecular hydrogen bond between the terminal carboxylic groups.

Saenger et al.[130] studied the X-ray crystal structure of complexes between alkali metal cations and polyethylene glycol ligands (ethylene oxide units = 3–11) with aromatic terminal groups. The configuration of the ligands around metal cations was found to be dependent on the chain length of the polyethers. Short ligands with five heteroatoms can wrap around the cation in a circular arrangement as shown in the complex of RbI with 1,5-bis(8-quinolyoxy)-3-oxapentane (Figure 3).

Ligands containing six to ten heteroatoms cannot fit circularly around the cation but have to adopt a helical structure. Figure 4 shows the complex of Rb^+ with 1,20-bis(8-quinolyoxy)-3,6,9,12,15,18 hexaoxaeicosane. The ligand is long enough to spherically wrap around the metal ion with more than one turn. Most of the heteroatoms occupy the "equatorial" region and the remaining heteroatoms are located near or on the "polar" region.

For ligands containing more than ten heteroatoms, it was found that the ligands do not spherically wrap around the cation in the complex of Rb^+ and 1,5-bis{2-[5-(2-nitrophenoxy)-3-oxapentyloxyl]-phenoxy}-3-oxapentane (Figure 5). The helical arrangement of the ligand holds only in a limited sense because the two K^+ cations are coordinated in circular complex-structures and are not stacked on top of each other but are side by side in an S-like configuration. These results demonstrate that acyclic polyethers are able to adopt a spiral configuration to chelate metal cations.

Adams et al.[131] studied the extraction of aurocyanide ion-pairs with alkali metals into various solvents in the presence of long-chain polyethers. The polyether is shown to coordinate to the alkali metal cation by the ether oxygen atoms, wrapping around the cation in a helical configuration.

The crystalline structure of poly(ethylene oxide) polymer chain has been determined by X-ray study[132,133,134]. It has a helical structure with a unit cell containing seven structural units ($-CH_2CH_2O-$) in two turns (Figure 6). The Raman spectra of the molten

Figure 3 X-ray crystal structure of the complex formed between RbI and 1,5-bis(8-quinolyloxy)-3-oxapentane[130].
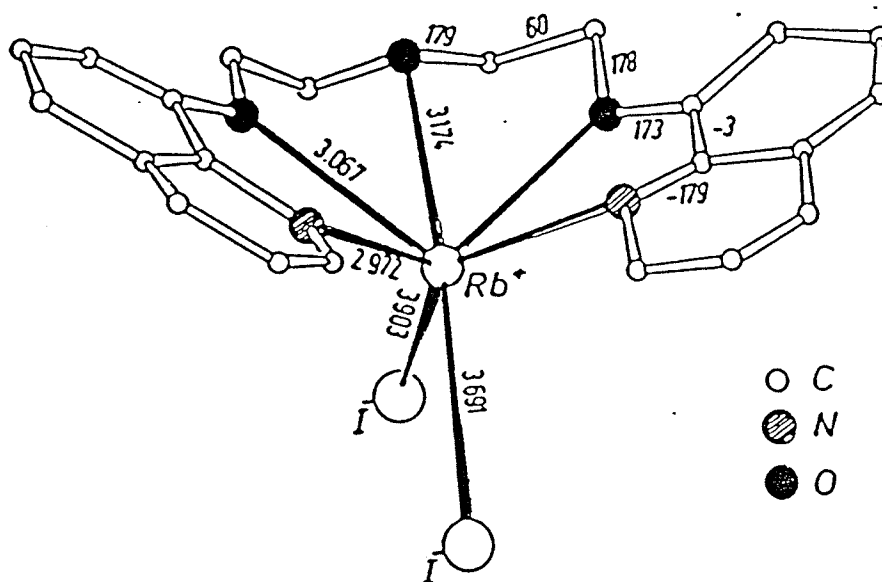
Figure 4   X-ray structure of the complex formed between Rb⁺ and 1,20-bis(8-quinolyoxy)-3,6,9,12,15,18 hexaoxaeicosane[130].
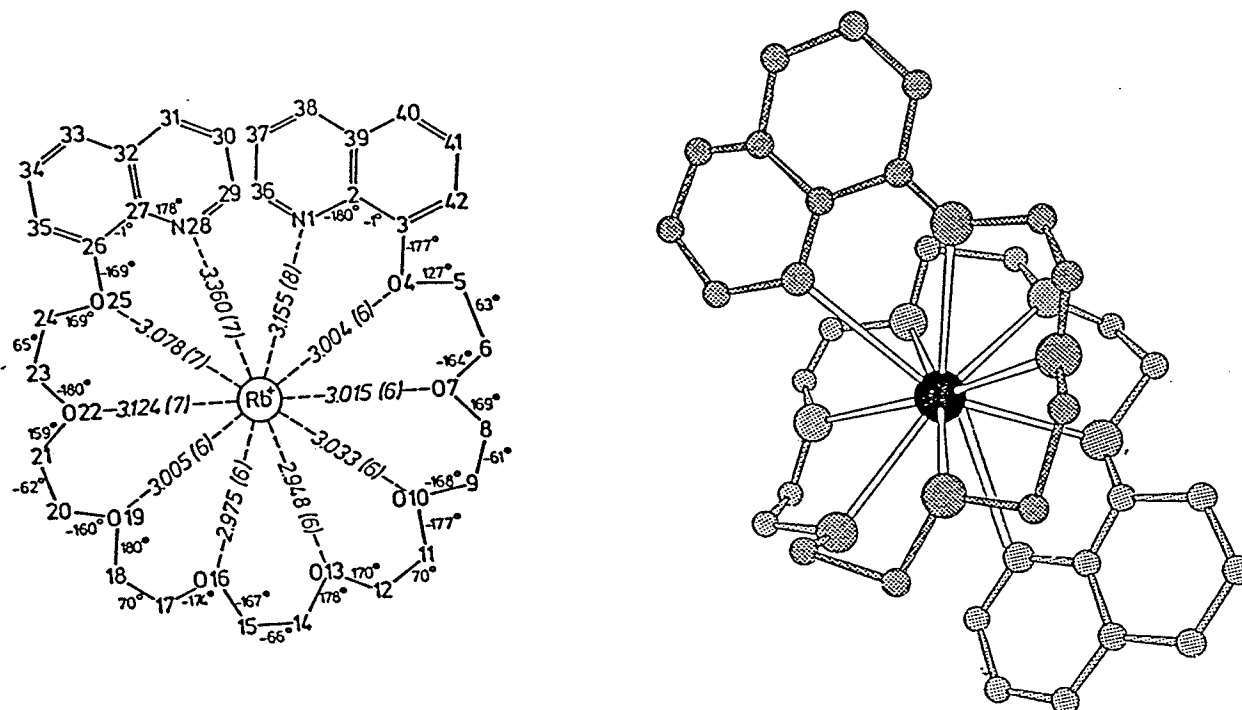
Figure 5   X-ray structure of the complex formed between 2 KSCN and 1,5-bis{2-[5-(2-nitrophenoxy)-3-oxapentyloxy]-phenoxy}-3-oxapentane[130].
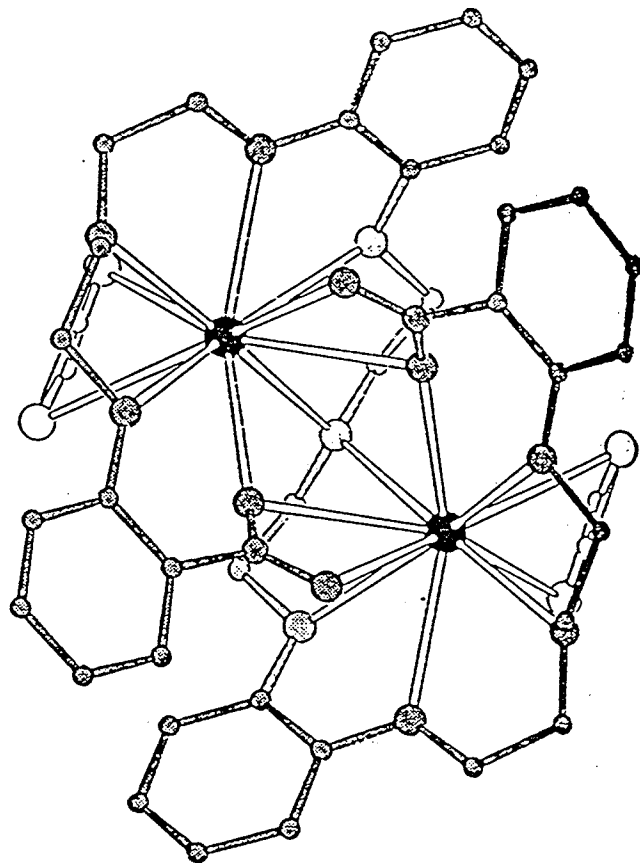
Figure 6   Skeletal model of poly(ethylene oxide) in crystalline state[132].

$$c = 19.3 \, \text{Å}$$
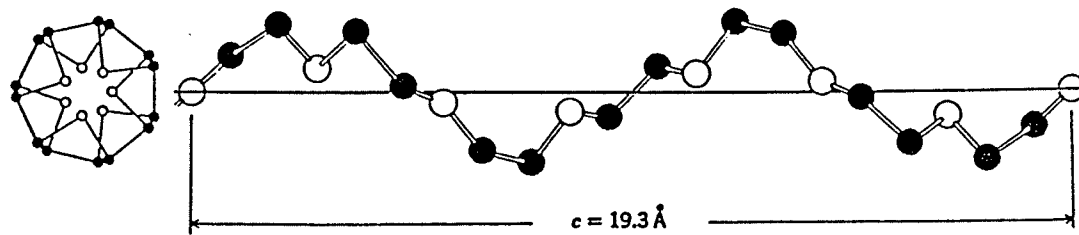
O   oxygen

● methylene

polymer and the chloroform solution suggest a disordered structure because additional Raman lines appear as a result of additional rotational isomers[135]. There is less structural change for the polymer in aqueous solution, however, indicating retention of some helical structure.

In polyols typical of flexible polyether-based polyurethane foam production, there may be 10–40 (CH_2CH_2O) units. It is reasonable to assume that the polyether portion of the foam can chelate a cation in a spiral wrap-around manner. Furthermore, many acyclic polyethers demonstrate cation selectivity; thus, it is possible for polyether foam to have similar properties. On the other hand, polyester foam has difficulty in adopting a helical configuration owing to the limited flexibility of the ester bond. Therefore it is less likely that a polyester chain can chelate a cation in a spiral wrap-around fashion. Accordingly, the possibility for polyester foam to have cation selectivity in terms of cation size is remote.

Hamon et al.[32] reported that polyether foam has high selectivity for K^+ with the extraction of $Co(SCN)_4^{2-}$. They proposed the cation chelation mechanism to account for the results. Other studies[34,35,37,38,42,48] have also been reported to support this mechanism. In these previous studies, a large excess of chelatable cations was used for the formation of extractable anionic metal complexes, and hence only the extraction of the anion was measured. In this present study, it was intended to keep the amount of chelatable cations close to that of the extractable anions so that the extraction of both cations and anions could be determined. Bulky organic anions have been known to form ion-pairs with cations, and moreover, these ion-pairs can be extracted into organic solvent. Therefore, the use of organic anions can eliminate the problem of using a large excess of chelatable cations and can provide a direct measurement of the extraction of the cations. Experiments were carried out to evaluate the extractability of various organic compounds in the presence of chelatable cations by polyether and polyester foams.

2.2 Experimental

2.2.1 Apparatus and Reagents

The following apparatus were used: a Fisher Accumet Model 520 pH meter, a Ross combination pH electrode, a Varian Model 634S UV-visible spectrophotometer, a Hewlett-Packard 5710A gas chromotograph, a Barnstead Nanopure II water purification system, extraction cells made of Pyrex glass (Figure 7)[136] and a muliple automatic squeezer (Figure 8)[136].

All the chemicals were of reagent grade.

2.2.2 Foam

Polyether type polyurethane foam (#1338M) was obtained from G. N. Jackson Ltd. (Winnipeg, Manitoba). Polyester type foam (DiSPo) was obtained from Canlab (Winnipeg, Manitoba).

2.2.3 General Procedure

2.2.3.1 Foam Washing

Foam plugs of approximately 0.4 g each were cut from a polyurethane sheet and were trimmed to the required weight after washing. These plugs were soaked in 1 M hydrochloric acid for 24 h with occasional squeezing to remove any possible inorganic contaminants and washed with water until acid free. They were then extracted with acetone

Figure 7   Extraction cell for equilibrating polyurethane foam with solution[136].
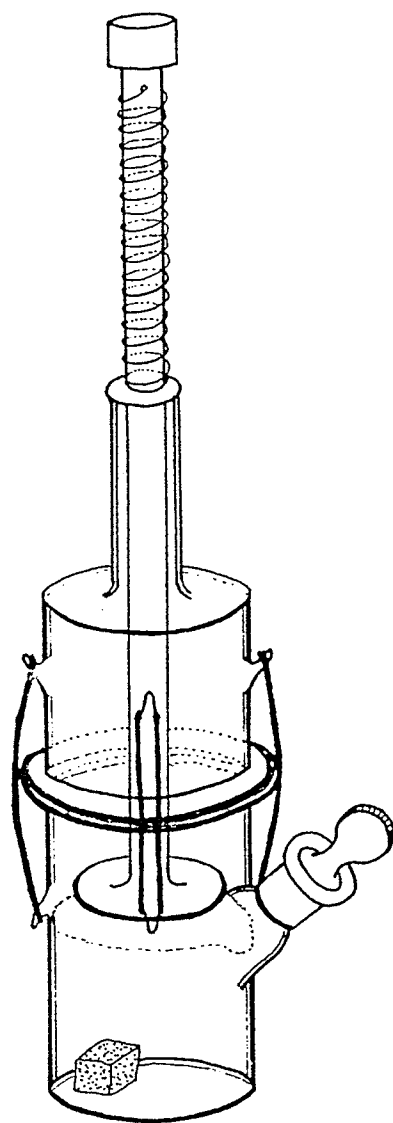
Figure 8   Automatic squeezing apparatus[136].
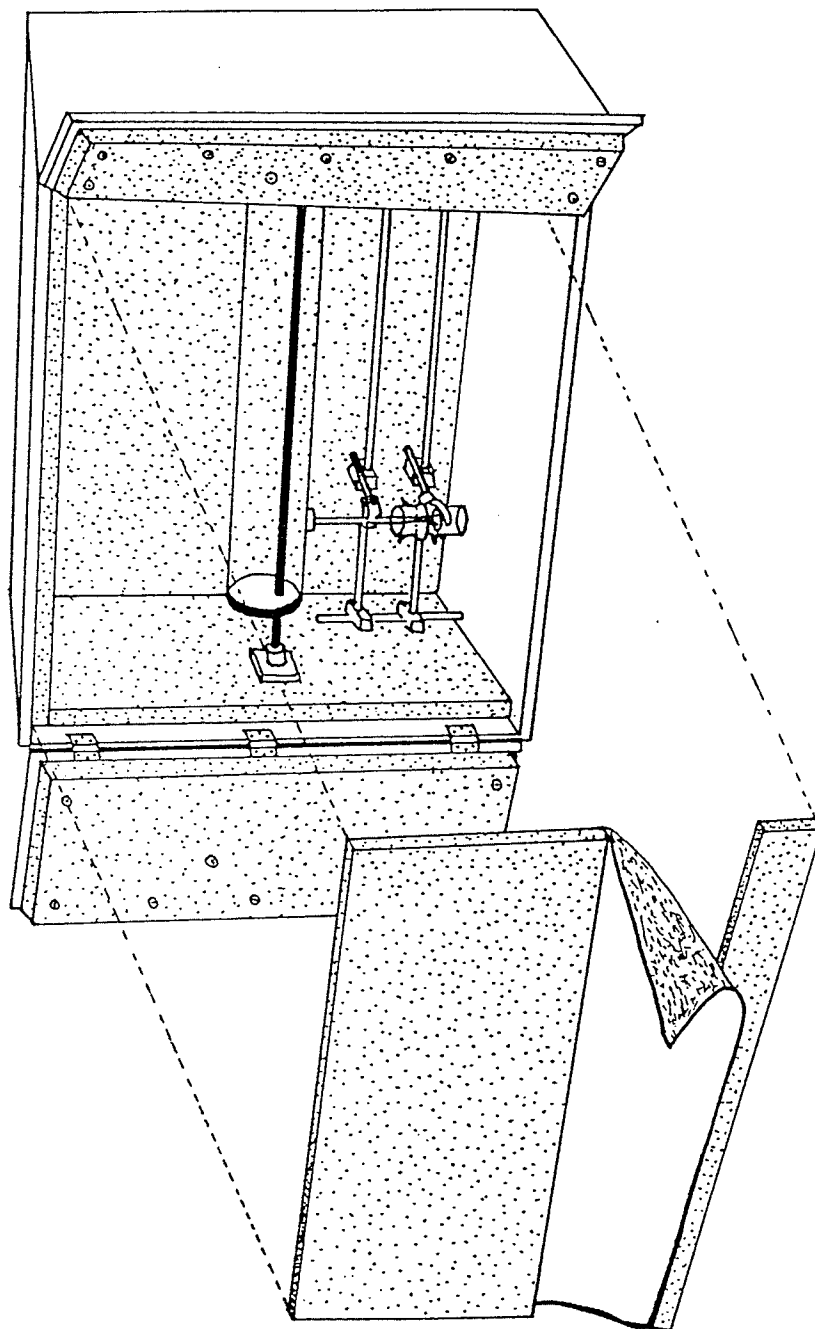
in a Soxhlet apparatus for 6 h to remove the organic contaminants and finally air dried in a 60°C oven.

2.2.3.2 Preparation of Sample Solutions

Sample solutions were freshly prepared by dissolving the appropriate amount of each compound in water into a 1 L volumetric flask. Pure water was obtained from a Barnstead Nanopure II water purification system using reverse osmosis purified water as the feed.

2.2.3.3 Extraction Procedure

The sample solution (100 mL) and the foam plug (0.300 ± 0.005 g) were placed in the extraction cell (Figure 7). The foam plug was squeezed by the automatic squeezing apparatus (Figure 8) at a rate of 24 strokes per minute.

2.2.3.4 Analytical Methods

Aromatic organic compounds were analysed by UV-visible spectrophotometry using a 1 cm cell. Table 1 shows the conditions for the measurement of the compounds. The wavelength used for absorbance measurements was that for the highest absorbance (λ_{max}) determined experimentally.

The aliphatic amine concentration was determined by gas chromatography. A flame ionization detector and a 1.8 m x 2 mm ID glass column packed with GP Carbopack B/4% Carbowax 20 M/0.8% KOH were used. A known amount of an amine was added to the sample solution as an internal standard. Then 200 μL solution of 4 M NaOH was added to

Table 1   Conditions for UV measurement of various organic compounds

Compunds	λ_{max} (nm)	Dilution
salicylic acid	296	2 to 25
8-hydroxyquinoline	239	1 to 25
cinnamic acid	272	1 to 25
1-amino-2-naphthol-4-sulfonic acid	235	0.5 to 25

2 mL of the amine solution to bring the resulting solution above pH 12 so that the amines were not ionized and could be vaporized after injection. An injection volume of 1 µL was used. A linear calibration curve of ratios of peak area (sample/internal standard) to the sample concentrations was obtained.

2.2.3.5 Calculations

The % extraction was calculated indirectly by determining the concentration of the species in solution after extraction, equation (17). The species removed from solution was assumed to have been extracted by the foam.

$$\% \text{ extraction} = (1 - C'/C_0) \times 100 \qquad (17)$$

$$C_0 = \text{concentration in solution before extraction}$$

$$C' = \text{concentration in solution after extraction}$$

The distribution coefficient (D) was calculated as follows:

$$D = \frac{\% \text{ extraction}}{(100 - \% \text{ extraction})} \times \frac{\text{volume of solution (L)}}{\text{weight of foam (kg)}} \qquad (18)$$

2.3 Results and Discussion

2.3.1 Preliminary Results

Experiments were carried out to determine the capability of polyurethane foam to extract simple aliphatic amines from aqueous solution. The extraction of various amines including methylamine, ethylamine, isopropylamine, isobutylamine, *n*-butylamine, *sec-*

butylamine and t-butylamine was studied. It was necessary to protonate the amines in 0.1 M sulphuric acid to prevent evaporation of the amines from solution. As the pH of the unacidified amine solution was 10.5, an appreciable amount of amine was in the neutral form which could evaporate from the unacidified solution. The pK_a values of the alkylammonium ions are given in Table 2.

A series of 100 mL solutions containing 100 μL/L of each of the amines in 0.1 M H_2SO_4 was extracted by 0.3 g foam. No extraction of the amines was observed for either polyester or polyether foam after 24 h. It is clear that these hydrophilic amines are not extractable from aqueous sulphuric acid solution. It has been reported that the hydrophobicity of the anions is important in the extraction of alkali metal ions from aqueous solution[138]. Thus the effect of several bulky organic compounds on the extraction of the amines was investigated.

2.3.2 Extraction of Salicylic Acid

2.3.2.1 Effect of Amines

To determine the extractability of salicylic acid, solutions (100 mL) containing 2.9 x 10^{-3} M of this acid were extracted with polyether and polyester foams (0.300 g). The pH of the solution was 3.15. Extraction equilibrium was reached within 1 h. The distribution coefficients were 96.9 $\pm$ 3.2 and 218 $\pm$ 4 L/kg for polyester and polyether foams respectively (Table 3).

To study whether the amines are extractable in the presence of salicylic acid, solutions (100 mL) containing different amines with varied concentrations and 2.9 x 10^{-3} M salicylic acid were extracted with both types of foams (0.300 g). The results are given in Table 3. Although salicylic acid is extractable, no extraction of the amines was

Table 2   pK_a values for the alkylammoniums[137]

Alkylammonium	pK_a
n-butylammonium	10.61
sec-butylammonium	10.60
t-butylammonium	10.68
isopropylammonium	10.64
isobutylammonium	10.72
ethylammonium	10.70
ammonium	9.25

Table 3 Effect of amines on the extraction of salicylic acid from aqueous solution by polyurethane foam

Amine	Concen-tration $(x10^{-3}\,M)$	Distribution coefficient (L/kg)		Equilibrium pH	
		Polyester	Polyether	Polyester	Polyether
none	0.00	96.9 ± 3.2	218 ± 4	3.20	3.25
sec-butylamine	0.50	83.9 ±1.2	185 ± 1	3.30	3.40
sec-butylamine	0.99	65.6 ± 2.6	139 ± 4	3.50	3.60
isobutylamine	0.99	67.3 ± 3.8	149 ± 2	3.45	3.55
sec-butylamine	1.98	31.9 ± 0.8	51.9 ± 0.8	3.90	4.05
ethylamine isopropylamine isobutylamine	1.06 1.16 0.99	0	0	9.60	9.60

Conditions: $2.9 \times 10^{-3}\,M$ salicylic acid, 0.300 g foam, 100 mL solution, 24 h extraction time.

observed. Salicylic acid extraction decreases with increasing amount of amine added. In the presence of the same amount of amine, the extraction coefficients for salicylic acid are about the same for both sec-butylamine and isobutylamine. As the total amount of amine is higher than salicylic acid present, pH increased markedly to 9.6 and no salicylic acid extraction was obtained. This observation suggests that the amount of amine added rather than the nature of the amines is important in the extraction of salicylic acid.

2.3.2.2 Effect of pH

An increase in amine added increases the pH of salicylic acid solution and decreases the distribution coefficient of salicylic acid (Table 3). It is likely that the decrease of salicylic acid extraction is due to pH change. Solutions of 2.9×10^{-3} M salicylic acid in 0.1 M and 2 M HCl solution were extracted with 0.300 g foam. The values of the distribution coefficient (D) at equilibrium pH from Table 3 along with those obtained for pH 1 and –0.3 were used to plot the graph of log D versus pH (Figure 9). Two regions are apparent from the graph. There are the plateau of roughly zero slope below pH 2.5 and the approximately linear segment with respective slopes of about –0.71 and –0.67 for polyether and polyester foams. This is consistent with the extraction of a system in which a molecular species is involved.

Suppose an organic acid, HA, is extracted from water to an organic solvent, o.

$$HA \rightleftharpoons HA_o \qquad (19)$$

In the aqueous phase, the acid is capable of dissociating as follows:

$$HA \rightleftharpoons H^+ + A^- \qquad (20)$$

The distribution constant can be defined as:

Figure 9   Plot of log D (distribution coefficient) versus pH for the distribution of

salicylic acid between foams and aqueous solution.
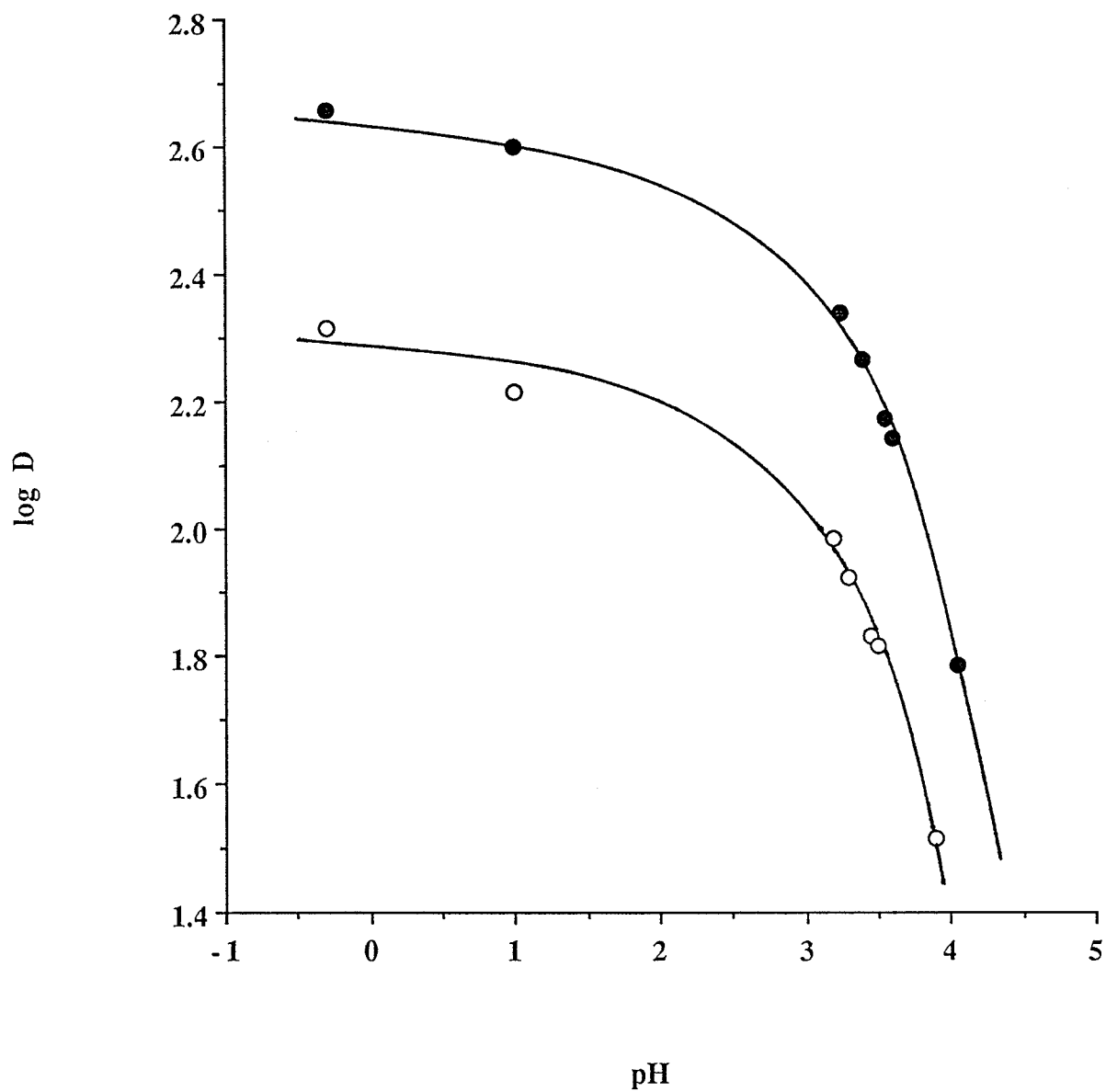
Conditions: $2.9 \times 10^{-3}\ M$ salicylic acid, 0.300g foam, 100 mL solution, 24 h extraction

time, (●) polyether foam, (o) polyester foam.

$$K = \frac{[HA]_0}{[HA]} \qquad (21)$$

and the acid dissociation constant, K_a, as:

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad (22)$$

The distribution coeficient, D, is expressed by,

$$D = \frac{[HA]_0}{[HA] + [A^-]} \qquad (23)$$

Substitution of Equations (21) and (22) into (23) results in

$$D = K \frac{[H^+]}{[H^+] + K_a} \qquad (24)$$

If $[H^+] \gg K_a$, then D = K. A plot of log D versus pH gives a straight line with slope 0. The solution is so acidic that no ionization occurs in the aqueous phase and HA acts as a simple neutral species which is distributed between the phases.

If $[H^+] = K_a$, then D = K/2, and D decreases when $[A^-]$ = [HA] because the concentration of undissociated HA in the aqueous phase is only 50% of the initial HA in solution.

If $[H^+] \ll K_a$, then D $\ll$ K and Equation (24) becomes

$$D \approx K[H^+] / K_a \qquad (25)$$

$$\log D \approx \log (K/K_a) - pH \qquad (26)$$

The log D against pH plot yields a straight line with a slope of −1. The concentration of HA in the aqueous phase is very low because of the ionization of the acid, and hence the amount extracted must be small. Figure 10 gives an example of the relationship between log D and pH of a weak acid over the whole pH range.

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Figure 10 Plot of log D (distribution coefficient) versus pH for a typical weak acid[139].
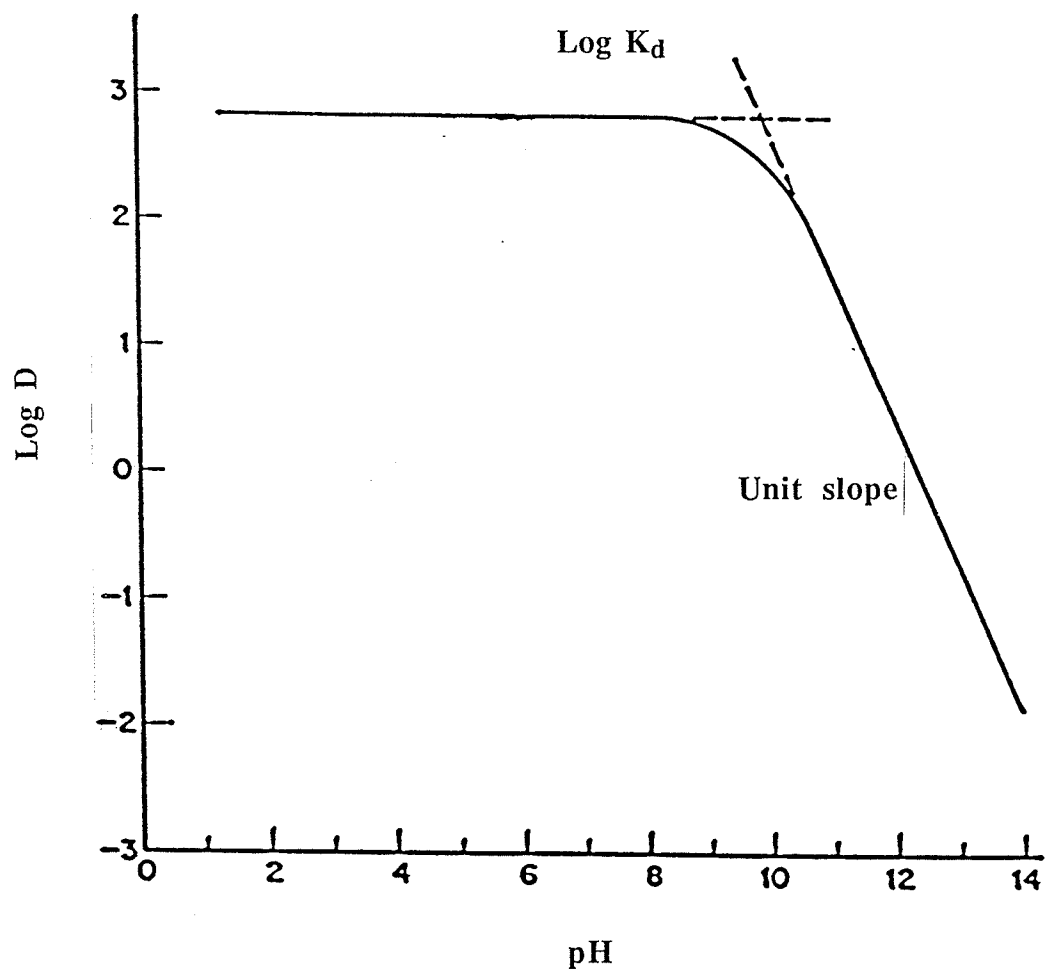
The pK_a value for salicylic acid is 2.75[137]. The slope of the straight lines are approximately equal to 0 and −1 for pH below 2 and above 3 respectively. The deviation of the values of the slopes from the theoretical values is likely due to the fact that the pH data points are close to the pK_a value of salicylic acid and the activity of the extractable species increases at lower pH. The results suggest that salicylic acid is extracted by a simple solvent extraction mechanism in which only the neutral molecular species is extractable.

2.3.2.3 Effect of Salts

It has been reported[32] that in the system where cation chelation mechanism is operating, polyether foam has high selectivity for NH_4^+ ion. Experiments were undertaken to test any change of salicylic acid extraction in the presence of NH_4Cl. NH_4Cl concentration was varied from 1.0 x 10^{-3} to 0.1 M. Table 4 shows that there is no significant difference in the amount of salicylic acid extracted in the presence of NH_4Cl with either polyester or polyether foams, although at 0.1 M NH_4Cl there is a slight decrease of salicylic acid extraction.

High salt concentration was generally used in the systems in which cation chelation is involved[32,34,35,37,38,42,48]. The inability of NH_4Cl to affect salicylic acid extraction may be due to the low NH_4Cl concentration used. The effect of various alkali metal chlorides (2 M) and alkaline earth metal chlorides (1 M) on salicylic acid extraction was studied. Table 5 demonstrates significant increases in salicylic acid extraction in the presence of LiCl, NaCl, KCl, $MgCl_2$ and $BaCl_2$ by both polyester and polyether foams. The following order of extraction: $Li^+ \approx Na^+ > K^+$, $Mg^{2+} > Ba^{2+}$ was observed. The extraction of salicylic acid increases with increasing charge density on the cation. This order is different from that for a cation chelation extraction system where K^+ produces a

Table 4   Effect of NH$_4$Cl concentration on the extraction of salicylic acid

Concentration (M)	Distribution coefficient (L/kg)	
	Polyester	Polyether
0.00	96.9 ± 3.2	218 ± 4
1.0 x 10^{-3}	94.2 ± 3.2	213 ± 5
3.0 x 10^{-3}	93.1 ± 1.7	212 ± 7
0.10	83.7 ± 1.7	189 ± 7

Conditions: 2.9 x 10^{-3} M salicylic acid, 0.300 g foam, 100 mL solution, 24 extraction time.

Table 5   Effect of salts on salicylic acid extraction

Salt	Concentr-ation (M)	Distribution coefficient (L/kg)		Equilibrium pH	
		Polyester	Polyether	Polyester	Polyether
none	0.0	96.9 ± 3.2	218 ± 4	3.20	3.25
LiCl	2.0	150 ± 2	321 ± 6	2.65	2.75
NaCl	2.0	150 ± 4	332 ± 8	2.80	2.85
KCl	2.0	125 ± 3	284 ± 8	3.05	3.10
$MgCl_2$	1.0	137 ± 3	256 ± 5	2.50	2.55
$BaCl_2$	1.0	111 ± 3	234 ± 7	2.65	2.75

Conditions: 2.9×10^{-3} *M* salicylic acid, 0.300 g foam, 100 mL solution, 24 h extraction time.

greater increase for anion extraction than Na^+ and Li^+. This effect is consistent with a solvent extraction mechanism with the salts acting as salting-out agents. Added ions increase the extraction of an organic compound into the organic phase by reducing the number of water molecules available to solvate the organic compound because some water molecules are used to solvate the ions. Ions with higher charge density are expected to exert a greater effect. The charge density for the cations studied is $Li^+ > Na^+ > K^+$ and $Mg^{2+} > Ba^{2+}$. Thus the influence of the salts can be explained by the salting-out effect on a solvent extraction system.

To confirm the salting-out effect of the salts, an extraction was carried out in 2.9 x $10^{-3} M$ salicylic acid solution containing 0.1 M HCl. At pH 1, 99% of the salicylic acid is in the neutral form. Comparing the results of Tables 5 and 6, the added salts increase the extraction of salicylic acid more in a solution at pH 1 than at higher pH owing to the increased amount of neutral salicylic acid. The effect of the salts remains the same with the sequence of $Li^+ > Na^+ > K^+$ and $Mg^{2+} > Ba^{2+}$.

It can be concluded that salicylic acid is only extractable in the neutral form. Anionic salicylates are too hydrophilic to effect the extraction of aliphatic amine cations from aqueous solution by either polyester or polyether foam.

2.3.3 Extraction of 8-hydroxyquinoline

8-Hydroxyquinoline is more hydrophobic than salicylic acid. To evaluate the extractability of 8-hydroxyquinoline, solutions (100 mL) of 1.0 x $10^{-3} M$ 8-hydroxyquinoline were extracted with 0.300 g foam for 1 h. Moreover, extractions of 8-hydroxyquinoline in the presence of 1.0 x $10^{-3} M$ methylamine and n-butylamine were also studied to determine whether the amines are extractable. Table 7 shows the amines have no effect on the extraction of 8-hydroxyquinoline. Both methylamine and *n*-butylamine were

Table 6   Effect of salts on salicylic acid extraction at pH 1

Salt	Concentration (M)	Distribution coefficient (L/kg)	
		Polyester	Polyether
none	0.0	164 ± 6	398 ± 14
LiCl	2.0	341 ± 9	818 ± 41
NaCl	2.0	312 ± 3	791 ± 29
KCl	2.0	260 ± 1	626 ± 23
$MgCl_2$	1.0	325 ± 8	780 ± 20
$BaCl_2$	1.0	275 ± 2	658 ± 18

Conditions: 2.9×10^{-3} M salicylic acid, 0.1 M HCl, 0.300 g foam, 100 mL solution, 24 h extraction time.

Table 7   Effect of amines on the extraction of 8-hydroxyquinoline

Amine	Concentration (M)	Distribution coefficient (L/kg)	
		Polyester	Polyether
none	0.0	173 ± 3	165 ± 3
methylamine hydrochloride	1.0×10^{-3}	170 ± 4	164 ± 3
n-butylamine HCl	1.0×10^{-3} 1.0×10^{-3}	156 ± 4	158 ± 2

Conditions: 1.0×10^{-3} M 8-hydroxyquinoline, 0.300 g foam, 100 mL solution, 1 h extraction time, pH = 6.4.

found to be nonextractable. The pK_a values for 8-hydroxyquinoline are 5.02 and 9.81[137]. At pH 6.4, the major species is in the molecular form. Therefore, no extraction of the amines was found. To ionize the (–OH)group of 8-hydroxyquinoline, a pH above 11 is required; however, at pH 11 undissociated amine is predominant. These difficulties prevent a proper investigation and no further studies on this compound were carried out.

2.3.4 Extraction of 1-Amino-2-naphthol-4-sulfonic Acid (ANS)

Experiments to test the ability of ANS to extract alkylamine cations with foam were carried out. Solutions (100 mL) of 1.0×10^{-3} M ANS containing methylamine or n-butylamine (1.0×10^{-3} M) were extracted with 0.300 g foam for 6 h. Table 8 shows that methylamine and butylamine have no effect on the distribution coefficient (D) of ANS.

The pK_a values for ANS shown as (12) in Figure 11, could not be found in the literature. The (–SO$_3$H) group is expected to be completely ionized. The pK_a for 1-naphthylamine, (13) in Figure 11 is 3.92[137]. In the presence of the (–SO$_3$H) group, the pK_a for the (–NH$_2$) group would be lowered. Thus at pH 3.5, the forms of ANS (14) and (15) may be present in comparable amount. Since there is no change of D with the addition of the amines, it is clear that the extraction of the possible ion-pair between the amine cation and (15) does not occur. Thus, the zwitterion form (14) must be the extractable species.

In order to determine whether K^+ and NH_4^+ can be extracted with ANS, extractions under varied KCl and NH$_4$Cl concentrations were studied. To verify that (14) is the extractable species, the extraction of ANS in 0.1 M HCl was also carried out. Table 9 demonstrates that there is no significant change of D for ANS with the addition of NH$_4$Cl and KCl up to 0.1 M. Thus, ANS is too hydrophilic to extract K^+ and NH_4^+ from aqueous solution. However, D increases in 0.1 M HCl solution. This can be the result of

Table 8   Effect of amines on 1-amino-2-naphthol-4-sulfonic acid (ANS) extraction

		Distribution coefficient (L/kg)	
Amine	Concentration (*M*)	Polyester	Polyether
none	0.0	9.3	30.8
methylamine hydrochloride	1.0×10^{-3}	8.1	28.2
n-butylamine HCl	1.0×10^{-3} 1.0×10^{-3}	11.1	32.1

Conditions: 1.0×10^{-3} *M* ANS, 0.300 g foam, 100 mL solution, 6 h extraction time, pH = 3.5.

Figure 11   Various forms of 1-amino-2-naphthol-4-sulfonic acid and 1-naphthylamine

(12)

(13)

(14)

(15)
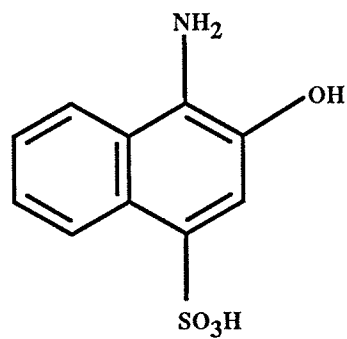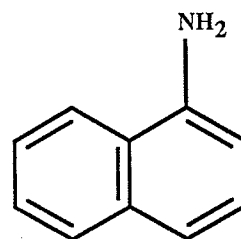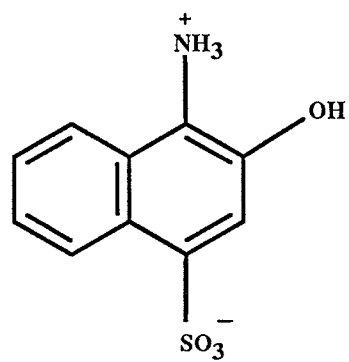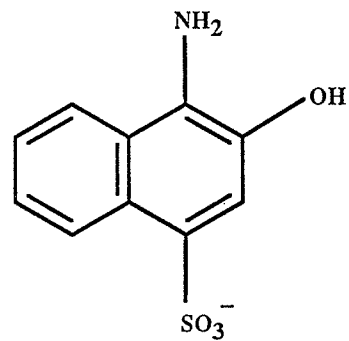
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Table 9   Effect of salt and pH on 1-amino-2-naphthol-4-sulfonic acid (ANS) extraction

Compound	Concentration (M)	Distribution coefficient (L/kg)	
		Polyester	Polyether
NH_4Cl	1.0×10^{-3}	9.0	29.2
NH_4Cl	0.10	4.7	25.3
KCl	1.0×10^{-3}	7.7	30.3
KCl	0.10	8.6	29.5
HCl	0.10	30.8	66.9

Conditions: 1.0×10^{-3} M ANS, 0.300 g foam, 100 mL solution, 6 h extraction time, pH = 3.5 for NH_4Cl and KCl solutions, pH = 1.0 for HCl solution.

the increased formation of the neutral species (14) at pH 1. This result is consistent with a solvent extraction mechanism.

2.3.5 Extraction of Cinnamic Acid

The extractability of cinnamic acid has also been studied. Solutions (100 mL) of 1.0×10^{-3} M cinnamic acid at pH 3.9 were extracted with 0.300 g foam for 24 h. Distribution coefficients of 195 ± 3 and 343 ± 4 L/kg for polyester and polyether foams respectively were obtained. Extraction of cinnamic acid in 1.0×10^{-2} M KOH was also carried out. The pH of the solution was above 12. No detectable amount of cinnamic acid was extracted. The pK_a value for cinnamic acid is 4.44[137], and therefore at pH 12, cinnamic acid is fully ionized. The results show that dissociated cinnamic acid is not extractable. At pH 3.9, 77.6% of cinnamic acid is in the neutral form. Thus, only the undissociated cinnamic acid is extractable.

Water is a solvent with high dielectric constant. Ions in aqueous solution are well solvated and so it is difficult for ions to form ion-pairs in aqueous solution. Ion-pair formation is facilitated in solvents with low dielectric constant. To determine whether ionized cinnamic acid is extractable in a low dielectric constant solvent, extractions of 1.0×10^{-3} M cinnamic acid with 1.0×10^{-2} M NaOH and KOH in 50% v/v dioxane solution at pH 10.4 were carried out. No extraction of the cinnamic acid was observed. It is apparent that cinnamic acid is too hydrophilic to form ion-pairs with Na^+ or K^+ in 50% dioxane solution.

2.3.6 Effect of Foam Types on the Extraction of the Organic Compounds

Schumack and Chow[67] examined the extraction of a wide variety of organic compounds by polyether and polyester foams. It was concluded that a solvent extraction mechanism is responsible for the extraction of these organic compounds. It was also found that compounds containing a (–OH) hydroxyl group are in general more extractable by polyether foam than by polyester foam. Hydrogen bonding between the (–OH) group on the organic compound and polyurethane foam can account for this observation because polyether foam is able to form stronger hydrogen bonds than polyester foam. In addition, when hydrogen bonding is prevented by placing a strongly intramolecular hydrogen bonding group adjacent to the (–OH) group as in the case of o-nitrophenol, salicylaldehyde and o-methoxyphenol, the extraction by polyester and polyether foams is about the same.

The various organic compounds used in this study all contain the (–OH) group. The distribution coefficients (D) of these compounds under different conditions with polyester and polyether foams are summarized in Table 10. With the exception of 8-hydroxyquinoline, the compounds are more extractable by polyether foam. The extractable forms of these compounds are given in Figure 12. It is possible that intramolecular hydrogen bonding takes place in 8-hydroxyquinoline, and hence no hydrogen bonding between it and the foam. For salicylic acid, there are two groups per molecule able to form hydrogen bonds as opposed to one group for cinnamic acid. The higher $D_{polyether}/D_{polyester}$ ratio for salicylic acid can be ascribed to greater hydrogen bonding between the compound and the foam. Although there are two groups per molecule capable of hydrogen bonding for salicylic acid and ANS, the $D_{polyether}/D_{polyester}$ ratio for ANS is higher than salicylic acid. It is possible that the ($-NH_3^+$) group can have an ion-dipole interaction with the foam in addition to hydrogen bonding, resulting in higher extraction for ANS. These results are consistent with those previously reported[67].

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Table 10   Comparison of the distribution coefficients of various organic compounds extracted by polyester and polyether foams

Compound	Distribution Coefficient (L/kg)		$D_{Polyether}/D_{Polyester}$
	Polyester	Polyether	
salicylic acid	96.9 ± 3.2	218 ± 4	2.2
8-hydroxyquinoline	173 ± 3	165 ± 3	1.0
cinnamic acid	195 ± 3	343 ± 4	1.8
1-amino-2-naphthol-4-sulfonic acid	9.3	30.8	3.3

Conditions: (1) salicylic acid: 2.9×10^{-3} M salicylic acid, 0.300 g foam, 100 mL solution, 24 h extraction, pH = 3.2.

(2) 8-hydroxyquinoline: 1.0×10^{-3} M 8-hydroxyquinoline, 0.300 g foam, 100 mL solution, 1 h extraction time, pH = 6.4.

(3) cinnamic acid: 1.0×10^{-3} M cinnamic acid, 0.300 g foam, 100 mL solution, 24 h extraction time, pH = 3.9.

(4) 1-amino-2-naphthol-4-sulfonic acid (ANS): 1.0×10^{-3} M ANS, 0.300 g foam, 100 mL solution, 6 h extraction time, pH = 3.5.

Figure 12 Extractable forms of the various organic compounds.
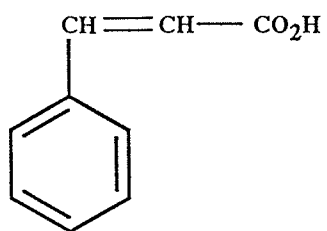
Cinnamic acid
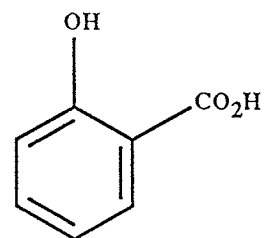
Salicylic acid
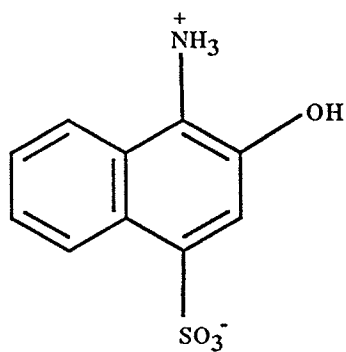
1-amino-2-naphthol-4-sulfonic acid
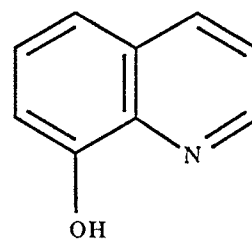
8-hydroxyquinoline

2.4 Conclusion

The study of the extraction of salicylic acid, 8-hydroxyquinoline, 1-amino-2-naphthol-4-sulfonic acid and cinnamic acid shows that these compounds are extracted in the neutral form by a solvent extraction mechanism. The anionic species are too hydrophilic to facilitate the extraction of alkylamines and alkali metal cations from aqueous solution. It was confirmed that hydrogen bonding and ion-dipole interactions between the extracted species and the foam are higher for polyether foam than for polyester foam.

The results demonstrate that polyurethane foam can extract relatively hydrophilic acids such as salicylic acid and cinnamic acid. With increased extractability for compounds able to form hydrogen bonds with the foam, organic acids and bases might be extracted by the proper adjustment of the pH of the solution. Thus, polyether foam appears to be well suited to apply for the removal of organic contaminants from aqueous solution.

CHAPTER 3

EXTRACTION OF ALKALI METAL AND
ALKYLAMMONIUM TETRAPHENYLBORATES

3.1 Introduction

Tetraphenylborate (TPB) was widely used as an analytical reagent during 1950–1960. It has been used to form precipitates with ammonium and alkali metal ions, and the insoluble salts have been separated by filtration or centrifugation. In 1960, Flaschka and Barnard[140] reviewed the applications of TPB.

The solubilities of potassium, rubidium, and cesium TPBs in water are not very different from each other; therefore, it is not possible to separate these ions by precipitation of the TPBs. Several attempts have been made to separate alkali metal ions by solvent extraction of their TPBs. Fix[141] reported the extraction of rubidium and cesium into nitrobenzene from aqueous 0.1 M sodium TPB solution, and Handley and Burros[142] studied the extraction of cesium TPB into amyl acetate.

Sekine and Dyrssen[143] studied the extraction of potassium, rubidium and cesium from aqueous solutions containing sodium TPB, sodium perchlorate, and perchloric acid into various organic solvents: nitromethane, nitroethane, nitrobenzene, methyl isobutyl ketone and tributyl phosphate. The highest distribution ratio and separation factor for the TPBs were obtained for extraction into nitrobenzene. The distribution ratio increases in the order sodium < potassium < rubidium < cesium. The results could be explained by assuming that TPBs are fully dissociated in both the aqueous and organic phases.

Koeva and Hala[144] examined the extraction of potassium, rubidium and cesium TPBs into nitrobenzene from mixed aqueous-organic solutions. The organic substances

used in the mixed solutions include methanol, ethanol, *n*-propanol, ethylene glycol, glycerine, ethylene glycol monomethyl ether, acetonitrile, dioxane, dimethylsulfoxide, dimethylformamide, pyridine, and urea. It was found that the extractability of alkali metal TPBs from mixed-organic solutions is always lower than from water irrespective of the nature of the organic component of the polar phase. The effect was ascribed to the increased solubility of TPB salts as well as the possible destruction of water structure in the mixed aqueous-organic phase.

Pivonkova and Kyrs[145] studied the distribution of alkaline earth TPBs between water and nitrobenzene. The extractability of alkaline earth TPBs follows the order: $Ba^{2+} > Sr^{2+} > Ca^{2+}$. The results can be explained by an extraction mechanism in which the salts are completely dissociated in the aqueous phase and partially dissociated in nitrobenzene.

Since polyurethane foam can be regarded as an organic phase for extraction, it is likely that various TPB salts can be extracted from aqueous solution into foam. Thus the extraction of alkali metal and various alkylamine TPBs was studied to assess the extractability of the cations.

3.2   Experimental

3.2.1   Apparatus and Reagents

The following apparatus were used: a Fisher Accumet Model 520 pH meter, a Ross combination pH electrode, a Waters Ion Chromatograph IIC-1, a Waters WISP auto-sampler, a Waters 740 data module, a Waters 590 solvent pump, a Waters 430 conductivity detector, a Hewlett-Packard Model 8452A diode-array spectrophotometer, a Barnstead Nanopure II water purification system, Micron Sep 0.22 μm cellulose acetate membrane filters, extraction cells (Figure 7), and a multiple automatic squeezer (Figure 8).

All the chemicals were of reagent grade.

3.2.2   Foam

Polyether type polyurethane foam (#1338M) was obtained from G. N. Jackson Ltd. (Winnipeg, Manitoba). Polyester type foam (DiSPo) was obtained from Canlab (Winnipeg, Manitoba).

3.2.3   General Procedure

3.2.3.1 Foam Washing

Foam plugs of approximately 0.4 g each were cut from a polyurethane sheet. These plugs were soaked in 1 M hydrochloric acid for 24 h with occasional squeezing to remove any possible inorganic contaminants and washed with water until acid free. They were then extracted with acetone in a Soxhlet apparatus for 6 h to remove the organic contaminants and finally air dried in a 60°C oven.

3.2.3.2 Preparation of Powdered Foam

Cleaned foam plugs were frozen in liquid nitrogen and ground in a stainless-steel container on a Waring™ blender.

3.2.3.3 Preparation of Sample Solutions

Stock solutions of 0.2 M various alkylamine hydrochlorides, 0.1 M NaOH and 0.01 M alkali metal chlorides were prepared. Sample solutions were freshly prepared by weighing in the necessary quantity of NaTPB solid and by pipetting the appropriate aliquots of stock solutions.

3.2.3.4 Extraction Procedure

For the extraction with foam plugs, the sample solution (100 mL) and the foam plug (0.300 ± 0.005 g) were placed in the extraction cell (Figure 7). The foam plug was squeezed by the automatic squeezing apparatus (Figure 8) at a rate of 24 strokes per minute.

For the extraction with powdered foam, the sample solution (100 mL) and powdered foam (0.300 ± 0.005 g for polyether foam and 0.800 ± 0.005 g for polyester foam) were placed in gas-tight plastic vials and were manually shaken periodically.

3.2.3.5 Analytical Methods

TPB was analysed by UV-visible spectrophotometry. Figure 13 shows the absorption spectrum of NaTPB and indicates that the absorbance changes less rapidly from 225 to 240 nm relative to lower wavelengths. Absorbance at 230 nm was chosen to measure the concentration of TPB. A 1 cm cell was used for the measurements.

The concentration of alkylammonium and alkali metal ions was determined by ion chromatography using a Waters cation guard column and a 4.6 mm (ID) x 5 cm Waters IC-PAK^{TM} plastic cation column. 2 mM HNO$_3$ was used as eluent at a flow rate of 1.2

Figure 13 Absorption spectrum of NaTPB in water.
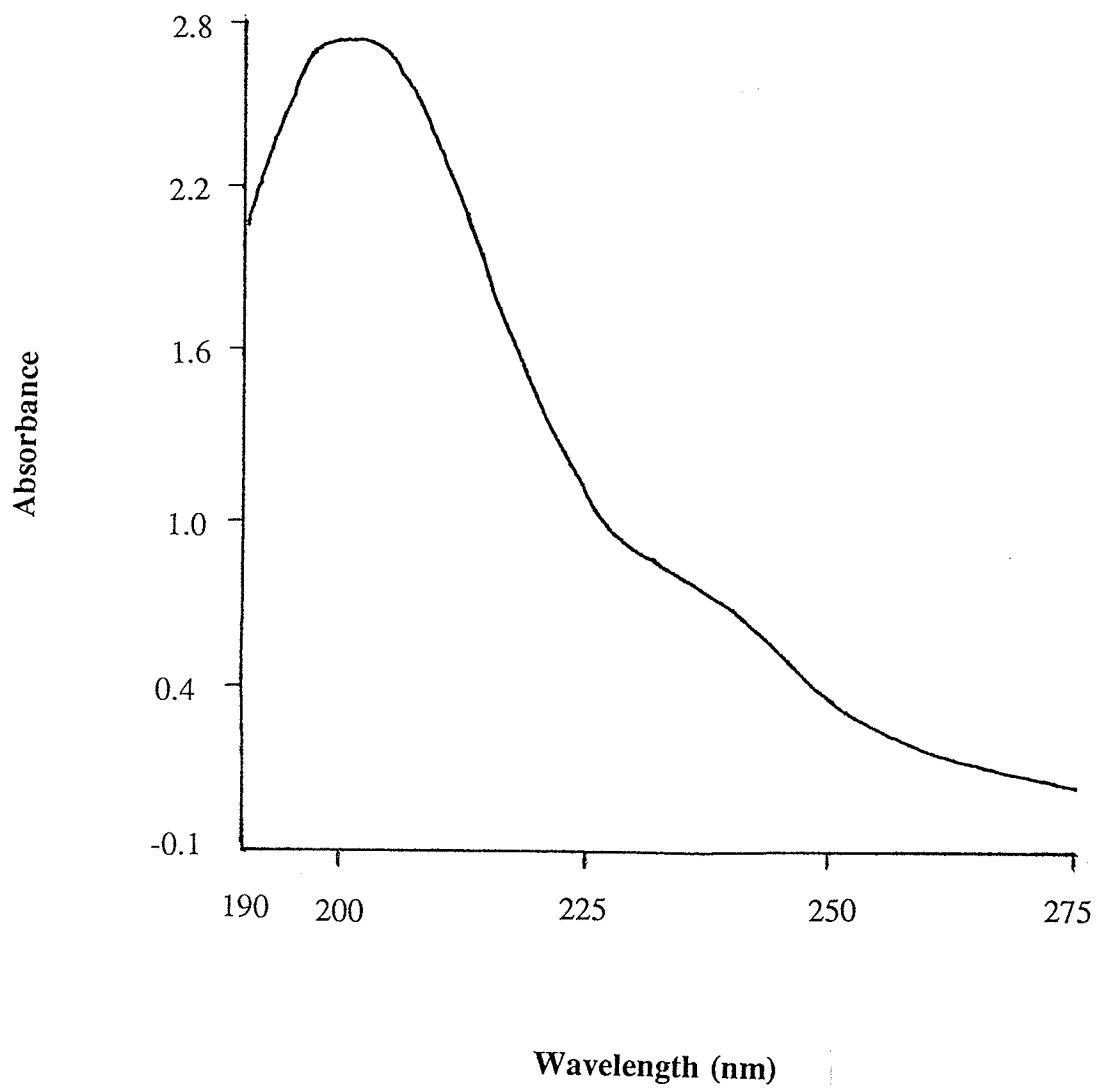
66

mL/min. 150 µL of the sample solution were injected for the analysis of the cations after filtering through a 0.22 µm cellulose acetate membrane filter.

3.2.3.6 Calculations

The % extraction was calculated indirectly by determining the concentration of the species in solution after extraction, equation (17). The species disappeared from solution was assumed to have been extracted by the foam.

$$\% \text{ extraction} = (\ 1 - C'/C_0\ ) \times 100 \qquad (17)$$

C_0 = concentration in solution before extraction

C' = concentration in solution after extraction

The distribution coefficient (D) was calculated as follows:

$$D = \frac{\% \text{ extraction}}{(100 - \% \text{ extraction})} \times \frac{\text{volume of solution (L)}}{\text{weight of foam (kg)}} \qquad (18)$$

Table 2 gives the pK_a values for the alkylammoniums and ammonium. At pH 9 about 98% of the amines is protonated, whereas only 64% of ammonia is protonated. In the calculation of C' (concentration after extraction) for ammonium, C' was corrected to be the concentration of NH_4^+ present in the solution after extraction rather than the concentration measured from ion chromatography (IC). In the IC analysis the eluent is 2 mM HNO_3 and unprotonated ammonia in the injected solution will become protonated after mixing with the acidic eluent.

3.3 Results and Discussion

3.3.1 Preliminary Results

To study whether NaTPB is extractable by foam, 1.0×10^{-3} M NaTPB solutions (100 mL) were extracted with polyether and polyester foams (0.300 g). The foam plugs were squeezed by the automatic squeezing apparatus. The pH of the solution changed from 8.5 to 7.0 after 24 h of extraction. The distribution coefficients of Na^+ and TPB^- ions for both types of foams are given in Table 11. It is evident that TPB^- can be used to extract Na^+. In contrast to the expected equal extraction of the cation (Na^+) and the anion (TPB^-), TPB^- is more extractable than Na^+. It should be noted that the species removed from solution was considered to be extracted by the foam. The decomposition of TPB^- with decomposition products which can be extracted by the foam but not necessarily along with Na^+ could result in the apparent higher extraction of TPB^-.

NaTPB solution has been known to be unstable and undergoes decomposition in acidic medium[140]. The TPB^- ion is attacked by H^+ to form benzene and triphenylboron (Equation 27).

$$B(C_6H_5)_4^- + H^+ \longrightarrow [HB(C_6H_5)_4] \longrightarrow B(C_6H_5)_3 + C_6H_6 \qquad (27)$$
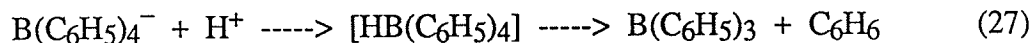
Triphenylboron undergoes hydrolysis to phenylboric acid or diphenylboric acid (Equations 28 and 29).

$$B(C_6H_5)_3 + 2H_2O \longrightarrow (C_6H_5)B(OH)_2 + 2C_6H_6 \qquad (28)$$

$$B(C_6H_5)_3 + H_2O \longrightarrow (C_6H_5)_2B(OH) + C_6H_6 \qquad (29)$$
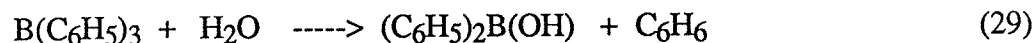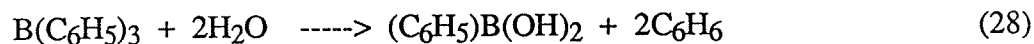
Table 11   Extraction of NaTPB with polyurethane foam

		Na$^+$	TPB$^-$
Polyester	% extraction	15.8 ± 0.5	25.4 ± 0.7
	Amount extracted (x 10^{-5} mol)	1.58 ± 0.05	2.54 ± 0.07
	Distribution coefficient (L/kg)	62.4 ± 2.5	113 ± 4
Polyether	% extraction	64.5 ± 0.5	81.5 ± 0.5
	Amount extracted (x 10^{-5} mol)	6.45 ± 0.05	8.15 ± 0.05
	Distribution coefficient (L/kg)	602 ± 11	1460 ± 60

Conditions: 1.0 x 10^{-3} M NaTPB, 0.300 g foam, 100 mL solution, 24 h extraction time, initial pH = 8.5, final pH = 7.0.

Cooper[146] reported that NaTPB solution is stable for at least several weeks if the pH of the solution is about 8 or 9.

The decomposition products of TPB$^-$ are highly hydrophobic and are likely to be extracted by foam. In addition, HTPB may also be extractable. To determine the effect of pH on the extraction, solutions (100 mL) containing 1.0×10^{-4} M NaTPB were extracted with 0.300 g foam at initial pH 3.8 and 5.2. Figure 14 shows the % extraction of the cation and the anion as a function of time. At pH 3.8 and after 1/2 h extraction, there is only 2% of Na$^+$ extracted but 96% of TPB$^-$ extracted, which may be a result of NaTPB decomposition and HTPB extraction. At pH 5.2 and after 1/2 h extraction, 35% of Na$^+$ and 84% of TPB$^-$ are extracted, suggesting lower NaTPB decomposition and HTPB extraction.

To prevent the decomposition of TPB$^-$, it is necessary to keep the pH of the solution above 8. From the extraction results of 1.0×10^{-3} M NaTPB, pH lowers from 8.5 to 7.0 after 24 h due to CO_2 absorption from air during the squeezing process. It was decided to raise the initial pH of the solution to higher pH by adding NaOH. Moreover, the extraction was carried out by bubbling N_2 through the solution to prevent CO_2 absorption in the set-up as shown in Figure 15. Solutions (100 mL) containing 1.0×10^{-4} M NaTPB and 1.0×10^{-4} M NaOH were extracted with 0.300 g polyether foam. The plot of amount extracted against extraction time is shown in Figure 16. There is a lowering of TPB$^-$ extracted compared with the extraction at lower pH. However, after reaching a maximum a decrease of Na$^+$ extraction still occurs with increasing extraction time. It is unlikely that TPB$^-$ decomposes since the final pH is 8.6. The pH change of the solution from 9.0 to 8.6 indicates that there may still be CO_2 absorption from air. The up and down motions of the plunger could bring solution into contact with air.and the dissolved CO_2 promotes the formation of H_3O^+ (Equation 30).

Figure 14   Effect of pH on the extraction of Na$^+$ and TPB$^-$.
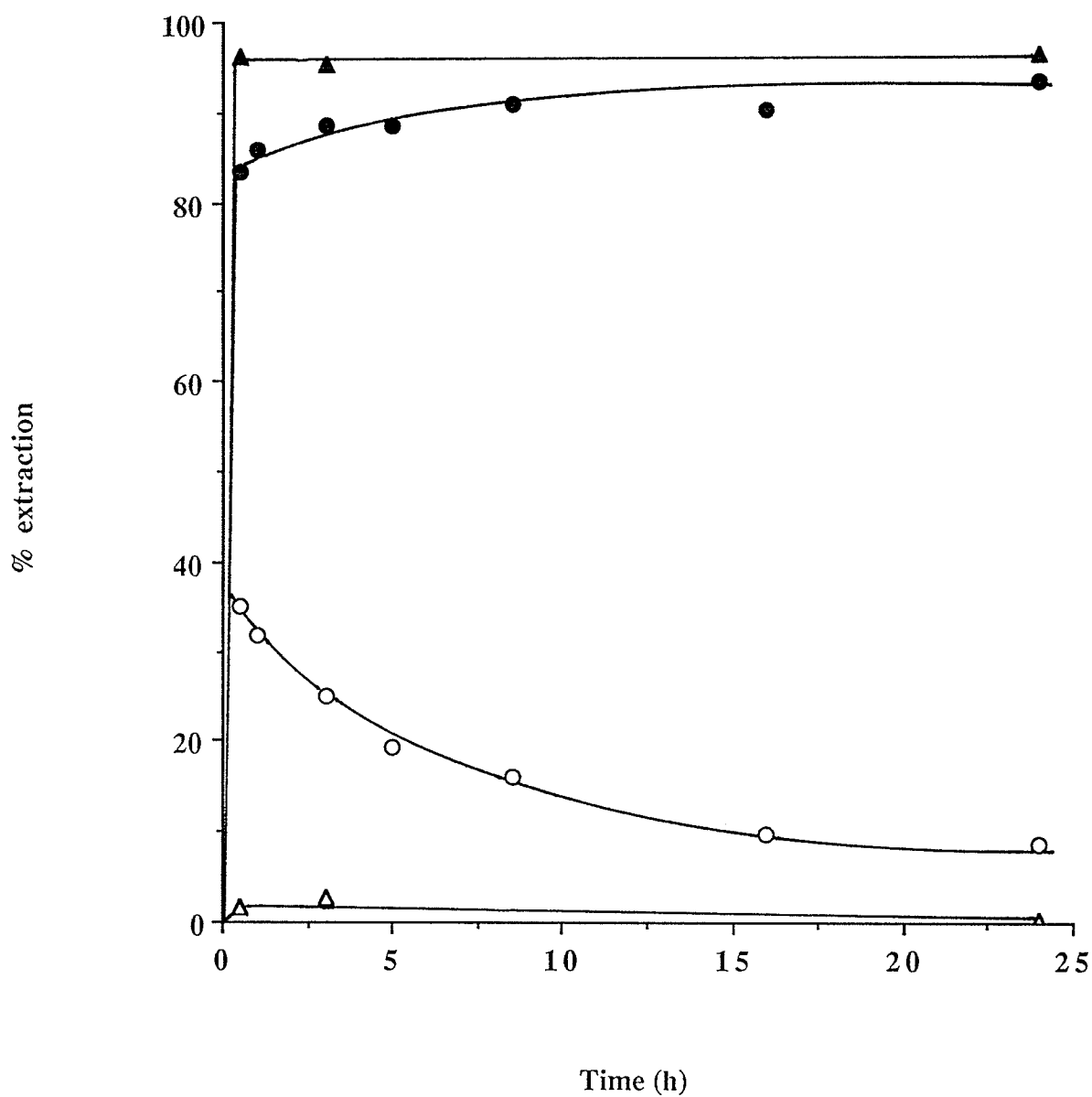
Conditions: 1.0 x 10^{-4} M NaTPB, 0.300 g polyether foam plug, 100 mL solution, ($\bullet$) TPB$^-$ extraction and (o) Na$^+$ extraction at initial pH = 5.2 and final pH = 6.3, ($\blacktriangle$) TPB$^-$ extraction and ($\triangle$) Na$^+$ extraction at initial pH = 3.8 and final pH = 4.3.

Figure 15 Set-up for the extraction of NaTPB with N_2 bubbling through solution.

N₂

glass tubing

cork

plastic tubing
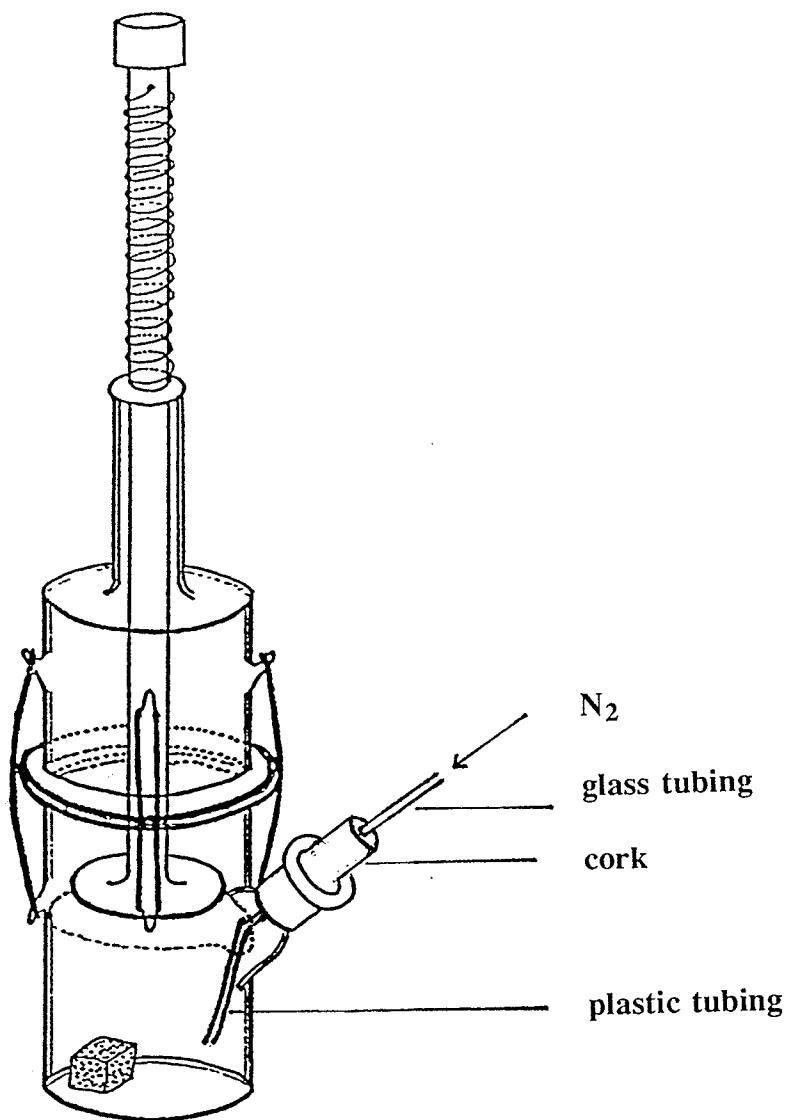
Figure 16 Extraction of NaTPB with N_2 bubbling through solution.
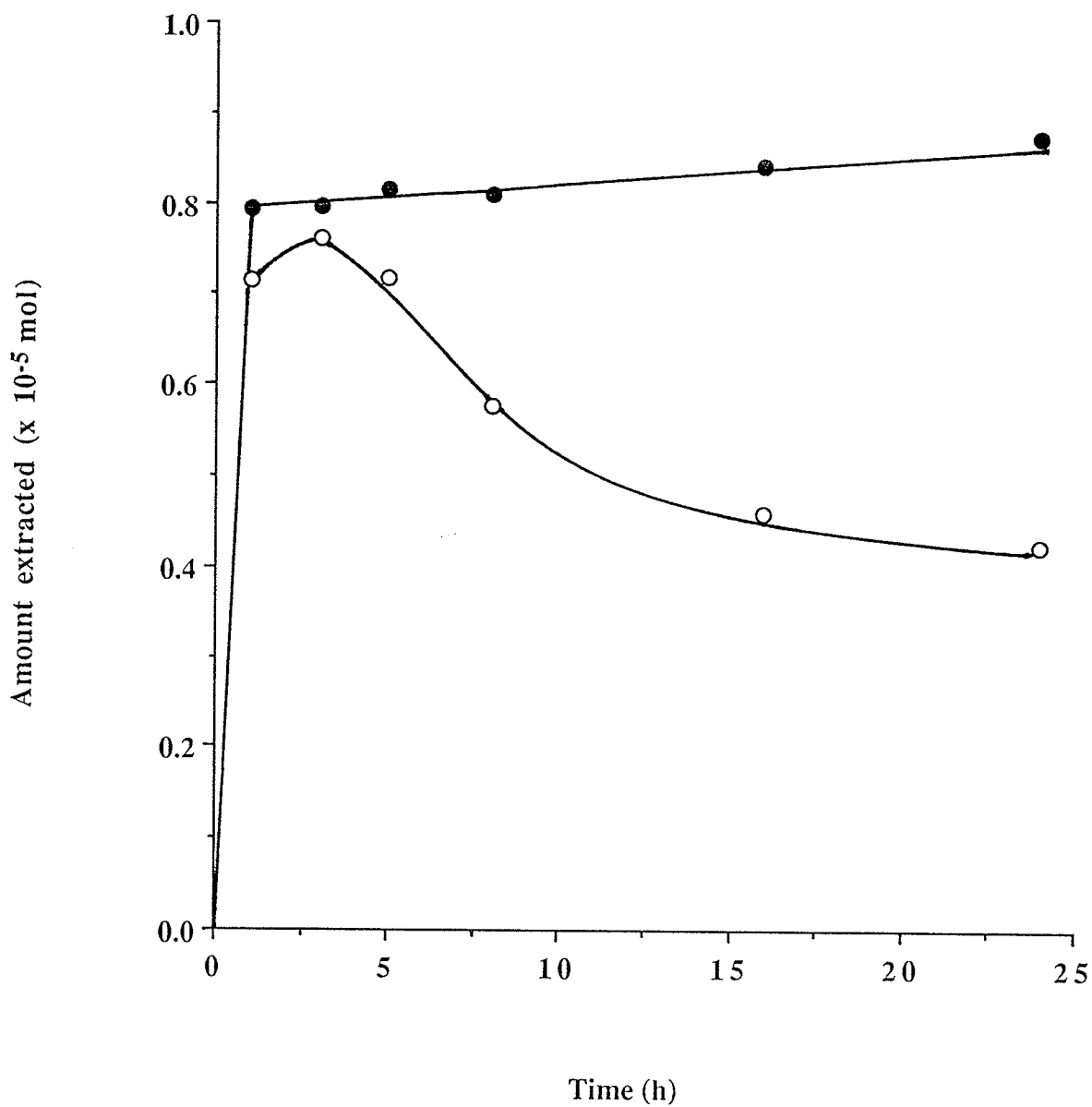
Conditions: 1.0×10^{-4} *M* NaTPB + 1.0×10^{-4} *M* NaOH, 0.300 g polyether foam plug, 100 mL solution, initial pH = 9.0, final pH = 8.6, (●) TPB^- and (o) Na^+.

$$2H_2O + CO_2 \rightleftharpoons H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^- \qquad (30)$$
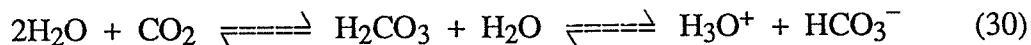
It is possible that H_3O^+ is more extractable than Na^+ and can displace Na^+ from the foam. This would result in the observed gradual decrease of Na^+ extraction as CO_2 absorption from air increased with time.

Izatt *et al.*[147] reported the preparation of a complex, $[OH_3,C_{20}H_{36}O_6^+][ClO_4^-]$, formed by H_3O^+ with a cyclic polyether. Behr *et al.*[148] determined the structure of the complex between tetracarboxylic 18-crown-6 and H_3O^+ by x-ray crystallography. The H_3O^+ cation is positioned in the center of the cavity by three OH^+–O hydrogen bonds with a pyramidal geometry as illustrated in Figure 17.

Heo and Bartsch[149] were also able to prepare the complex between 18-crown-6 and H_3O^+. They attempted to prepare solid H_3O^+ complexes with tetraglyme, an acyclic polyether; and with 15-crown-5. It was found that H_3O^+ only complexes with tetraglyme. They suggested that the greater flexibility of acyclic polyether allows the oxygens to provide a better arrangement for the formation of hydrogen bonds with the pyramidal H_3O^+, and hence increases complexation.

Kolthoff *et al.*[150] determined the complexation constants of H_3O^+ and K^+ with 18-crown-6 (L) and with dibenzo-18-crown-6 (L') in acetonitrile. The dibenzo groups are electron withdrawing which lower the electron-density of the oxygen binding sites. Therefore the complexation constants for (L'H_3O^+) and (L'K^+) are lower than that for (LH_3O^+) and (LK^+). The dibenzo effect can be calculated as [$K(LH_3O^+) - K(L'H_3O^+)$] and [$K(LK^+) - K(L'K^+)$] for H_3O^+ and K^+ respectively (K is the association constant). This effect on (LH_3O^+) is two orders of magnitude greater than that on (LK^+). It was concluded that H_3O^+ is strongly bound to the ether oxygens by hydrogen bonding in addition by ion-dipole interaction, whereas K^+ is bound only by the latter.

Figure 17 Diagrammatic representation of mode of binding of H_3O^+ to 18-crown-6[149].
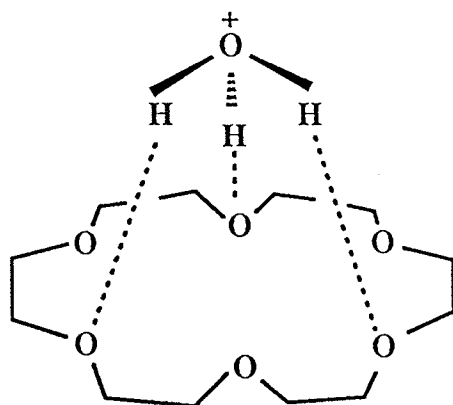
Dashed lines represent hydrogen bonds

It is evident that H_3O^+ can complex with crown ethers and acyclic polyethers by hydrogen bonding and ion-dipole interaction. It appears that similar interaction of H_3O^+ with foam can take place because polyether and polyester foams can be considered as acyclic polymers with flexible chains.

Since CO_2 absorption from air may cause the displacement of cations and lowering pH of the solution, further extractions were carried out in gas-tight plastic vials to minimize CO_2 absorption. Powdered foam was used to provide a better contact between foam and solution, and the vials were periodically shaken manually. It should be noted that further discussion of the imbalance of the cation and the anion extracted will be given in Chapter 5.

3.3.2   Extraction by Polyether Foam

3.3.2.1   Alkali Metal TPB

Results of the extraction of 1.0×10^{-3} M NaTPB demonstrate that 0.300 g polyether foam extracts 6.5×10^{-5} mol Na^+ and 8.2×10^{-5} mol TPB^-. Due to the low solubility of TPB salts with K^+ and other alkali metal ions, a maximum of 1.0×10^{-4} M NaTPB was used for further experiments. The total amount of TPB^- present in 100 mL solution is 1.0×10^{-5} mole. Thus, 0.300 g polyether foam is enough to extract a 100 mL solution containing 1.0×10^{-4} M TPB^-.

3.3.2.1.1   Time Dependence of the Extraction

To determine the time required to reach equilibrium, the extraction of solutions (100 mL) containing 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 2.0×10^{-5} M NaCl with 0.3 g foam was studied as a function of time. The results are given in Figure 18. TPB^-

Figure 18   Extraction of NaTPB with polyether foam as a function of time.
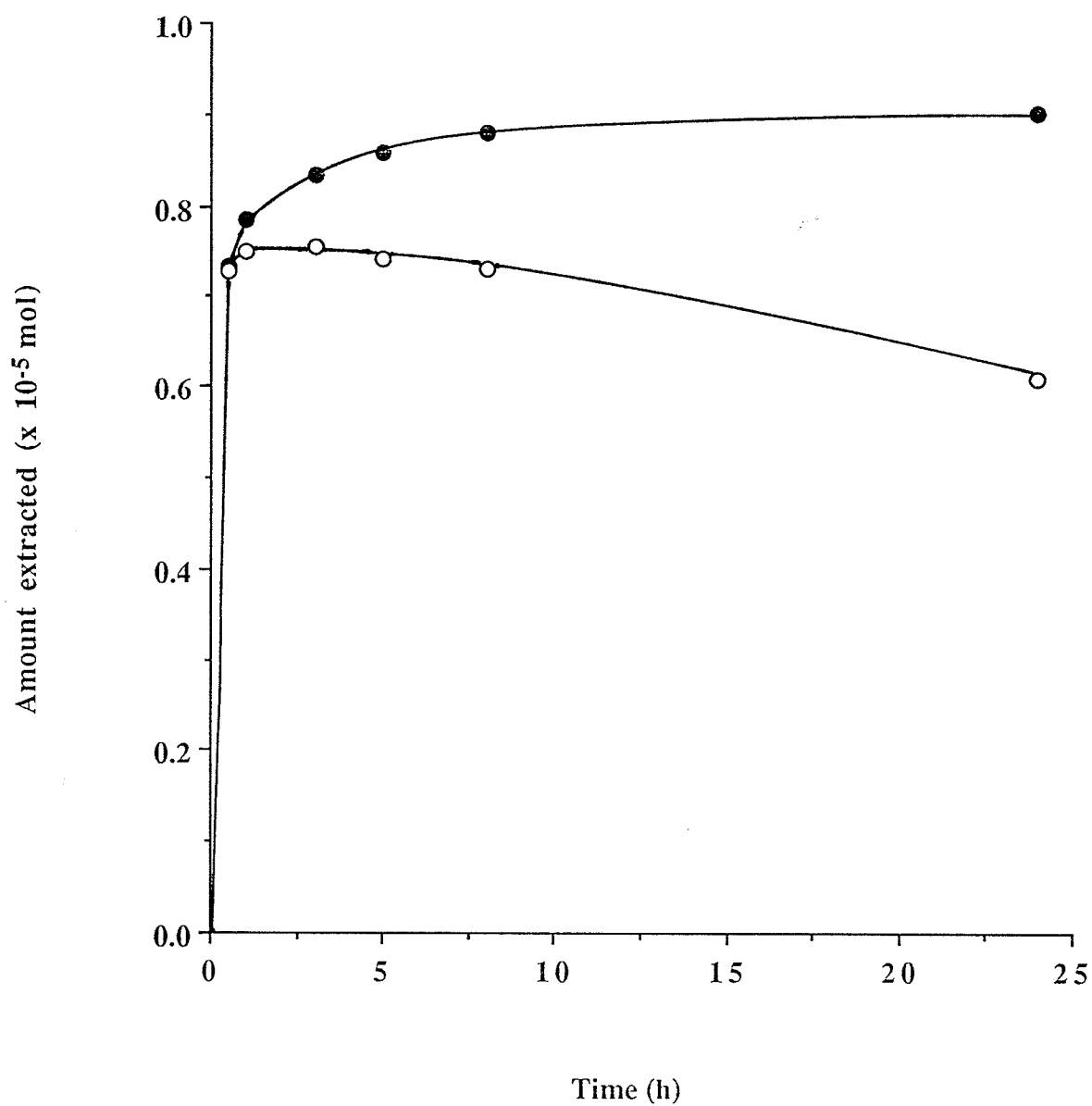
Conditions: 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 2.0×10^{-5} M NaCl, 0.300 g

powdered polyether foam, 100 mL solution, pH = 9.0, ($\bullet$) TPB$^-$ and (o)

Na$^+$.

extraction increases rapidly to 79 % after 1 h and then slowly to 90 % after 24 h. Na^+

extraction reaches a maximum of 34 % after 1 h and decreases to 28 % after 24 h. No

decomposition of TPB^- should take place as the pH of the solution is 9.0. Although the

extraction was carried out in closed containers, CO_2 could still diffuse into the container.

The decrease of Na^+ extracted may be because of a slow continuous CO_2 absorption from

air. Table 12 gives the ratio of cation extracted / anion extracted (Na^+ extracted / TPB^-

extracted) as a function of time. The precisions obtained for determining the concentration

were estimated to be 5.0 % and 2.4 % of the % extraction for the cation and the anion

respectively (Section 4.3.3.2.2). Thus, the random error for the ratio of cation extracted /

anion extracted is ± 0.05. The ratio is very close to 1 for the first hour of extraction. It is

reasonable to assume that no decomposition or displacement of cations take place if the

ratio of cation extracted / anion extracted is 1. Although a time for the cation extraction

reaching equilibrium could not be obtained, the extractability of different cations can still be

evaluated by comparing the values of cation extraction at which cation / anion is about 1.

The extraction of 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 2.0×10^{-5} M alkali

metal chloride solutions (100 mL) with 0.300 g foam for different extraction times was

carried out. The results are given in Figures 19, 20 and 21. The extraction characteristic is

similar to that shown in Figure 18. The extraction of total cations (Na^+ + alkali metal ion)

maximizes at about 1 h and decreases with time. The ratios of cation extracted / anion

extracted with time are listed in Table 13.

3.3.2.1.2 Selectivity for Alkali Metal Ions

Figures 22 and 23 show the % extraction of the cation and anion as a function of

time for potassium, rubidium and cesium TPBs. Tables 14 and 15 give the % extraction

Table 12   Ratio of Na^+ extracted / TPB^- extracted as a function of time for the extraction of NaTPB with polyether foam

Time (h)	Na^+ extracted / TPB^- extracted
0.5	0.99
1.0	0.95
3.0	0.91
5.0	0.86
8.0	0.83
24.0	0.68

Conditions: 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 2.0×10^{-5} M NaCl, 0.300 g powdered polyether foam, 100 mL solution, pH = 9.0.

Figure 19   Extraction of NaTPB and KCl with polyether foam as a function of time.

Time (h)
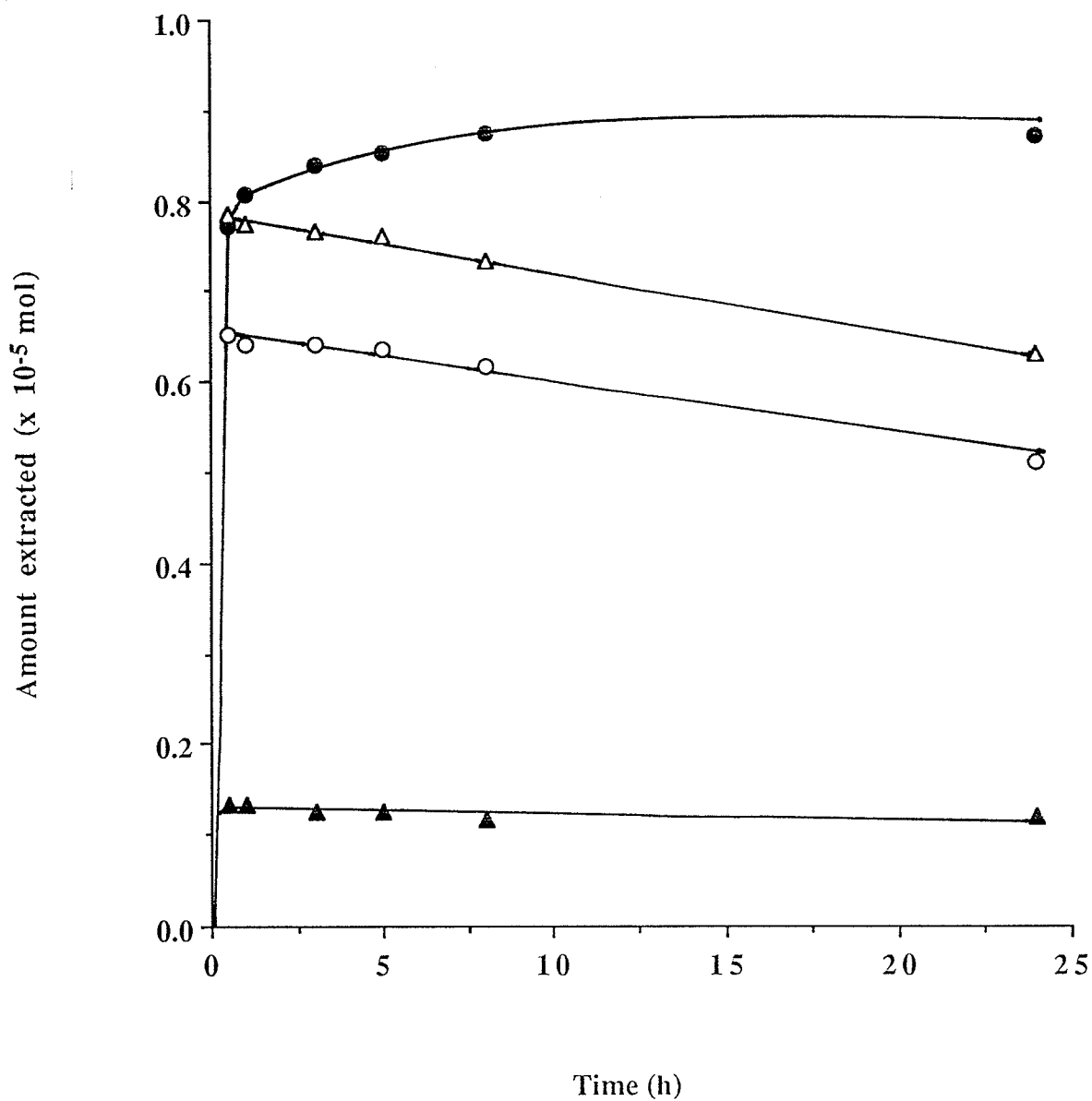
Conditions: 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 2.0×10^{-5} M KCl, 0.300 g

powdered polyether foam, 100 mL solution, pH = 9.0, (●) TPB^-, (o) Na^+,

(▲) K^+ and (Δ) total cations ($Na^+ + K^+$).

Figure 20   Extraction of NaTPB and RbCl with polyether foam as a function of time.
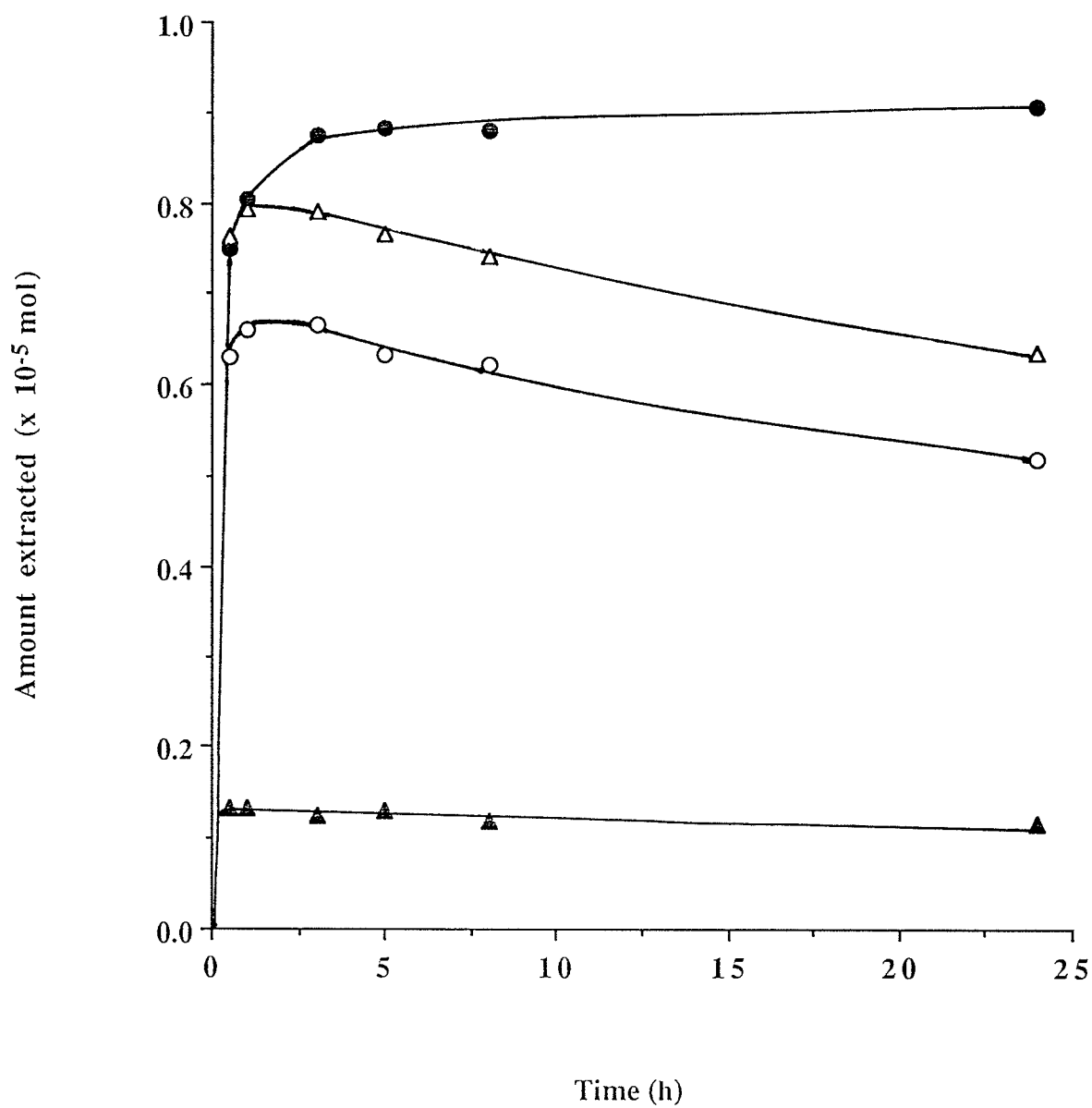
Conditions: 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 2.0×10^{-5} M RbCl, 0.300 g

powdered polyether foam, 100 mL solution, pH = 9.0, (●) TPB$^-$, (o) Na$^+$,

(▲) Rb$^+$ and (Δ) total cations (Na$^+$ + Rb$^+$).

Figure 21 Extraction of NaTPB and CsCl with polyether foam as a function of time.
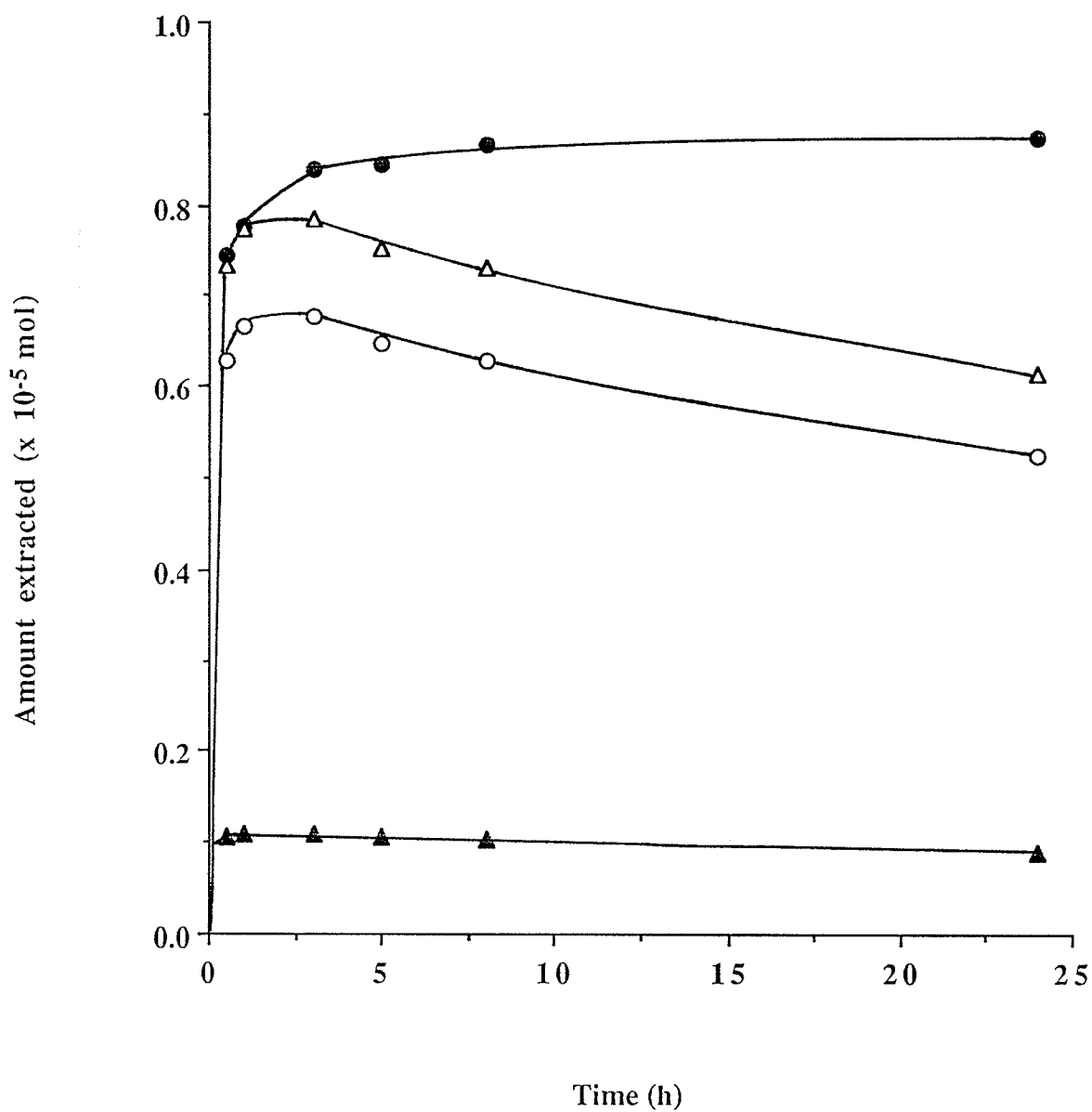
Conditions: $1.0 \times 10^{-4}\ M$ NaTPB + $1.0 \times 10^{-4}\ M$ NaOH + $2.0 \times 10^{-5}\ M$ CsCl, 0.300 g powdered polyether foam, 100 mL solution, pH = 9.0, (●) TPB$^-$, (o) Na$^+$, (▲) Cs$^+$ and (Δ) total cations (Na$^+$ + Cs$^+$).

Table 13   Ratio of total cations extracted / TPB^- extracted for the extraction of NaTPB and alkali metal chlorides with polyether foam as a function of time

Time (h)	$(Na^+ + Na^+)\,/$ TPB^-	$(Na^+ + K^+)\,/$ TPB^-	$(Na^+ + Rb^+)\,/$ TPB^-	$(Na^+ + Cs^+)\,/$ TPB^-
0.5	0.99	1.02	1.02	0.98
1.0	0.95	0.96	0.99	0.99
3.0	0.91	0.91	0.91	0.94
5.0	0.86	0.89	0.87	0.89
8.0	0.83	0.87	0.84	0.84
24.0	0.68	0.72	0.70	0.70

Conditions: $1.0 \times 10^{-4}\ M$ NaTPB + $1.0 \times 10^{-4}\ M$ NaOH + $2.0 \times 10^{-5}\ M$ alkali metal chloride, 0.300 g powdered polyether foam, 100 mL solution, pH = 9.0.

Figure 22   Plot of % cation extraction as a function of time for the extraction of NaTPB and alkali metal chlorides with polyether foam.

Time (h)
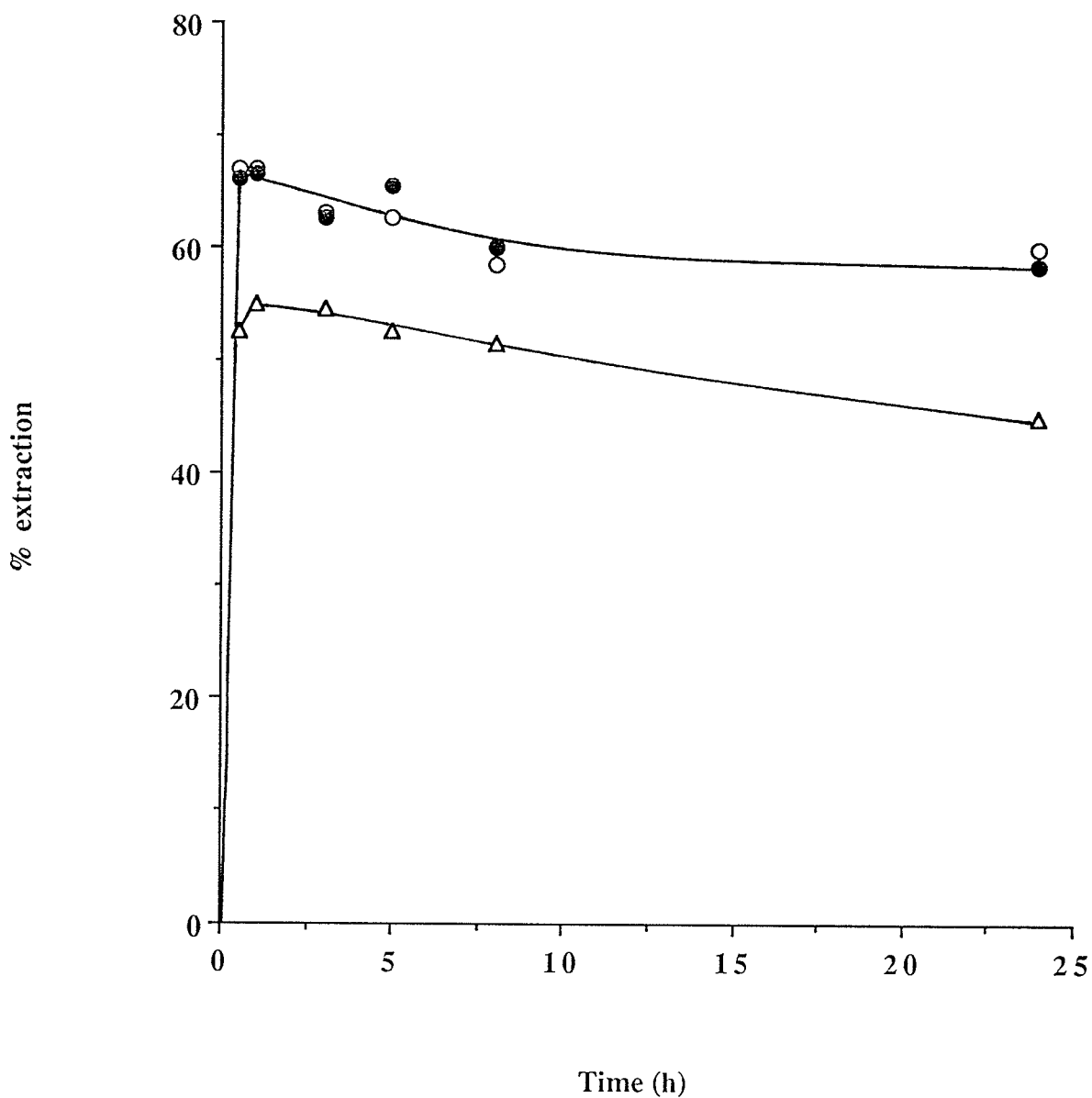
Conditions: 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 2.0×10^{-5} M alkali metal chloride, 0.300 g powdered polyether foam, 100 mL solution, pH = 9.0, (o) K^+, (●) Rb^+ and (Δ) Cs^+.

Figure 23   Plot of % TPB⁻ extraction as a function of time for the extraction of NaTPB and alkali metal chlorides with polyether foam.

Time (h)
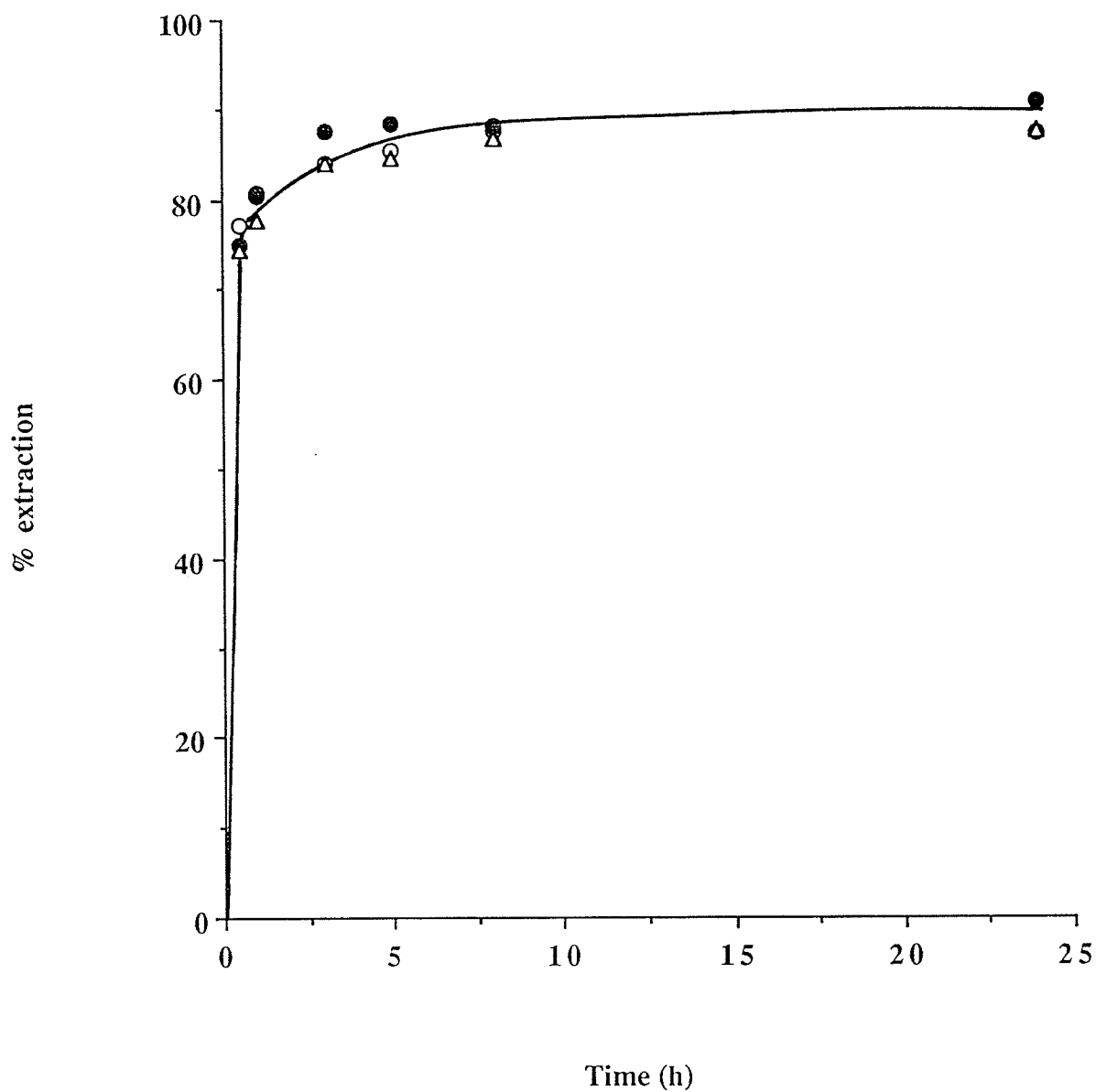
Conditions: 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 2.0×10^{-5} M alkali metal chloride, 0.300 g powdered polyether foam, 100 mL solution, pH = 9.0, (o) TPB⁻ extraction for solution with KCl, (●) TPB⁻ extraction for solution with RbCl and (Δ) TPB⁻ extraction for solution with CsCl.

Table 14   Distribution coefficient and % extraction of alkali metal ions at total cations extracted / TPB⁻ extracted ≈ 1 for the extraction of NaTPB and alkali metal chlorides with polyether foam

Cation	% extraction	Distribution coefficient (L/kg)
K^+	67.0	669
Rb^+	66.5	660
Cs^+	55.0	404

Conditions: 1.0×10^{-4} *M* NaTPB + 1.0×10^{-4} *M* NaOH + 2.0×10^{-5} *M* alkali metal chloride, 0.300 g powdered polyether foam, 100 mL solution, pH = 9.0.

Table 15   Distribution coefficients of cations and TPB$^-$ at total cations extracted / TPB$^-$ extracted $\approx$ 1 for the extraction of NaTPB and alkali metal chlorides with polyether foam

Alkali metal	Distribution coefficient (L/kg)		
	Cation	Na$^+$	TPB$^-$
K$^+$	669	157	1340
Rb$^+$	660	164	1380
Cs$^+$	404	166	1170

Conditions: 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 2.0×10^{-5} M alkali metal chloride, 0.300 g powdered polyether foam, 100 mL solution, pH = 9.0.

and distribution coefficient (D) of the cations at which the ratio of total cations extracted / anion extracted (Na^+ + alkali metal ions extracted / TPB^- extracted) is about 1. It should be noted that the distribution coefficients of TPB^- and the cations are not necessarily the same because of the different initial concentrations of TPB^- and the cations in solution (Table 15) although the absolute amounts of total cations extracted and that of TPB^- extracted are the same when the ratio of total cations extracted / TPB^- extracted is 1.

From Figures 22, 23 and Tables 14, 15 the extractability follows the order of $K^+ \approx Rb^+ > Cs^+$. Assuming that alkali metal ions form ion-pairs with TPB^-, Cs^+ and Rb^+ are expected to form ion-pairs with TPB^- more readily than K^+ because the Cs^+ and Rb^+ salts are less soluble than the K^+ salt as shown in Table 16. The higher extractability of K^+ than Cs^+ must be due to some stronger interaction between K^+ and foam. This can be explained by the cation chelation mechanism because K^+ fits well in the cavity in the foam, and hence stronger interaction.

3.3.2.2 Alkylammonium TPB

From Table 16, it can be seen that the alkylammonium TPB salts are generally more soluble than the alkali metal salts. 1.0×10^{-4} M alkylammonium chloride as opposed to 2.0×10^{-5} M alkali metal chloride was used in the extraction to keep the concentration of the alkylammonium cation and TPB^- the same. For this study, 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 1.0×10^{-4} M alkylammonium chloride solutions (100 mL) were extracted with 0.300 g foam.

Table 16   Solubilities of various TPB salts in water[151]

TPB salt	Concentration (x 10^{-4} M)
rubidium	0.23
cesium	0.28
potassium	1.8
ammonium	2.9
trimethylammonium	3.9
n-propylammonium	9.0
n-butylammonium	11.2
dimethylammonium	16.3
ethylammonium	28.3
methylammonium	36.3

3.3.2.2.1 Time Dependence of the Extraction

Figure 24 shows the extraction of 1.0 x 10^{-4} M NaTPB + 1.0 x 10^{-4} M NaOH + 1.0 x 10^{-4} M t-butylammonium chloride as a function of time. Similar to the alkali metal TPB extraction, the cation extraction decreases after reaching a maximum. The decrease may be because of the displacement of the cation by H_3O^+ resulting from CO_2 absorption from air. Other alkylammonium TPBs also exhibit similar extraction characteristics. Table 17 lists the ratio of total cations (Na^+ + alkylammonium ion) / anion versus extraction time. The ratio is generally close to 1 for the first hour of extraction.

3.3.2.2.2 Selectivity for Alkylammonium Ions

According to the cation chelation mechanism a hole-size / cation-diameter relationship is responsible for the selectivity for cations. It was believed that alkylammonium cations with chains of different length and branching may exert different effects on the complexation with foam. Long and highly branched side chains are expected to offer more steric hindrance for the cations to fit in the cavity of the foam. Thus, the extraction of n-butylammonium, t-butylammonium, n-propylammonium, isopropylammonium, ethylammonium, dimethylammonium, trimethylammonium and ammonium chloride as well as potassium chloride was studied for comparison with NaTPB.

No equilibrium time for the cation extraction was observed from time dependence studies. However, the maximum for the cation extraction generally occurs after 1 h of extraction and the ratio of cation / anion is about 1 indicating no displacement of the cation. Therefore, the maximum values of the cation extracted were used to compare the extractability of the various alkylammonium cations and are listed in Tables 18 and 19.

Figure 24   Extraction of NaTPB and *t*-butylammonium with polyether foam as a function of time.
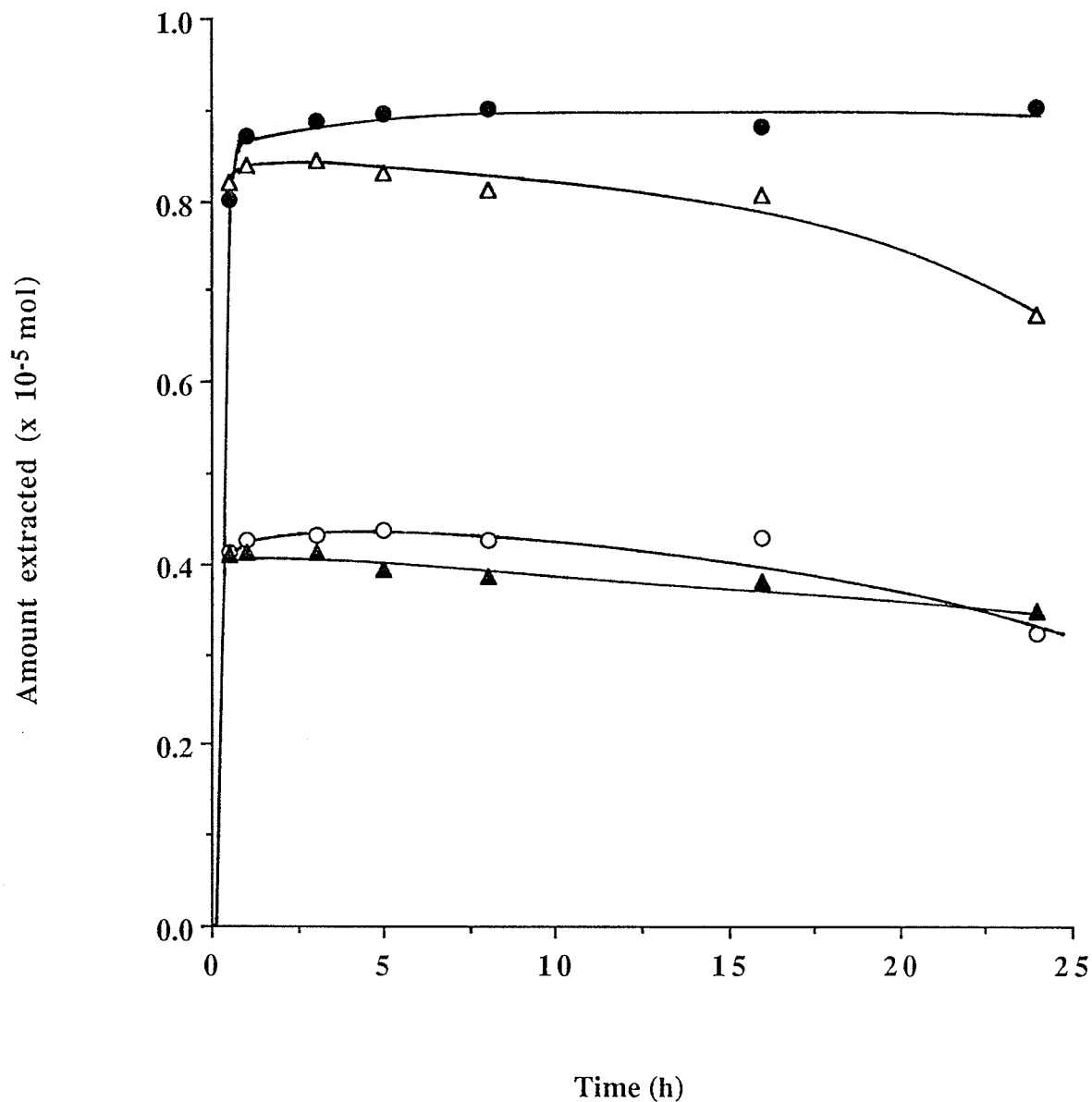
Conditions: $1.0 \times 10^{-4} \, M$ NaTPB + $1.0 \times 10^{-4} \, M$ NaOH + $1.0 \times 10^{-4} \, M$ *t*-butylammonium, 0.300 g powdered polyether foam, 100 mL solution, pH = 9.0, (●) TPB⁻, (o) Na⁺, (▲) *t*-butylammonium and (Δ) total cations (Na⁺ + *t*-butylammonium).

Table 17   Ratio of total cations extracted / TPB⁻ extracted for the extraction of NaTPB, and alkylammonium, potassium and ammonium chlorides with polyether foam as a function of time

	Time (h)					
	0.5	1.0	3.0	5.0	8.0	24.0
n-butylammonium	1.03	1.05	0.94	0.95	0.90	0.83
n-propylammonium	1.03	1.02	0.93	0.97	0.92	0.78
potassium	1.01	1.01	0.96	0.96	0.94	0.80
ammonium	1.00	0.96	0.89	0.83	0.79	0.70
t-butylammonium	1.03	0.96	0.95	0.93	0.90	0.74
isopropylammonium	1.01	1.00	0.99	0.94	0.92	0.78
ethylammonium	1.01	1.04	0.98	0.92	0.87	0.74
methylammonium	1.02	1.02	0.93	0.88	0.88	0.77
dimethylammonium	0.97	0.96	0.95	0.96	0.88	0.78
trimethylammonium	0.99	0.94	0.94	0.88	0.87	0.72

Conditions: 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 1.0×10^{-4} M alkylammonium, potassium or ammonium chloride, 0.300 g powdered polyether foam, 100 mL solution, pH = 9.0.

Table 18   Distribution coefficient and % extraction of the cations at total cations extracted / TPB⁻ extracted ≈ 1 for the extraction of NaTPB, and alkylammonium, potassium and ammonium chlorides with polyether foam

Cation	% extraction	Distribution coefficient (L/kg)
n-butylammonium	59.1	481
n-propylammonium	52.4	369
potassium	48.1	310
ammonium	37.8	294
t-butylammonium	41.4	235
isopropylammonium	41.3	235
ethylammonium	40.9	232
methylammonium	34.5	176
dimethylammonium	23.6	104
trimethylammonium	15.5	61

Conditions: 1.0×10^{-4} *M* NaTPB + 1.0×10^{-4} *M* NaOH + 1.0×10^{-4} *M* alkylammonium, potassium or ammonium chloride, 0.300 g powdered polyether foam, 100 mL solution, pH = 9.0.

Table 19   Distribution coefficients of the cations and TPB⁻ at total cations / TPB⁻ ≈ 1 for the extraction of NaTPB, and alkylammonium, potassium and ammonium chlorides with polyether foam

TPB salt	Distribution coefficient (L/kg)		
	Cation	Na^+	TPB⁻
n-butylammonium	481	62	2490
n-propylammonium	369	86	2900
potassium	310	88	2770
ammonium	294	102	2360
t-butylammonium	235	90	2250
ispropylamine	235	100	2290
ethylammonium	232	120	2330
methylammonium	176	125	2240
dimethylammonium	104	146	2180
trimethylammonium	61	181	2210

Conditions: 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 1.0×10^{-4} M alkylammonium, potassium or ammonium chloride, 0.300 g powdered polyether foam, 100 mL solution, pH = 9.0.

The following factors can be considered to affect the extraction of the cations:

(1) Steric effect

(2) Hydrophobic interaction

(3) Inductive effect of alkyl groups

Alkylammoniums with branched side chains are expected to exert higher steric hindrance to fitting into the cavity of the foam. The extractabilities of various alkylammonium cations with the same chain length but different branching were compared and the following trend was obtained: *n*-butylammonium > *t*-butylammonium, propylamine > isopropylammonium > trimethylammonium, ethylammonium > dimethylammonium. The results show that the branched alkylammoniums are less extractable than the unbranched alkylammoniums, and therefore it appears that the steric effect may affect the extraction.

The alkyl side chain can interact with the non-polar portion of the foam through hydrophobic interaction. The interaction increases with increasing length of the alkyl side chain. The extractability of the unbranched alkylammoniums decreases in the order: *n*-butylammonium > *n*-propylammonium > ethylammonium > methylammonium. It suggests that hydrophobic interaction plays an important role in the extraction of the alkylammoniums.

Hydrophobic interaction is stronger with straight chains than with branched chains because branched chains would be more spherical in shape. Thus, the higher extractability of the straight chain alkylammoniums compared to the branched chain alkylammoniums as follows: *n*-butylammonium > *t*-butylammonium, *n*-propylammonium > isopropylammonium > trimethylammonium, ethylammonium > dimethylammonium, may result from the higher hydrophobic interaction of the less branched alkylammoniums rather than steric effect. It may also be due to a combination of both hydrophobic interaction and steric effect.

The interaction of protonated amines with crown ethers has been studied. It is different from that for metal cations; the binding of metal cations and crown ethers is mainly by ion-dipole interaction, whereas protonated amine complexes are stabilized by hydrogen bonding in addition to ion-dipole interaction. Timko *et al.*[152] estimated the relative contributions of hydrogen bonding and electrostatic interactions as 75% and 25% respectively for the complexation between NH_4^+ and $HOCH_2CH_2OH$. X-ray crystallography studies[153,154] have shown the complexation of RNH_3^+ with 18-crown-6 corresponds to the simplified structure in Figure 25. Therefore, for strong RNH_3^+ complexation the oxygens of the crown ether should align to allow a tripod hydrogen-bond arrangement.

Similarly, the formation of strong hydrogen bonding is required for strong interaction between alkylammonium group and foam. The number and length of the alkyl side chain (R) attaching to the nitrogen atom of the amine cation affect the polarity of the N–H bond which, in turn, determines the strength of hydrogen bonding with foam. R is electron donating and it tends to reduce the positive charge at the electron-deficient nitrogen. The reduced positive charge at the nitrogen lowers the N–H bond polarity resulting in the weaker hydrogen bonding with foam. The electron-releasing effect increases with increasing length of R. Therefore, hydrogen-bond strength decreases with increasing length of R. It is expected that the magnitude of hydrogen bonding with foam decreases in the order: methylammonium > ethylammonium > *n*-propylammonium > *n*-butylammonium. However, the results show the reverse sequence of extractability, i.e., *n*-butylammonium > *n*-propylammonium > ethylammonium > methylammonium. It is evident that hydrophobic interaction is more important than hydrogen bonding for these amines.

In addition to the length of R, the number of R groups attaching to the nitrogen of the amine group affects the magnitude of hydrogen bonding with foam. In general, the

Figure 25 Diagrammatic representation of the binding between RNH_3^+ and 18-crown-6^{153}.
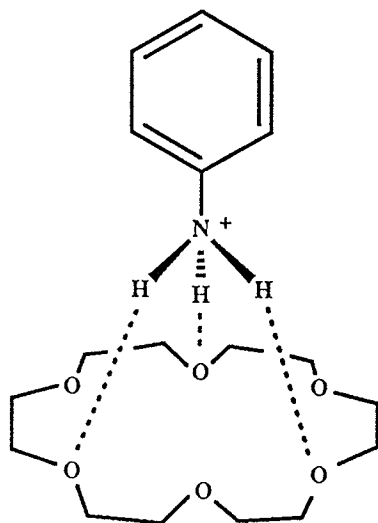
Dashed lines represent hydrogen bonds

inductive effect weakens steadily with increasing distance from the substituent; this can explain the low inductive effect of the longer alkyl group of the primary amines. However, the number of alkyl groups directly adjacent to the nitrogen of the amine group increases to two and three respectively for secondary and tertiary amines; this could have a higher inductive effect from the result of lowering the N–H bond polarity of secondary and tertiary amines. Moreover, the number of N–H groups able to form hydrogen bonds with foam reduces to two and one for protonated secondary and tertiary amines respectively. Thus, the low extraction values for dimethylammonium and trimethylammonium can be a result of weaker N–H polarity and lower number of N–H groups for hydrogen bonding.

It should be noted that NH_4^+ is more extractable than t-butylammonium, isopropylammonium, ethylammonium and methylammonium. Without hydrophobic interaction, the high extractability of NH_4^+ must be due to strong hydrogen bonding with foam. This effect can be because of the absence of electron-donating alkyl groups in NH_4^+. Furthermore, there are four N–H bonds capable of forming hydrogen bonds with foam for NH_4^+ and the polyether chains should be quite flexible in aqueous solution. It is possible that NH_4^+ can form four hydrogen bonds with foam as compared to three for protonated primary alkylamines. The additional hydrogen bond could result in a stronger interaction between NH_4^+ and foam. The ionic diameter of NH_4^+ (2.84 Å) is close to that of K^+ (2.66Å)[155] and the high extractability of K^+ has been explained by the cation chelation mechanism. By the same token, the NH_4^+ ion dimension matches that of the cavities in the foam and may also be explained by the cation chelation mechanism.

3.3.3 Extraction by Polyester Foam

From the preceding experiments, it was determined that 0.300 g polyester foam can extract 2.5×10^{-5} mol TPB$^-$ and 1.6×10^{-5} mol Na$^+$ from 100 mL of 1.0×10^{-3} M

NaTPB. The total amount of TPB$^-$ present in 100 mL of 1.0×10^{-4} M NaTPB solution is 1.0×10^{-5} mol. The capacity of the foam is not exceeded in using 0.300 g polyester foam to extract 100 mL of 1.0×10^{-4} M NaTPB. However, the extraction of TPB$^-$ was found to be rather low, about 50 %. The cation extraction would also be low if TPB$^-$ extraction is low, and therefore it would be difficult to compare the extractability of the cations if the extractions were low and very close to one another. For this reason, it was decided to increase the weight of foam to 0.800 g and to reduce the volume of solution extracted to 50 mL so that the extraction of TPB$^-$ increased to about 90 %.

3.3.3.1 Alkali Metal TPB

Solutions (50 mL) of 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 0.2×10^{-4} M alkali metal chloride were extracted with 0.800 g foam.

3.3.3.1.1. Time Dependence of the Extraction

Figure 26 shows the extraction of 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 0.2×10^{-4} M NaCl as a function of time. The same phenomenon of a decrease of Na$^+$ extraction after reaching a maximum was observed. Table 20 gives the ratio of Na$^+$ extracted / TPB$^-$ extracted versus time. It should be noted that the maximum ratio is only about 0.9 as opposed to about 1.0 for the extraction with polyether foam. The pH of the solution decreased to 8.4 from 9.0 which indicates that there is a residual amount of H$_3$O$^+$ present in the foam. Pivonkova and Kyrs[145] reported that the extraction of NaTPB from water into nitrobenzene is pH independent above 9.0 because of the competitive extraction of HTPB that occurs at lower pH. For this study, the extraction of HTPB may take place

Figure 26   Extraction of NaTPB with polyester foam as a function of time.

Time (h)
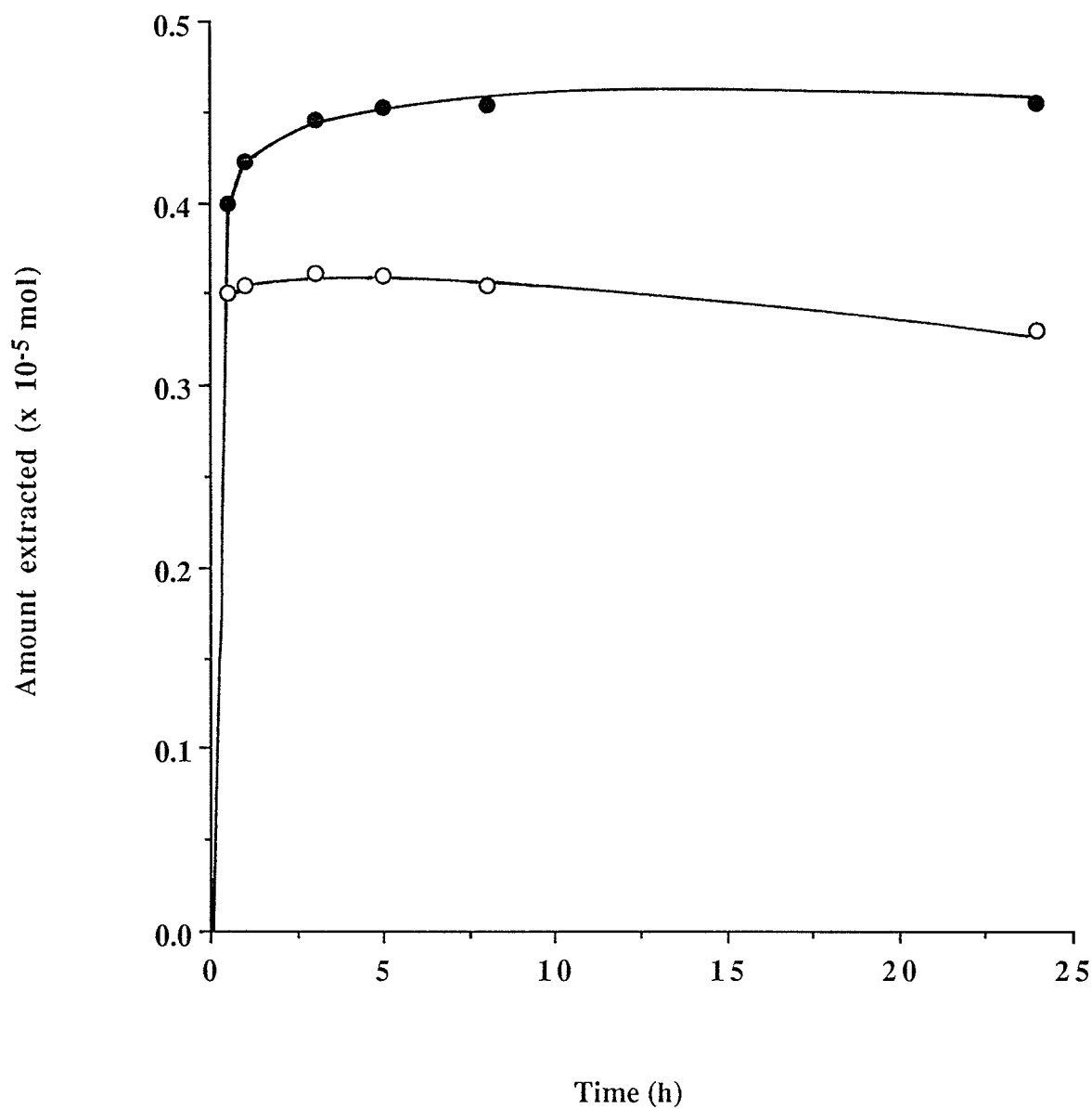
Conditions: 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 2.0×10^{-5} M NaCl, 0.800 g

polyester foam plug, 50 mL solution, initial pH = 9.0, final pH = 8.4, (●)

TPB$^-$ and (o) Na$^+$.

Table 20   Ratio of Na^+ extracted / TPB^- extracted for the extraction of NaTPB with polyester foam as a function of time

Time (h)	Na^+ extracted / TPB^- extracted
0.5	0.88
1.0	0.84
3.0	0.82
5.0	0.80
8.0	0.78
24.0	0.73

Conditions: 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 2.0×10^{-5} M NaCl, 0.800 g powdered polyester foam, 50 mL solution, initial pH = 9.0, final pH = 8.4.

because the final pH of 8.4 is lower than that suggested. Thus, the maximum ratio of Na^+ extracted / TPB^- extracted is only about 0.9. A more detailed discussion of the imbalance of the cation and the anion extracted will be given in Chapter 5.

The results for the extraction of 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 0.2×10^{-4} M alkali metal chloride (50 mL) with 0.800 g foam against time are shown in Figures 27, 28 and 29. Table 21 gives the ratio of total cations extracted / TPB^- extracted as a function of time. The maximum ratio of total cations extracted (Na^+ + alkali metal ion) / TPB^- extracted is again about 0.9. It should be noted that only Na^+ is displaced but not K^+, Rb^+ and Cs^+. It is possible that the interaction of Na^+ with the foam is relatively weaker than that of K^+, Rb^+ and Cs^+. Therefore, only Na^+ is displaced. A more detailed discussion of the displacement of the cations will be given in Section 4.3.6.

3.3.3.1.2 Selectivity for Alkali Metal Ions

From Table 21, the maximum ratio of total cations extracted / TPB^- extracted is about 0.9 indicating displacement of the cations. However, only Na^+ is displaced (Figures 27, 28 and 29). The amount of K^+, Rb^+ and Cs^+ extracted levels off after 1 h of extraction. Figures 30 and 31 show the % extraction of the cation and the anion as a function of time for the extraction of potassium, rubidium and cesium TPBs. Table 22 gives the maximum extraction and distribution coefficient of the cations. The extractability sequence of the cations is : $K^+ \approx Rb^+ \approx Cs^+$. This order is different from that obtained from polyether foam of $K^+ \approx Rb^+ > Cs^+$. As polyester foam does not normally adopt a helical structure, there cannot be any hole-size / cation-diameter relationship. The relative strength of the interaction between K^+ and polyester foam compared with Rb^+ and Cs^+ is

Figure 27   Extraction of NaTPB and KCl with polyester foam as a function of time.

Time (h)
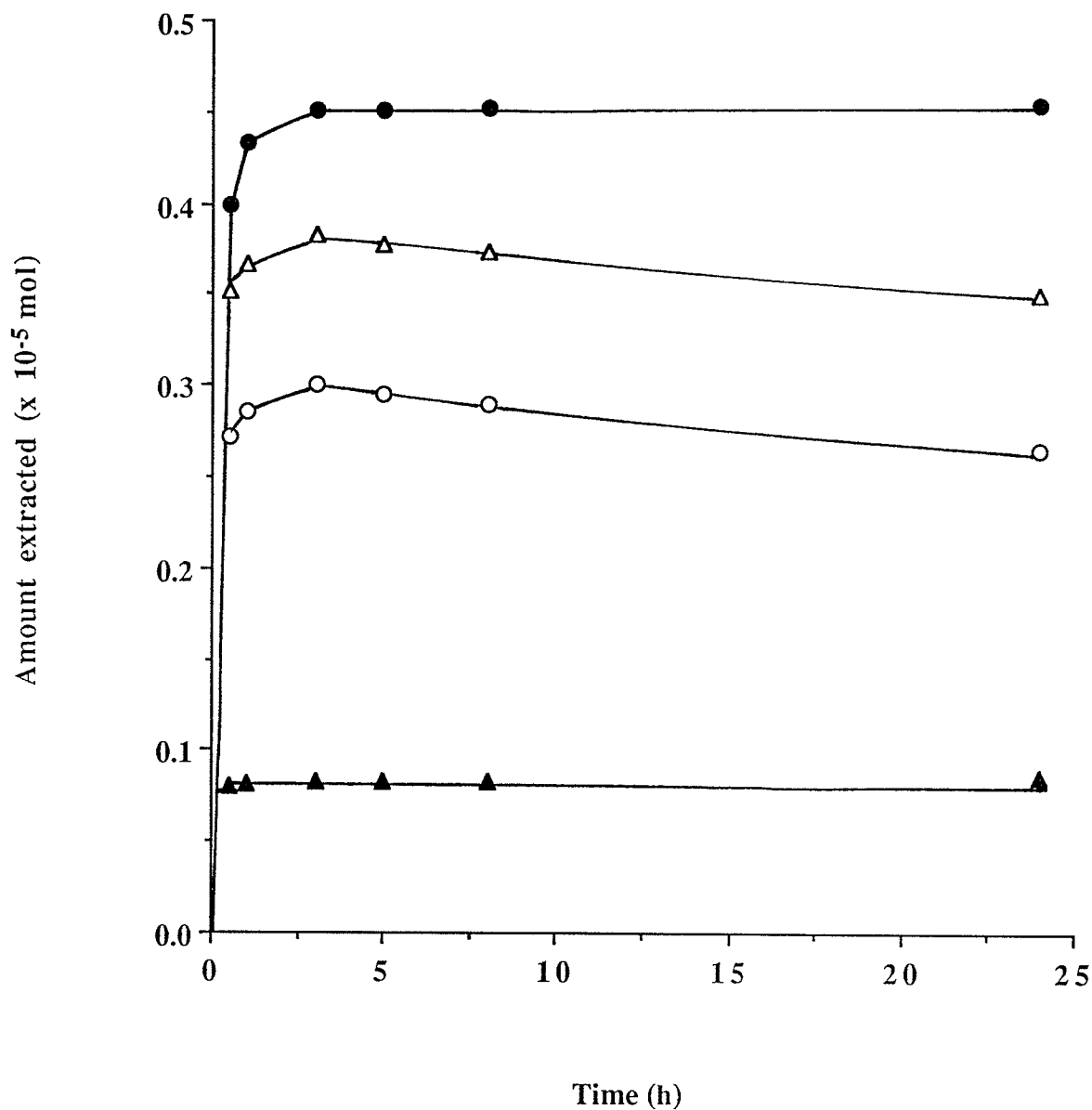
Conditions: $1.0 \times 10^{-4}\ M$ NaTPB + $1.0 \times 10^{-4}\ M$ NaOH + $2.0 \times 10^{-5}\ M$ KCl, 0.800 g

powdered polyester foam, 50 mL solution, initial pH = 9.0, final pH = 8.4,

(●) TPB⁻, (o) Na⁺, (▲) K⁺ and (Δ) total cations (Na⁺ + K⁺).

Figure 28   Extraction of NaTPB and RbCl with polyester foam as a function of time.
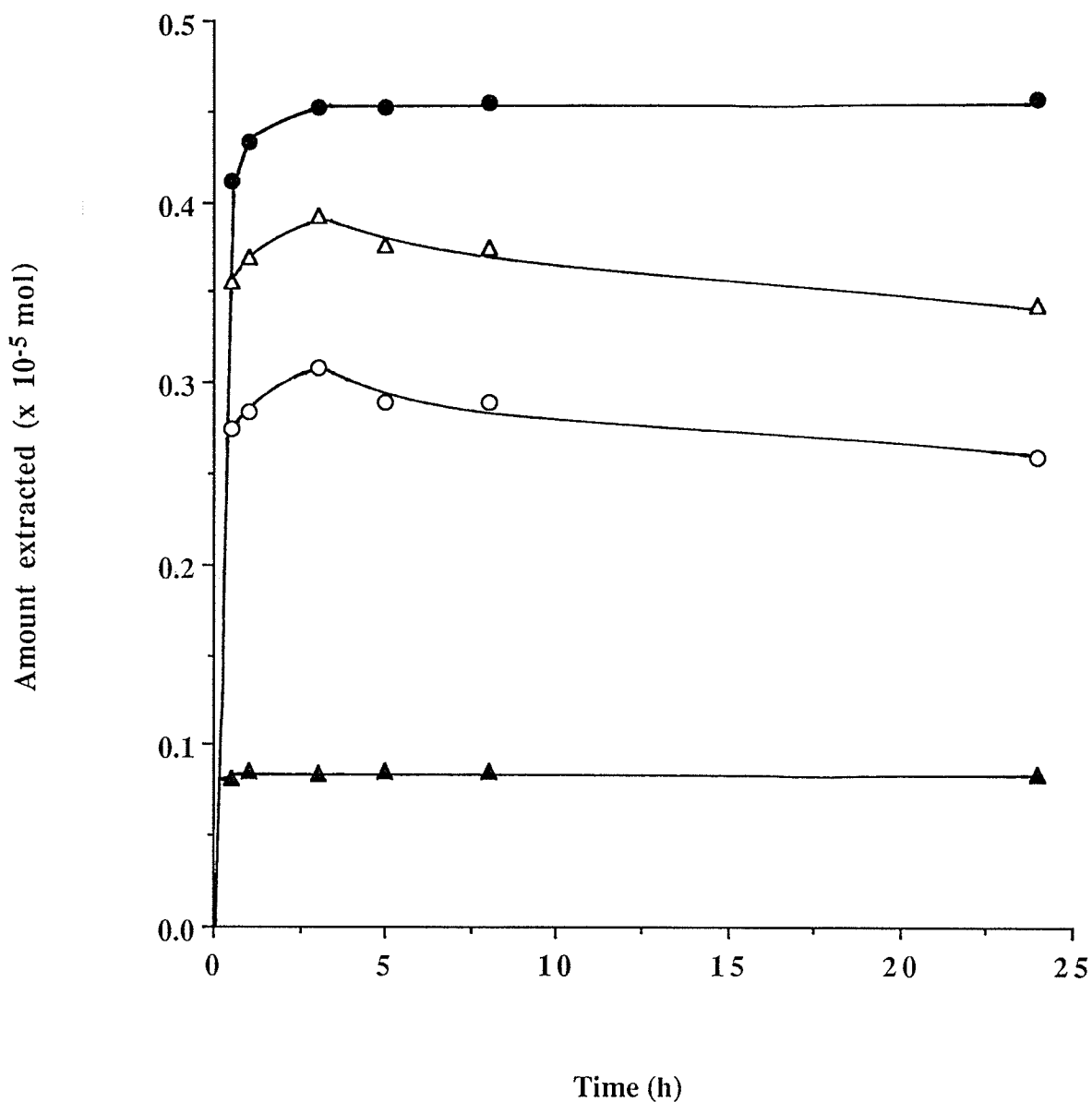
Conditions: 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 2.0×10^{-5} M RbCl, 0.800 g

powdered polyester foam, 50 mL solution, initial pH = 9.0, final pH = 8.4,

(●) TPB^-, (o) Na^+, (▲) Rb^+ and (Δ) total cations ($Na^+ + Rb^+$).

Figure 29   Extraction of NaTPB and CsCl with polyester foam as a function of time.
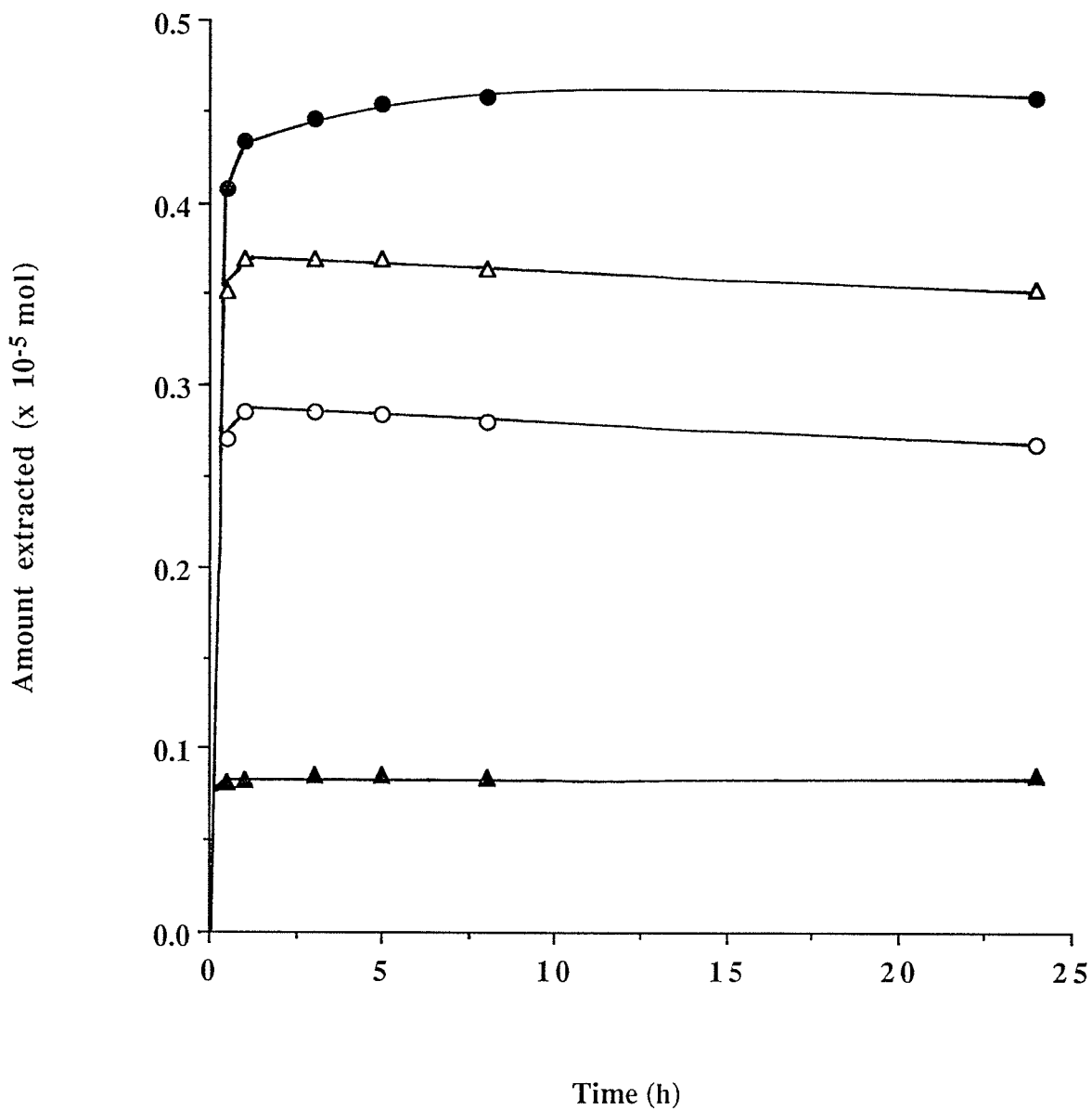
Conditions: $1.0 \times 10^{-4}\ M$ NaTPB + $1.0 \times 10^{-4}\ M$ NaOH + $2.0 \times 10^{-5}\ M$ CsCl, 0.800 g

powdered polyester foam, 50 mL solution, initial pH = 9.0, final pH = 8.4,

(●) TPB⁻, (o) Na⁺, (▲) Cs⁺ and (Δ) total cations (Na⁺ + Cs⁺).

Table 21 Ratio of total cations extracted / TPB$^-$ extracted for the extraction of NaTPB and alkali metal chlorides with polyester foam as a function of time

Time (h)	$(Na^+ + Na^+)/$ TPB$^-$	$(Na^+ + K^+)/$ TPB$^-$	$(Na^+ + Rb^+)/$ TPB$^-$	$(Na^+ + Cs^+)/$ TPB$^-$
0.5	0.88	0.88	0.86	0.86
1.0	0.84	0.85	0.85	0.85
3.0	0.82	0.845	0.87	0.83
5.0	0.80	0.84	0.83	0.81
8.0	0.78	0.82	0.82	0.80
24.0	0.73	0.77	0.75	0.77

Conditions: 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 2.0×10^{-5} M alkali metal chloride, 0.800 g powdered polyester foam, 50 mL solution, initial pH = 9.0, final pH = 8.4.

Figure 30   Plot of % cation extraction as a function of time for the extraction of NaTPB

and alkali metal chlorides with polyester foam.
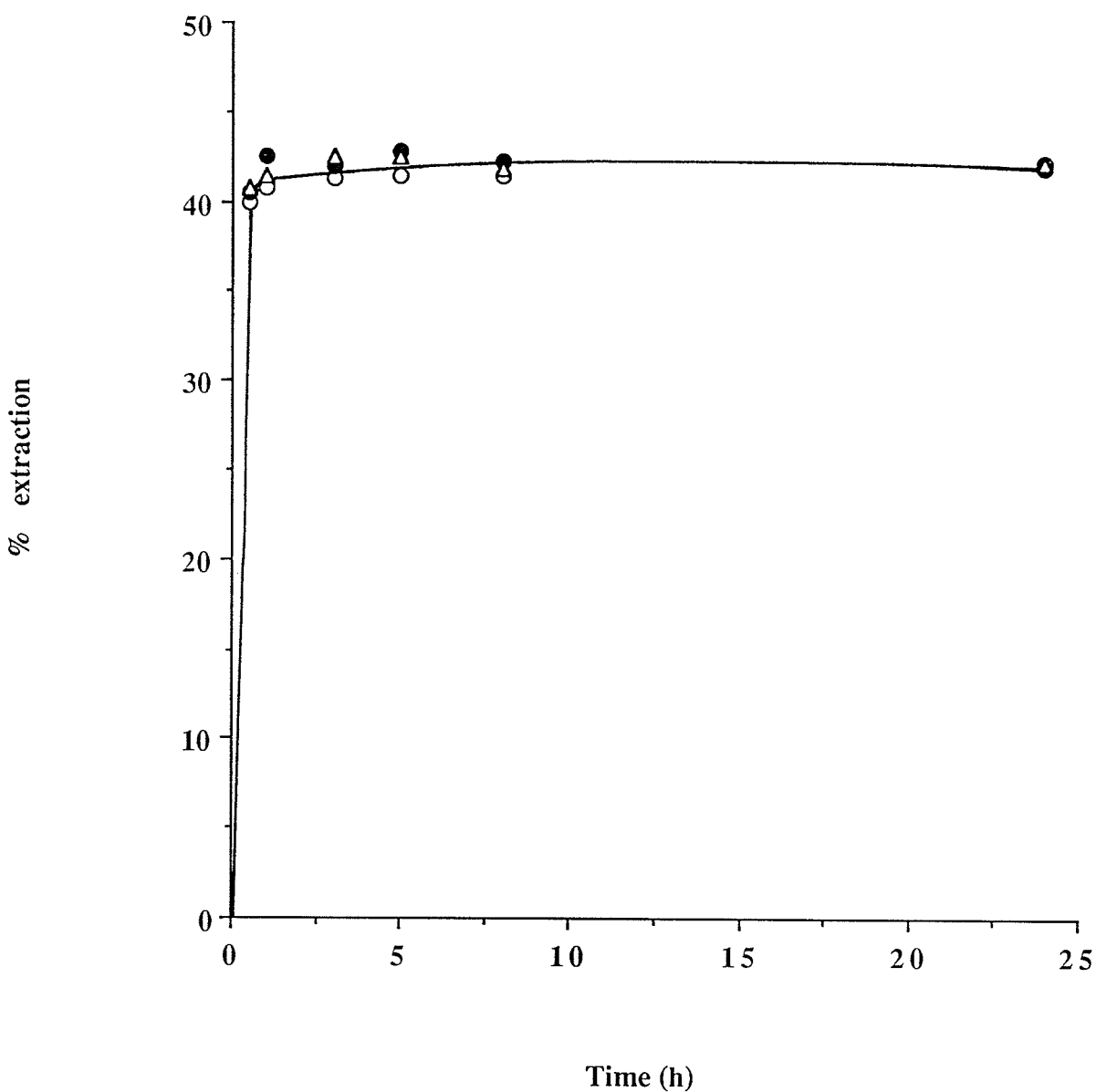
Conditions: $1.0 \times 10^{-4}\ M$ NaTPB + $1.0 \times 10^{-4}\ M$ NaOH + $2.0 \times 10^{-5}\ M$ alkali metal

chloride, 0.800 g powdered polyester foam, 50 mL solution, initial pH =

9.0, final pH = 8.4, (o) K^+, (●) Rb^+ and (Δ) Cs^+.

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Figure 31   Plot of % TPB⁻ extraction as a function of time for the extraction of NaTPB

and alkali metal chlorides with polyester foam.

Time (h)
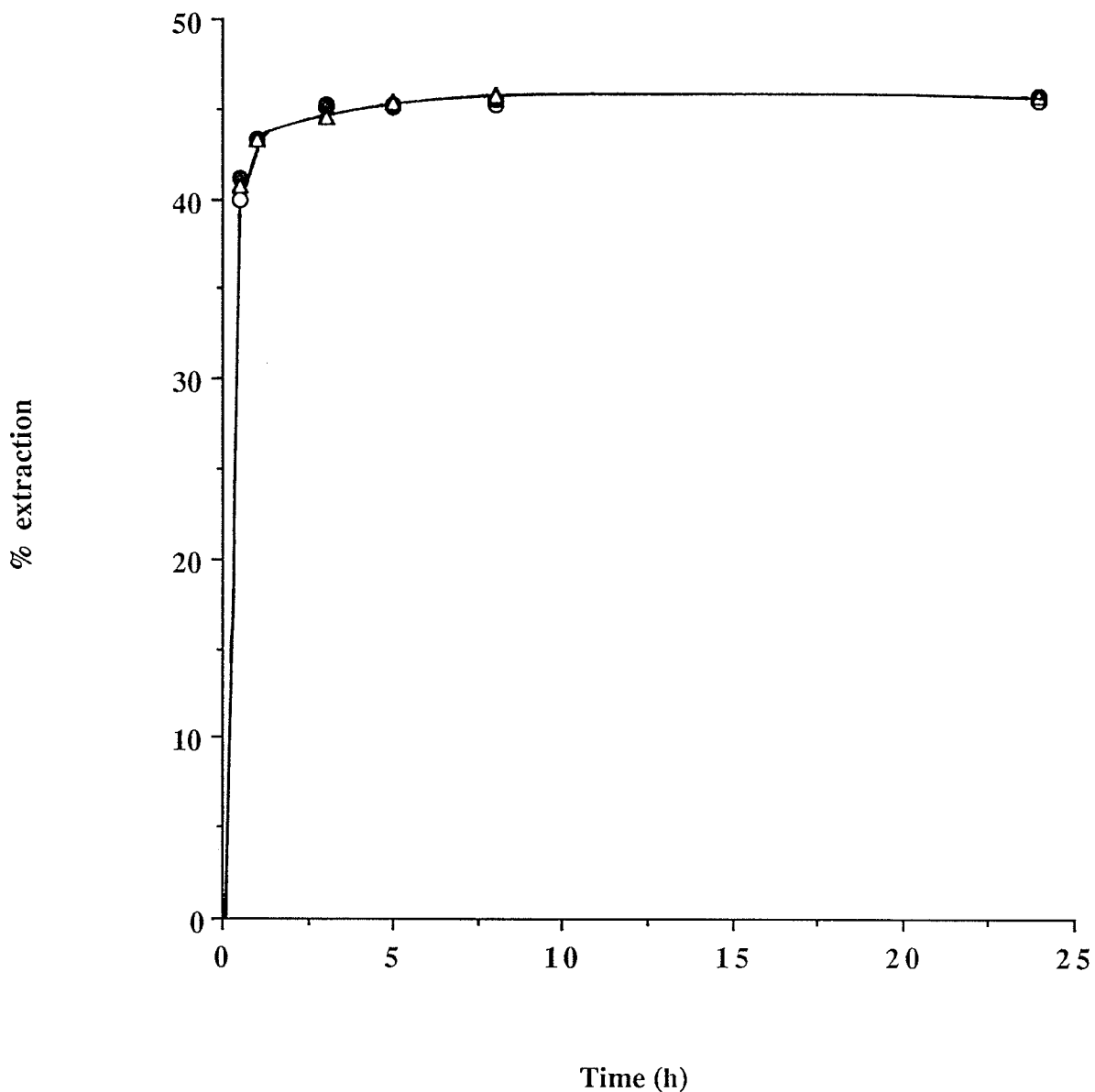
Conditions: 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 2.0×10^{-5} M alkali metal

chloride, 0.800 g powdered polyester foam, 50 mL solution, initial pH =

9.0, final pH = 8.4, (o) TPB⁻ extraction for solution with KCl, (●) TPB⁻

extraction for solution with RbCl and (Δ) TPB⁻ extraction for solution with

CsCl.

Table 22   Maximum % extraction and distribution coefficient of the cations for the extraction of NaTPB and alkali metal chlorides with polyester foam

Cation	% extracted	Distribution coefficient (L/kg)
K^+	42.3	335
Rb^+	42.0	322
Cs^+	42.3	339

Conditions: 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 2.0×10^{-5} M alkali metal chloride, 0.800 g powdered polyester foam, 50 mL solution, initial pH = 9.0, final pH = 8.4, 24 h extraction time.

not as high as in the case for polyether foam. Thus, the extractability of K^+, Rb^+ and Cs^+ is about the same for polyester foam. These results are consistent with the cation chelation mechanism.

3.3.3.2 Alkylammonium TPB

The concentration of alkylammonium was increased to 1.0×10^{-4} M to keep the concentration of the alkylammonium cation and TPB^- the same. Solutions (50 mL) containing 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 1.0×10^{-4} M alkylammonium chloride were extracted with 0.800 g polyester foam.

3.3.3.2.1. Time Dependence of the Extraction

Figure 32 shows the extraction of 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 1.0×10^{-4} M t-butylammonium chloride as a function of time. It resembles the extraction of NaTPB in the presence of other alkali metal ions. Only Na^+ is displaced. This could be due to the relatively weak interaction of Na^+ with polyester foam compared with t-butylammonium. The ratio of total cations (Na^+ + alkylammonium ion) extracted / TPB^- extracted against time is given in Table 23. The maximum ratio of total cations extracted / TPB^- extracted is also about 0.9 and the pH of the solution decreased to 8.4. The imbalance of the cation and the anion extracted may be attributed to residual H_3O^+ on the foam and the competitive extraction of HTPB. The extraction of other alkylammoniums as a function of time was also studied. Similar Na^+ displacement behavior was observed except for the alkylammonium ions.

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Figure 32   Extraction of NaTPB and t-butylammonium with polyester foam as a function of time.
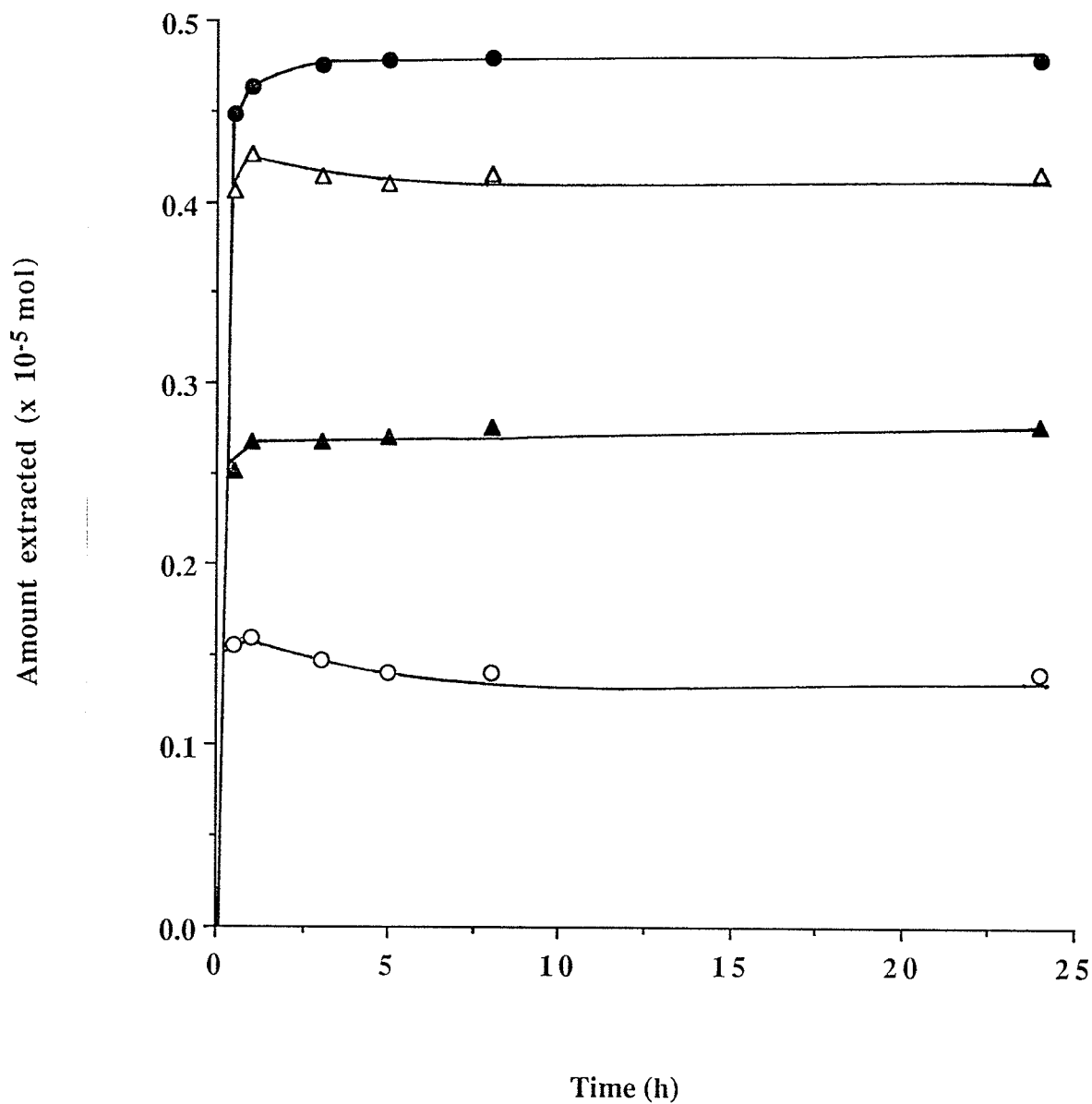
Conditions: 1.0 x 10^{-4} M NaTPB + 1.0 x 10^{-4} M NaOH + 1.0 x 10^{-4} M t-butylammonium, 0.800 g powdered polyester foam, 50 mL solution, initial pH = 9.0, final pH = 8.4, (●) TPB⁻, (o) Na⁺, (▲) t-butylammonium and (△) total cations (Na⁺ + t-butylammonium).

Table 23   Ratio of total cations extracted / TPB⁻ extracted for the extraction of NaTPB, and alkylammonium, potassium and ammonium chlorides with polyester foam as a function of time

TPB salt	Time (h)					
	0.5	1.0	3.0	5.0	8.0	24.0
n-butylammonium	0.89	0.88	0.86	0.87	0.86	0.88
n-propylammonium	0.88	0.88	0.87	0.85	0.85	0.86
potassium	0.89	0.90	0.88	0.88	0.86	0.85
t-butylammonium	0.90	0.92	0.87	0.86	0.87	0.87
isopropylammonium	0.88	0.87	0.85	0.84	0.85	0.86
ammonium	0.89	0.88	0.88	0.88	0.87	0.85
ethylammonium	0.90	0.91	0.84	0.88	0.86	0.89
methylammonium	0.90	0.91	0.91	0.88	0.88	0.89
dimethylammonium	0.89	0.87	0.88	0.87	0.85	0.87
trimethylammonium	0.90	0.90	0.89	0.88	0.87	0.81

Conditions: $1.0 \times 10^{-4}\ M$ NaTPB + $1.0 \times 10^{-4}\ M$ NaOH + $1.0 \times 10^{-4}\ M$ alkylammonium, potassium or ammonium chloride, 0.800 g powdered polyester foam, 50 mL solution, initial pH = 9.0, final pH = 8.4.

3.3.3.2.2. Selectivity for Alkylammonium Ions

Tables 24 and 25 give the maximum extraction and distribution coefficient (D) of the cations. Table 26 compares the maximum D of the alkylammoniums for the extraction with polyether and polyester foams. The distribution coefficients are lower for polyester foam than for polyether foam. Ester group is more polar than ether group and it is expected that protonated alkylamines should interact more strongly with the ester group than with the ether group. However, because the ether group is more easily protonated than the ester group it is more strongly hydrogen bonded. Therefore, stronger hydrogen bonding can account for the higher extraction for polyether foam.

Polyurethane foam is prepared from polyols of polyether or polyester joined together by urethane and urea links. Polyether foam is prepared from poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO) or a mixture of the two. Polyester foam is generally made of poly(ethylene adipate) (PEA). Table 27 gives the structure and typical number of monomer units in prepolymer chain for the different types of polyols. The oxygens in polyester foam are more widely spaced than in polyether foam. These more separated oxygens may not be able to provide as ideal a binding arrangement for hydrogen bonding with the protonated amine group. The number of oxygens to coordinate with alkali metal cations may also be lowered. These effects could result in the lower complexing strength of polyester foam.

The extractability sequence of the alkylammoniums for polyester foam is similar to that for polyether foam. It can be explained by the steric effect, hydrophobic interaction and the inductive effect as discussed in Section 3.3.2.2.2. However, the extractability sequence changes from NH_4^+ > t-butylammonium > isopropylammonium > ethylammonium > methylammonium for polyether foam to isopropylammonium ≈ t-butylammonium > NH_4^+ > ethylammonium > methylammonium for polyester foam. Since

Table 24   Maximum % extraction and distribution coefficient of the cations for the extraction of NaTPB, and alkylammonium, potassium and ammonium chlorides with polyester foam

Cation	% extraction	Distribution coefficient (L/kg)
n-butylammonium	69.8	144
n-propylammonium	58.9	89.6
potassium	58.9	89.2
t-butylammonium	55.3	77.6
isopropylammonium	54.9	76.1
ammonium	50.0	71.3
ethylammonium	51.9	67.9
methylammonium	46.7	54.9
dimethylammonium	44.2	50.0
trimethylammonium	28.4	24.8

Conditions: 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 1.0×10^{-4} M alkylammonium, potassium or ammonium chloride, 0.800 g powdered polyester foam, 50 mL solution, initial pH = 9.0, final pH = 8.4, 24 h extraction time.

Table 25   Maximum distribution coefficients of the cations and TPB⁻ for the extraction of NaTPB, and alkylammonium, potassium and ammonium chlorides with polyester foam

TPB salt	Distribution coefficient (L/kg)		
	Cation	Na^+	TPB^-
n-butylammonium	144	5.0	1770
n-propylammonium	89.6	8.4	1380
potassium	89.2	8.0	1440
t-butylammonium	77.6	10.2	1460
isopropylammonium	76.1	9.9	1350
ammonium	71.3	11.2	1060
ethylammonium	67.9	12.4	1230
methylammonium	54.9	14.5	1060
dimethylammonium	50.0	14.8	1130
trimethylammonium	24.8	19.5	856

Conditions: 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 1.0×10^{-4} M alkylammonium, potassium or ammonium chloride, 0.800 g powdered polyester foam, 50 mL solution, initial pH = 9.0, final pH = 8.4, 24 h extraction time.

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Table 26   Comparison of the maximium distribution coefficients of the cations for the extraction of NaTPB, and alkylammonium, potassium and ammonium chlorides with polyether and polyester foams

	Distribution coefficient (L/kg)	
Cation	Polyester	Polyether
n-butylammonium	144	481
n-propylammonium	89.6	369
potassium	89.2	310
t-butylammonium	77.6	235
isopropylammonium	76.1	235
ammonium	71.3	294
ethylammonium	67.9	232
methylammonium	54.9	176
dimethylammonium	50.0	104
trimethylammonium	24.8	61

Conditions: $1.0 \times 10^{-4}\ M$ NaTPB + $1.0 \times 10^{-4}\ M$ NaOH + $1.0 \times 10^{-4}\ M$ alkylammonium, potassium or ammonium chloride,

For extraction with powdered polyether foam: 0.300 g foam, 100 mL solution, pH = 9.0.

For extraction with powdered polyester foam: 0.800 g foam, 50 mL solution, initial pH = 9.0, final pH = 8.4.

Table 27   Comparison of polyols of different types[102]

	Poly (ethylene-oxide) (PEO)	Poly (propylene-oxide) (PPO)	Poly (ethylene adipate) (PEA)
Structure	$-(-CH_2CH_2O-)_n-$	$\overset{CH_3}{-(-\overset{\shortmid}{C}HCH_2O-)_n-}$	$-(-CH_2CH_2O-\overset{O}{\overset{\shortparallel}{C}}-(-CH_2)_4-\overset{O}{\overset{\shortparallel}{C}}-O-)_n-$
Typical number of mononer units in prepolymer chain	11–45	9–35	6–17
Crystalline state	helical	planar zigzag	planar zigzag

hydrogen bonding in polyester foam is weaker than in polyether foam, the hydrophobic interaction of isopropylammonium and t-butylammonium with the foam may increase their extractability more than that of NH_4^+. The chains of polyester foam cannot readily assume a planar zigzag structure and may allow the formation of only three hydrogen bonds with NH_4^+ rather than four for polyether foam. These effects could cause the decrease of extractability of NH_4^+. However, the strength of hydrogen bonding with polyester foam must still be an important factor because when the hydrophobic interaction is relatively weak for lower alkylammoniums, NH_4^+ is still more extractable than ethylammonium and methylammonium.

3.4. Conclusion

This study demonstrates that both polyether and polyester foams are able to extract alkali metal and alkylammonium cations in the presence of bulky TPB^- anions. There is a characteristic decrease of the cation extracted on foam after reaching a maximum with extraction time. Polyether foam is a better extractor than polyester foam for alkali metal and various alkylammonium ions. The orders of extractability of alkali metal ions are: $K^+ \approx Rb^+ > Cs^+$ for polyether foam and $K^+ \approx Rb^+ \approx Cs^+$ for polyester foam. These results suggest that the cation chelation mechanism may take place in polyether foam but not in polyester foam. The extractions of the alkylammoniums show that a combination of steric effect, hydrophobic interaction and inductive effect determines the relative extractability of these alkylammoniums.

CHAPTER 4

EXTRACTION OF ALKALI METAL

AND ALKYLAMMONIUM DIPICRYLAMINATES

4.1 Introduction

In addition to tetraphenylborate, dipicrylaminate (DPA) has been widely employed as an ion-pairing agent for the extraction of alkali metals and organic bases. Schill and Danielsson[156] reported that the complex of dipicrylaminate with quaternary ammonium can be extracted from aqueous solution with organic solvents such as chloroform or methylene chloride. The complexes have high molecular extinctions and hence very small amounts of quaternary ammonium compounds can be determined by direct photometric measurements. They noted that the extraction has to be carried out at high pH to prevent the extraction of the free acid hexanitrodiphenylamine (HDPA).

Iwachido and Toei[157] studied the extraction of potassium ion in the form of potassium dipicrylaminate from aqueous solution into nitrobenzene. The potassium ion was stripped from nitrobenzene with a hydrochloric acid solution and determined gravimetrically with sodium tetraphenylborate.

Kyrs and Kadlecova[158] described the exchange of cesium(I) for calcium(II) in a nitrobenzene solution of calcium dipicrylaminate with a slightly alkaline aqueous cesium(I) solution (Equation 31).

$$2Cs^+_{(aq)} + Ca^{2+}_{(org)} \rightleftharpoons 2Cs^+_{(org)} + Ca^{2+}_{(aq)} \tag{31}$$
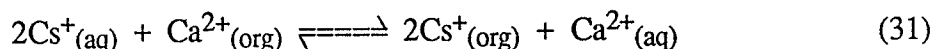
This extraction can be used for the determination of cesium labelled with ^{137}Cs. Kyrs and Selucky[159] reported two indirect methods determining cesium using the same extraction

system. Instead of using radioactively-labelled cesium, cesium concentration was determined indirectly by adjusting the solution to pH 8–11 with lithium hydroxide and the calcium content in the aqueous phase was determined with EDTA. Alternatively, the calcium was determined in the extract after back-extraction with dilute mineral acid and the cesium concentration calculated. They said that these methods are less time-consuming than the cation-exchange method.

Motomizu et al.[160] determined the association constants of the ion-pairs of dipicrylamines with alkali metal cations in nitrobenzene by conductivity measurements and in water by the solvent extraction method. The association constant in nitrobenzene decreases in the order: Li > Na > K > Rb > Cs. However, in nitrobenzene saturated with water, the constants vary from 2 to 4. In water the association constants range from 10 to 400 with the reverse sequence: Li < Na < K < Rb < Cs. It was concluded that in aqueous solution the association depends mainly on the hydrated radius of the alkali metal ion, and the ion-pairs are formed between dipicrylaminate and the hydrated alkali metal cation. The extractability of the alkali metal increases with an increase in the values of the association constant of the ion-pair in nitrobenzene. The same authors[161] derived an equation for the extraction separation of alkali metals with dipicrylaminate which is in good agreement with the experimental data for the extraction of sodium and potassium with dipicrylaminate. Sano et al.[162] determined the association constants of the ion-pairs between dipicrylaminate and alkali metal cations based on the difference in the adsorbability of the anions and of the ion-pairs on a filter paper. The results are in fairly good agreement with those obtained by the solvent extraction method[160].

Iwachido[163] studied various aromatic compounds with an acidic group, such as –OH, –SH, –COOH, –SO$_3$H, >NH, >CH and $\equiv$B$^-$ as extracting agents for potassium. It was found that the highest extraction of potassium is attained with the acids of amine

derivatives and tetraphenylborate. Bulky and electron-attracting substituents, such as nitro or halogen group, are effective in enhancing the extractability.

Rais *et al.*[164] investigated the extraction of univalent metal (M) dipicrylaminates into nitrobenzene. The distribution is shown to be controlled by the following equilibria:

$$M^+ + DPA^- \rightleftharpoons M^+_{(org)} + DPA^-_{(org)} \qquad (32)$$

$$M^+ + DPA^- \rightleftharpoons MDPA_{(org)} \qquad (33)$$

The results can be explained by the mechanism in which MDPA is completely dissociated in the aqueous phase and partially dissociated in nitrobenzene.

Iwachido[165] examined the extraction of potassium salts with dipicrylaminate, *N*-(2,4,6-trinitrobenzo)-2,4-dinitro-1-naphthylamine, and 1,3,7,9-tetranitrophenothiazine-5-oxide in aqueous solution by nitrobenzene. The dissociation constants in the aqueous phase and the distribution constants of the acids were estimated from the analysis of the curve obtained by plotting the distribution ratios of the metal or the acids against pH. The results show that the salts are mainly in the dissociated form in both phases.

Jawaid and Ingman[166] investigated the extraction of ion-pairs formed by the Na^+, K^+ and Ca^{2+} complexes of dicyclohexyl-18-crown-6 and β- and γ-dinitrophenol, picric acid and dipicrylamine in aqueous solution by dichloromethane. The extraction increases in the order of $Ca^{2+} < Na^+ < K^+$. The bulkier ligands are less hydrophilic and are more extractable. The extraction sequence follows: dipicrylamine > picric acid > dinitrophenol. However, the selectivity for cations decreases with increasing hydrophobicity of the anions. For example, the separation factor for sodium and potassium is over 100 for picric acid but is about 2 for dipicrylamine.

Dipicrylaminate salts are highly extractable by organic solvents, and therefore it is likely that they are extracted by polyurethane foam. Futhermore, unlike tetraphenylborate,

the free dipicrylamine acid is stable and does not decompose. The alkali metal dipicrylamine salts can be prepared by neutralizing the free dipicrylamine acid with the corresponding alkali metal hydroxide. The extraction of these salts alone can be studied as opposed to the tetraphenylborate system in which sodium ions are always present because tetraphenylborate has to be added as sodium tetraphenylborate. Thus the extractions of alkali metal and various alkylammonium dipicrylaminates were conducted in this study.

4.2 Experimental

4.2.1 Apparatus and Reagents

The following apparatus were used: a Hewlett-Packard Model 8452A diode-array spectrophotometer, a Fisher Accumet Model 520 pH meter, a Ross combination pH electrode, a Waters Ion Chromatograph IIC-1, a Waters WISP auto-sampler, a Waters 740 data module, a Waters 590 solvent pump, a Waters 430 conductivity detector, a Barnstead Nanopure II water purification system, a Burell wrist-action shaker, and Micron Sep 0.22 μm cellulose acetate membrane filters.

All the chemicals were of reagent grade.

4.2.2 Foam

Polyether type polyurethane foam (#1338M) was obtained from G. N. Jackson Ltd. (Winnipeg, Manitoba). Polyester type foam (DiSPo) was obtained from Canlab (Winnipeg, Manitoba). 100% polypropylene oxide polyether foam (27CGS-44-2A) was obtained from Union Carbide.

4.2.3   General Procedure

4.2.3.1 Foam Washing

Foam plugs of approximately 0.4 g each were cut from a polyurethane sheet. These plugs were soaked in 1 M hydrochloric acid for 24 h with occasional squeezing to remove any possible inorganic contaminants and washed with water until acid free. They were then extracted with acetone in a Soxhlet apparatus for 6 h to remove the organic contaminants and finally air dried in a 60°C oven.

4.2.3.2 Preparation of Powdered Foam

Cleaned foam plugs were frozen in liquid nitrogen and ground in a stainless-steel container on a Waring™ blender.

4.2.3.3 Preparation of Dipicrylaminate Salts

Dipicrylamine was purified by the following procedure[156]. 20 g dipicrylamine (50 % water) was dissolved in 2 L sodium borate buffer of pH 9. The solution was extracted with 400 mL CHCl$_3$ five times. The technique removed the pentanitrodiphenylamine impurity. The aqueous phase was acidified with HCl to precipitate dipicrylamine which was filtered off and washed several times with water.

Dipicrylaminate salts of potassium, rubidium and cesium were prepared by dissolving dipicrylamine in an aqueous solution containing a slight excess of the corresponding alkali metal hydroxide with the pH about 11 for the resulting solutions. The precipitates were filtered and recrystallized twice from ethanol. The salts were dried at

60°C. Sodium and lithium dipicrylaminates are so soluble in water that no precipitate was formed after neutralization. The aqueous solution was extracted with equal volumes of nitrobenzene for three and six times for sodium and lithium salts respectively. The salts were obtained by slowly evaporating the nitrobenzene solvent. All the alkali metal dipicrylaminates were stored in a vacuum desiccator.

Attempts were made to prepare the alkylammonium dipicrylaminate salts. However, the n-butylammonium and isobutylammonium salts produced were viscous liquids which could not be separated from the aqueous solution.

4.2.3.4 Preparation of Sample Solutions

Stock solutions of 0.2 M various alkylammonium hydrochlorides, 0.1 M NaOH and 0.1 M alkali metal hydroxides were prepared. Sample solutions were freshly prepared by weighing in the necessary quantity of alkali metal dipicrylaminate solid and by pipetting the appropriate aliquots of stock solutions.

4.2.3.5 Extraction Procedure

The sample solution (100 mL) and powdered foam (0.050 ± 0.005 g) for polyether foam and (0.100 ± 0.005 g) for polyester foam were placed in gas-tight plastic vials and were shaken by a mechanical wrist-action shaker.

4.2.3.6 Analytical Methods

Dipicrylaminate was analysed by UV-visible spectrophotometry. The highest UV absorbance (λ_{max}) at 426 nm was used for absorbance measurements in a 1 cm cell.

Atomic absorption spectrometry was used for the analysis of alkali metals. The instrument settings used from the Varian Handbook[167] are listed in Table 28.

The concentration of alkylammoniums was determined by ion chromatography using a Waters cation guard column and a 4.6 mm (ID) x 5 cm Waters IC-PAK™ plastic cation column. 2 mM HNO_3 was used as eluent at a flow rate of 1.2 mL/min. 150 μL of the sample solution were injected for the analysis of the cations after filtering through a 0.22 μm cellulose acetate membrane filter.

4.2.3.7 Calculations

It is the same as in Section 3.2.3.6.

4.3 Results and Discussion

4.3.1 Preliminary Results

To study whether DPA salts can be extracted by foam, solutions (100 mL) containing 0.5 x 10^{-4} M KDPA + 0.5 x 10^{-4} M KOH at pH 9 were extracted with 0.025 g powdered polyether foam. The solution was stirred with a magnetic stirrer in a gas-tight vial and was extracted for 1 h. 0.265 x 10^{-5} mol (53%) DPA$^-$ was extracted. The extraction is rather low and it was expected that the extraction of lithium and sodium DPAs would be even lower. It was decided to increase the foam weight to 0.050 g to extract 100 mL of 0.5 x 10^{-4} M KDPA + 0.5 x 10^{-4} M KOH solution in which the amount of DPA$^-$ present is 0.5 x 10^{-5} mol. Increasing the foam weight to 0.05 g ensures that the capacity of the foam for DPA$^-$ is not exceeded and the extraction of DPA$^-$ increases to about 80%.

Table 28   Instrument settings of the atomic absorption spectrometer for the analysis of alkali metals[167]

Operating conditions	Instrument Settings				
	Li	Na	K	Rb	Cs
Lamp current (mA)	5	5	5	20	20
Wavelength (nm)	670.8	589.0	769.9	780.0	852.1
Spectral band pass (nm)	1.0	0.5	1.0	0.2	1.0
Flame type	air-acetylene oxidizing	air-acetylene oxidizing	air-acetylene oxidizing	air-acetylene oxidizing	air-acetylene oxidizing
Modifier	2000 ppm K	2000 ppm K	1000 ppm Cs	2000 ppm K	none

The extraction of a solution (100 mL) containing 0.5×10^{-4} M CsDPA + 0.5 x 10^{-4} M CsOH with 0.200 g powdered polyester foam was carried out. 0.44×10^{-5} mol (88%) DPA$^-$ was extracted. To make sure that the capacity of the foam was not exceeded, 0.100 g polyester foam was used to extract 100 mL solution containing 0.2×10^{-4} M alkali metal DPA (0.2×10^{-5} mol DPA$^-$ in solution) for further experiments.

To compare the extractability of DPA$^-$ and TPB$^-$, extractions of 100 mL solutions containing 0.5×10^{-4} M NaDPA + 0.5×10^{-4} M NaOH with 0.050 g powdered polyether foam and 0.2×10^{-4} M NaDPA + 0.2×10^{-4} M NaOH with 0.100 g powdered polyester foam were conducted. The results are given in Table 29. The equilibrium between an aqueous solution containing the monovalent metal M$^+$, the anion A$^-$ and the foam can be written as

$$M^+ + A^- \rightleftharpoons MA_f \tag{34}$$

$$K_{ex} = [MA]_f / [M^+][A^-] \tag{35}$$

where MA denotes the ion-pair. The overall extraction equilibrium can be described by the following constituent equilibria:

(i) ion-pair formation in aqueous solution

$$M^+ + A^- \rightleftharpoons MA \tag{36}$$

$$K_1 = [MA] / [M^+][A^-] \tag{37}$$

(ii) extraction of the ion-pair into the foam

$$MA \rightleftharpoons MA_f \tag{38}$$

$$K_{1ex} = [MA]_f / [MA] \tag{39}$$

Table 29   Comparison of the extractability of TPB$^-$ and DPA$^-$ for the extraction with polyether and polyester foam

	Distribution coefficient (L/kg)	
Anion	Polyether	Polyester
TPB$^-$	3030	631
DPA$^-$	2960	1200

Conditions: TPB$^-$, polyether foam:

      1.0 x 10^{-4} M NaTPB + 1.0 x 10^{-4} M NaOH + 2.0 x 10^{-5} M NaCl, 0.300 g powdered polyether foam, 100 mL solution, pH = 9.0, 24 h extraction time.

      TPB$^-$, polyester foam:

      1.0 x 10^{-4} M NaTPB + 1.0 x 10^{-4} M NaOH + 2.0 x 10^{-5} M NaCl, 0.800 g powdered polyester foam, 50 mL solution, initial pH = 9.0, final pH = 8.4, 24 h extraction time.

      DPA$^-$, polyether foam:

      0.5 x 10^{-4} M NaDPA + 0.5 x 10^{-4} M NaOH, 0.050 g powdered polyether foam, 100 mL solution, pH = 9.0, 24 h extraction time.

      DPA$^-$, polyester foam:

      0.2 x 10^{-4} M NaDPA + 0.5 x 10^{-4} M NaOH, 0.100 g powdered polyester foam, 100 mL solution, pH = 9.0, 24 h extraction time.

(iii) dissociation of the ion-pair in the foam

$$MA_f \rightleftharpoons M^+_f + A^-_f \qquad (40)$$

$$K_2 = [M^+]_f [A^-]_f / [MA]_f \qquad (41)$$

The distribution ratio is then expressed as

$$D_{A^-} = \frac{[MA]_f + [A^-]_f}{[MA] + [A^-]} \qquad (42)$$

From equations 37, 39 and 41, D_{A^-} can be described as

$$[MA]_f = K_1 K_{1ex}[M^+][A^-] \qquad (43)$$

$$[A^-]_f = K_1 K_{1ex} K_2 [M^+][A^-] / [M^+]_f \qquad (44)$$

$$[MA] = K_1[M^+][A^-] \qquad (45)$$

$$D_{A^-} = \frac{K_1 K_{1ex}[M^+][A^-] + K_1 K_{1ex} K_2 [M^+][A^-][M^+]_f^{-1}}{K_1[M^+][A^-] + [A^-]}$$

$$= \frac{K_1 K_{1ex}[M^+] + K_1 K_{1ex} K_2 [M^+][M^+]_f^{-1}}{K_1[M^+] + 1} \qquad (46)$$

It is reasonable to assume that A^- rather than MA is the dominant species in aqueous solution at low ionic concentration, equation (46) becomes,

$$D_{A^-} = K_1 K_{1ex}[M^+] + K_1 K_{1ex} K_2 [M^+][M^+]_f^{-1} \qquad (47)$$

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Equation 47 shows that D_{A^-} is dependent on $[M^+]$ and $[M^+]_f$. In addition, K_1, K_2 and K_{1ex} are not known, therefore it is not possible to predict the dependence of A^- on M^+ concentration.

Generally, the distribution coefficient (D) is independent of the phase ratio. However it was found that D of the anion increased with increasing foam weight (Figure 33). It appears that a residual amount of H_3O^+ in the foam which is proportional to foam weight could enhance the anion extraction because of the extraction of HDPA or HTPB. It may also indicate that additional dissociation of the extracted species takes place in the foam on dilution. However, it is not likely the higher D for DPA^- than TPB^- with polyester foam is due to the additional dissociation of the extracted species because the ratio of DPA^- extracted / foam (1.10×10^{-2} mol / kg) is higher than that of TPB^- extracted / foam (0.56×10^{-2} mol / kg). It is not clear that the higher extraction of DPA^- than TPB^- with polyester foam is because of the M^+ concentration effect or of the stronger interaction of DPA^- with the foam.

4.3.2 Extraction by Polyether Foam

4.3.2.1 Alkali Metal DPA

Alkali metal DPA salts can be prepared, and hence the extraction of each alkali metal DPA in the presence of the corresponding hydroxide was studied as opposed to the extraction of TPB in which sodium ion is always present.

Figure 33   Effect of foam weight on the distribution coefficient of the extraction of

CsDPA with polyester foam.
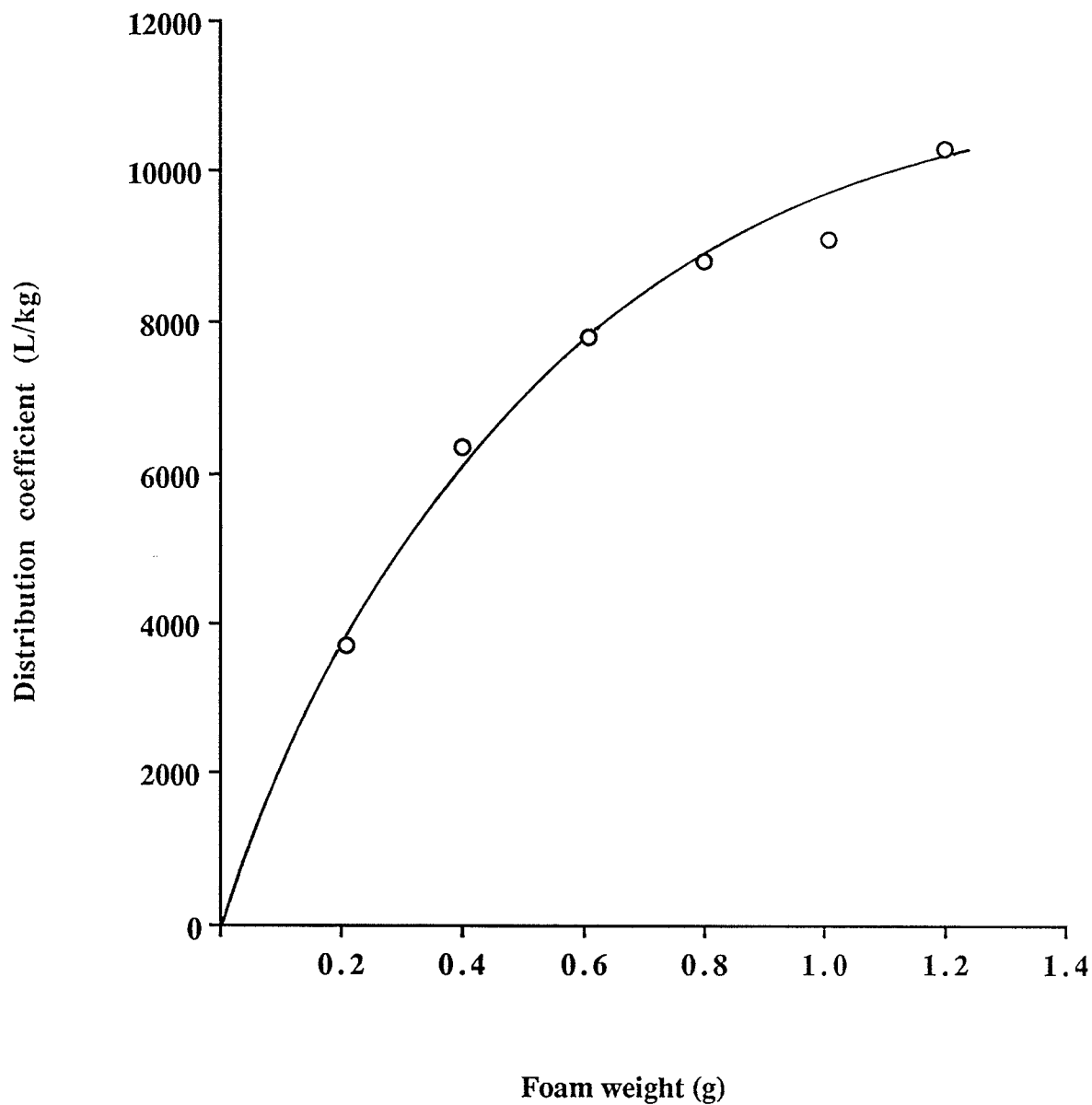
Conditions: 0.5×10^{-4} *M* CsDPA + 0.5×10^{-4} *M* CsOH, 100 mL solution, pH = 9.0,

extraction time = 4 h.

4.3.2.1.1 Time Dependence of the Extraction

To determine the time required to reach equilibrium, the extraction of solutions (100 mL) containing 0.5×10^{-4} M alkali metal DPA $+ 0.5 \times 10^{-4}$ M alkali metal hydroxide with 0.050 g foam as a function of time was studied. The results are given in Figures 34-38. DPA$^-$ extraction increases rapidly after 1/2 h and then slowly up to 24 h. The cation extraction reaches a maximum after 1 or 2 h and decreases with extraction time. A more detailed discussion of the imbalance of the cation and the anion extracted will be given in Chapter 5. Table 30 gives the ratios of cation extracted / DPA$^-$ extracted as a function of time. The ratio is very close to 1 for the first 2 h of extraction with the exception of the extraction of LiDPA. There is no imbalance of the cation and the anion extracted when the ratio of cation extracted / DPA$^-$ extracted ≈ 1, and hence the extractions of the cations are compared at this ratio about 1.

4.3.2.1.2 Selectivity for Alkali Metal Ions

Figures 39 and 40 show the cation and the anion extracted as a function of time for the alkali metal DPAs. Table 31 gives the extraction and distribution coefficient (D) of the cations and DPA$^-$ at which the ratio of cation extracted / DPA$^-$ extracted is about 1. Although this ratio is only 0.87 for the LiDPA extraction, it does not affect the order of extractability of the cations because Li$^+$ extraction is much less than for the other cations.

The extractability of the alkali metal DPAs follows the order of K$^+$ $\approx$ Rb$^+$ > Cs$^+$ > Na$^+$ > Li$^+$. This sequence is the same as that obtained for alkali metal TPBs and is consistent with the cation chelation mechanism.

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Figure 34   Extraction of LiDPA with polyether foam as a function of time.
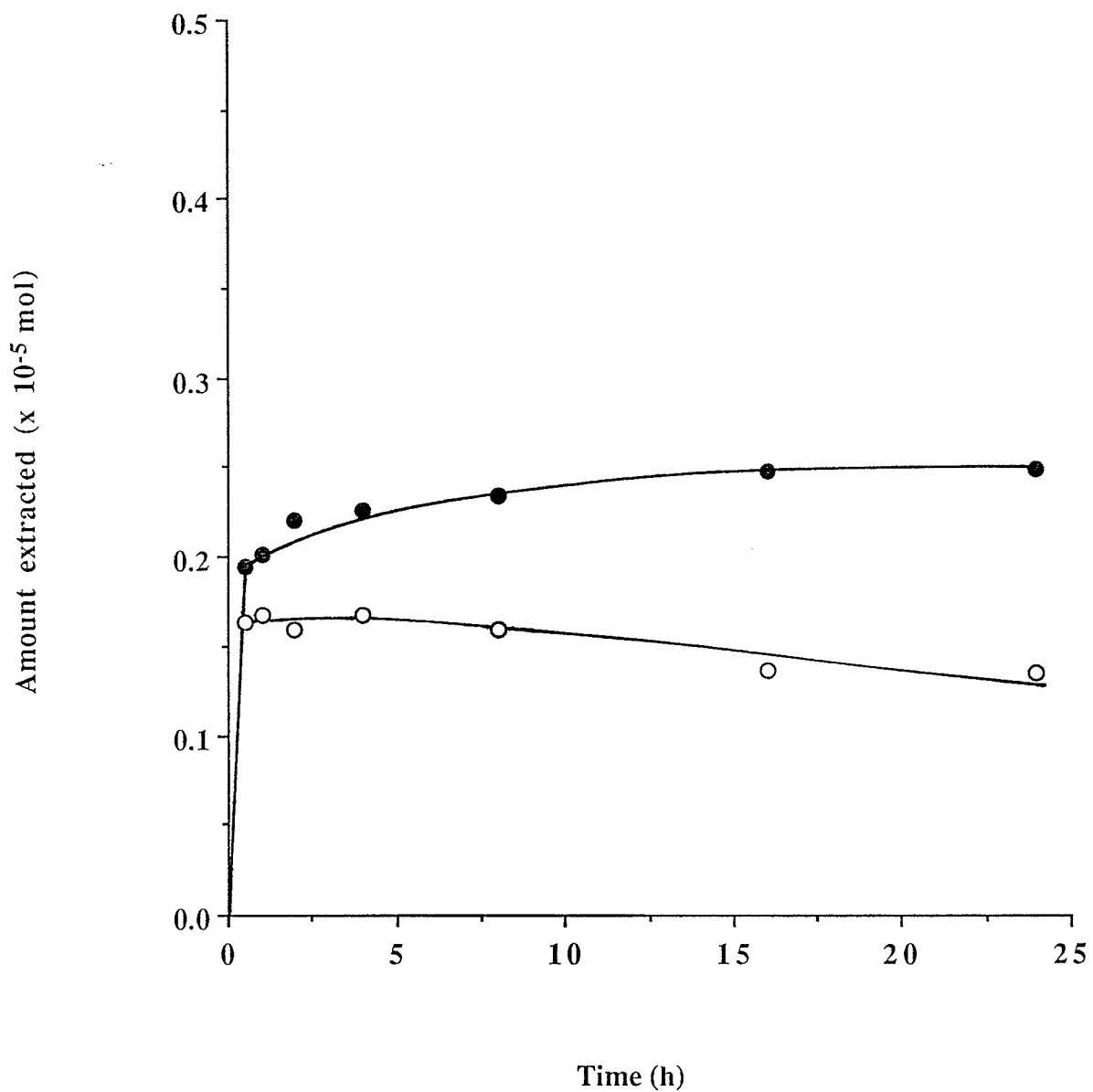
Conditions: $0.5 \times 10^{-4}\ M$ LiDPA + $0.5 \times 10^{-4}\ M$ LiOH, 0.050 g powdered polyether

foam, 100 mL solution, pH = 9.0, (●) DPA^-, (o) Li^+.

Figure 35   Extraction of NaDPA with polyether foam as a function of time.
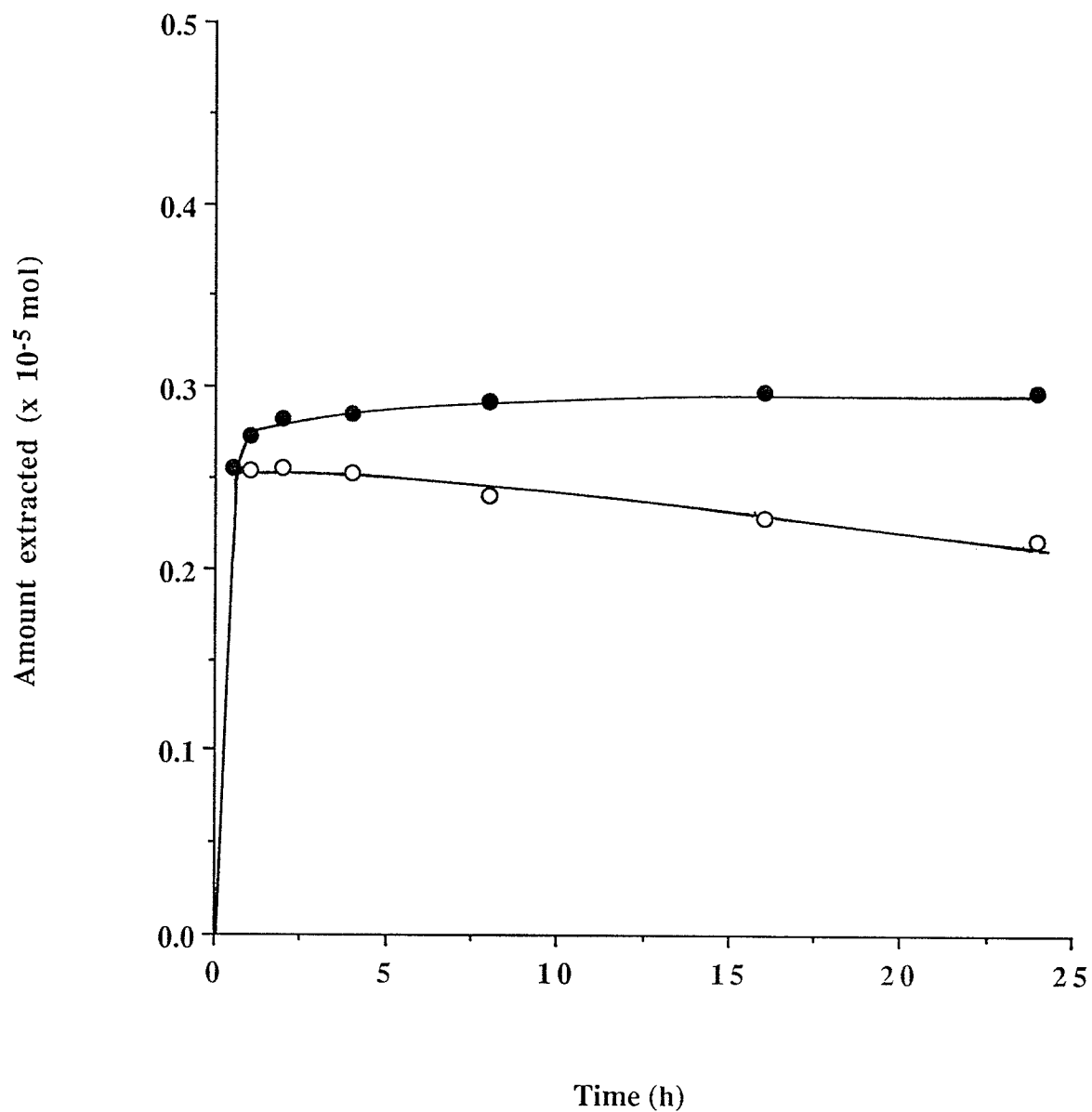
Conditions: 0.5×10^{-4} M NaDPA + 0.5×10^{-4} M NaOH, 0.050 g powdered polyether

foam, 100 mL solution, pH = 9.0, (●) DPA⁻, (o) Na⁺.

Figure 36   Extraction of KDPA with polyether foam as a function of time.
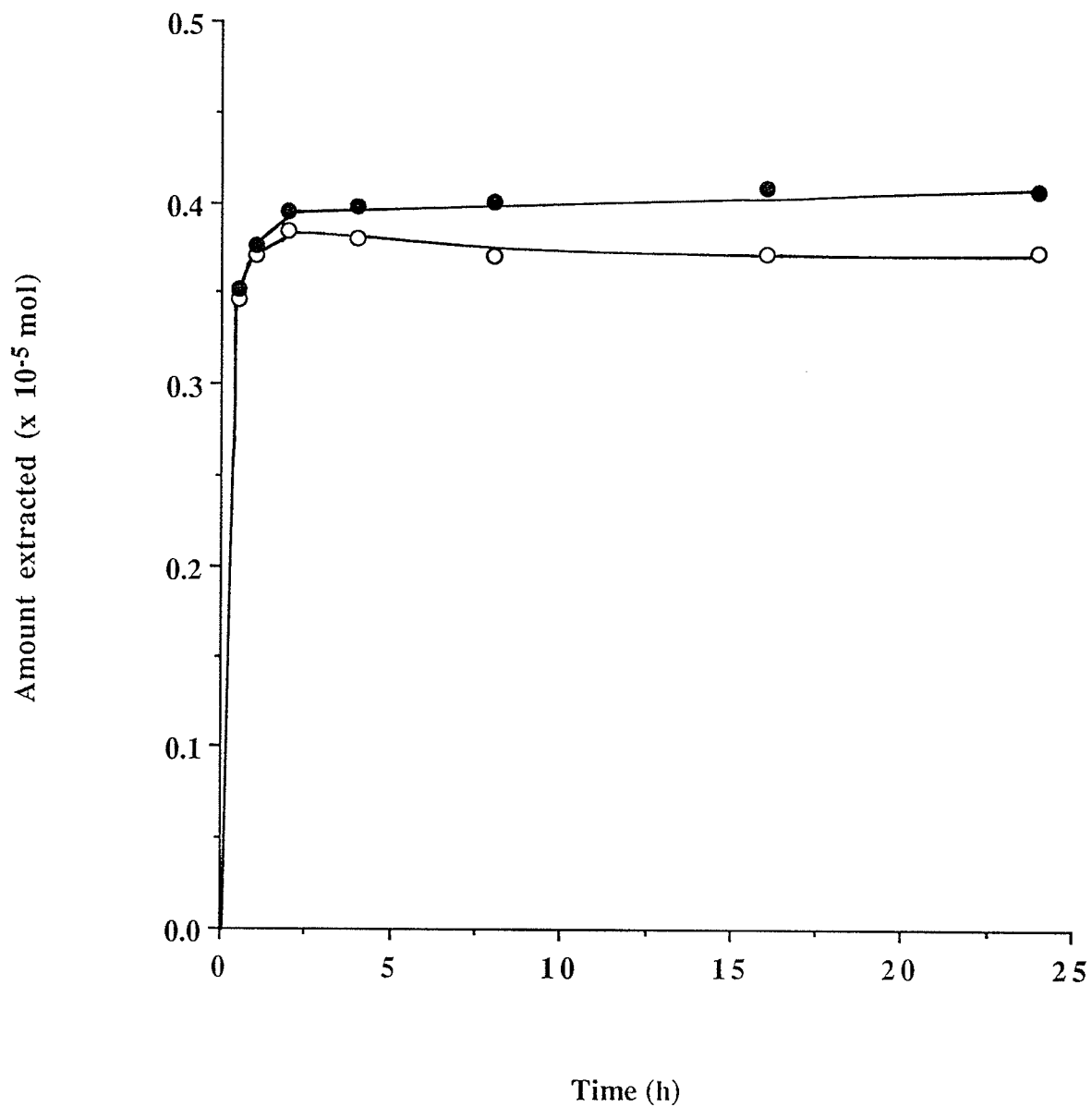
Time (h)

Conditions: 0.5×10^{-4} M KDPA + 0.5×10^{-4} M KOH, 0.050 g powdered polyether foam, 100 mL solution, pH = 9.0, (●) DPA⁻, (o) K⁺.

Figure 37   Extraction of RbDPA with polyether foam as a function of time.

Time (h)
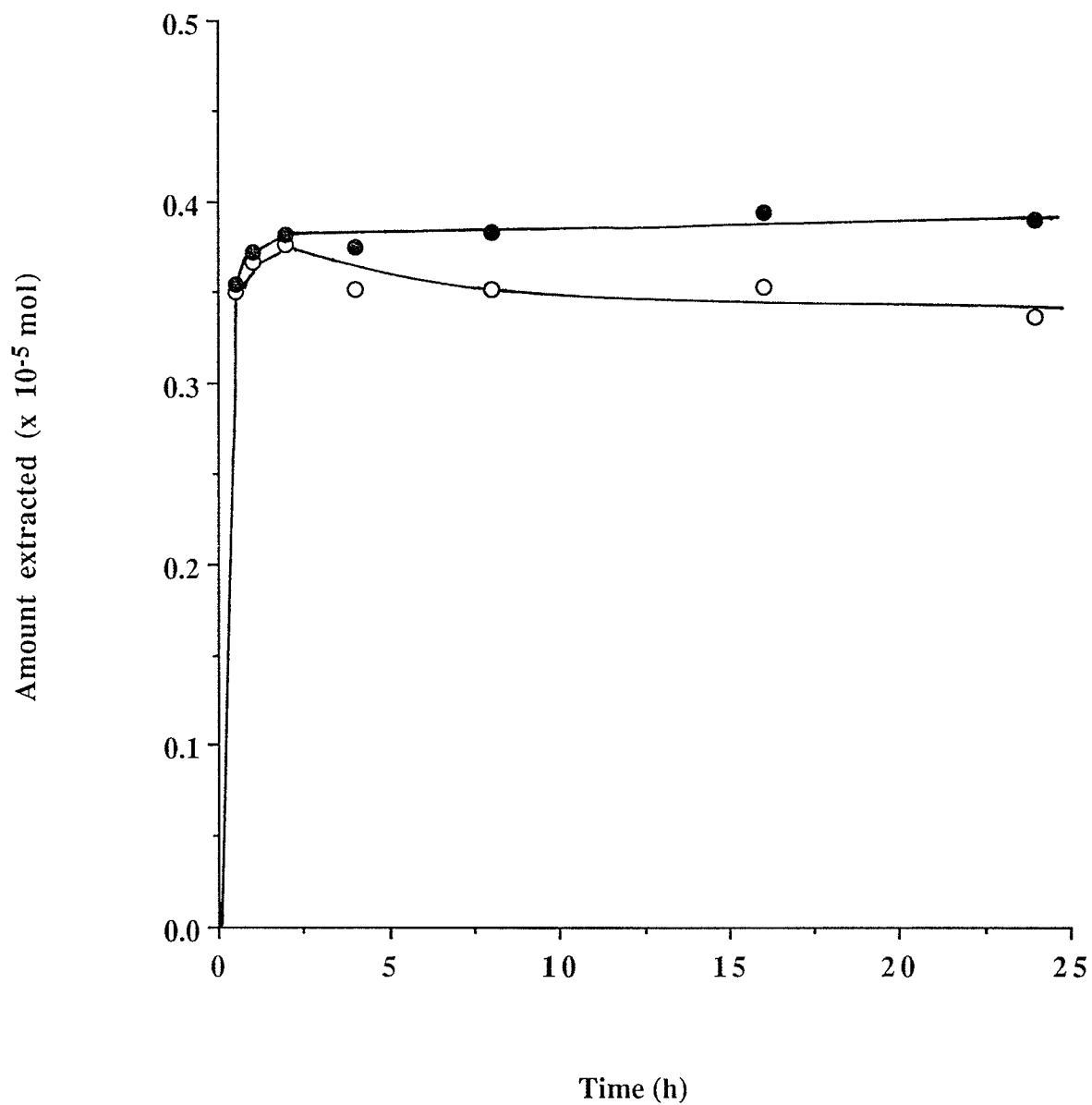
Conditions: 0.5×10^{-4} *M* RbDPA + 0.5×10^{-4} *M* RbOH, 0.050 g powdered polyether

foam, 100 mL solution, pH = 9.0, (●) DPA⁻, (o) Rb⁺.

Figure 38 Extraction of CsDPA with polyether foam as a function of time.
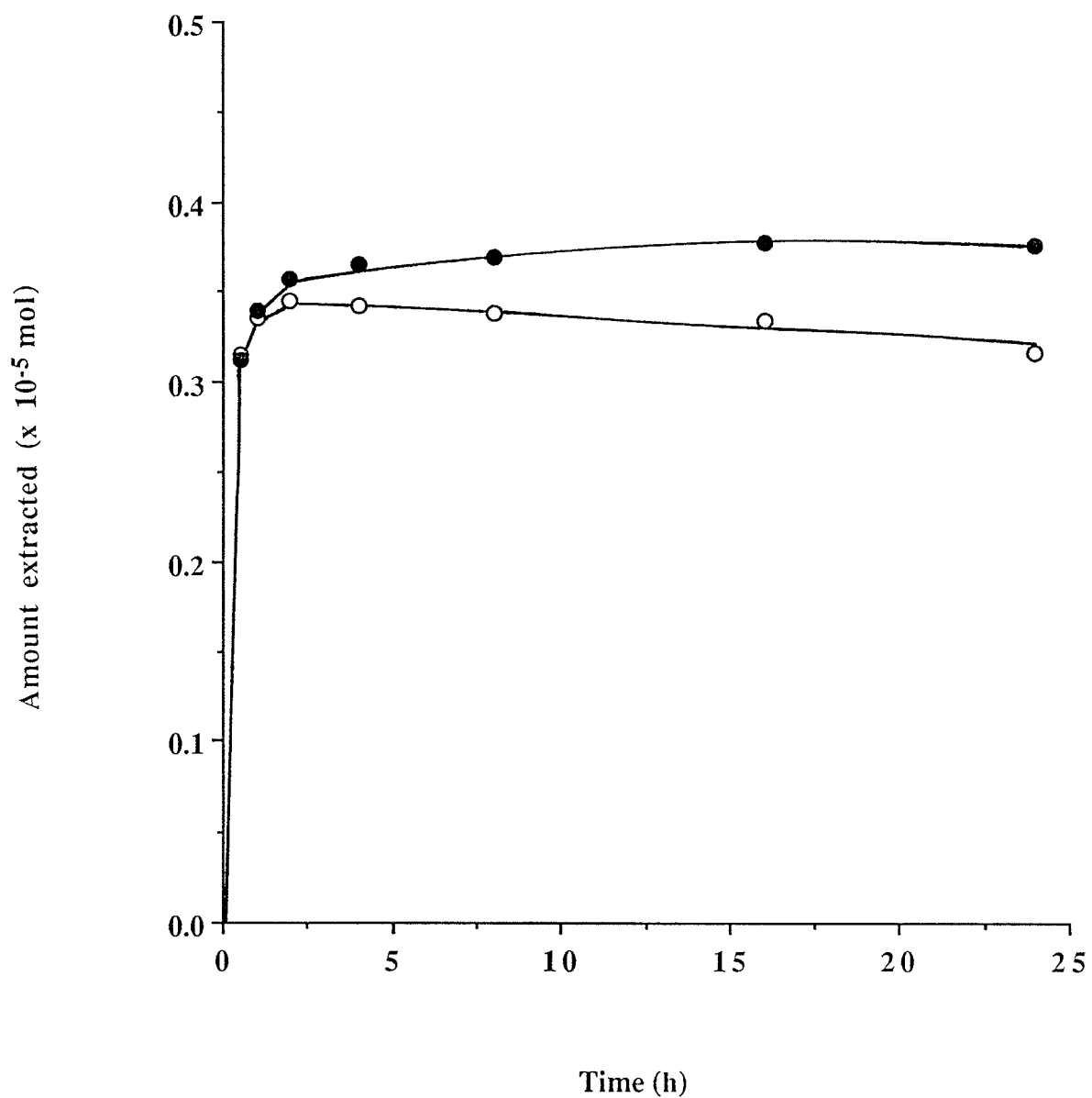
Conditions: 0.5×10^{-4} M CsDPA + 0.5×10^{-4} M CsOH, 0.050 g powdered polyether foam, 100 mL solution, pH = 9.0, (●) DPA⁻, (o) Cs⁺.

Table 30   Ratio of cation extracted / DPA⁻ extracted as a function of time for the extraction of alkali metal DPAs with polyether foam

Time (h)	Cation extracted / DPA⁻ extracted				
	LiDPA	NaDPA	KDPA	RbDPA	CsDPA
0.5	0.88	1.00	0.99	0.99	1.00
1.0	0.87	0.93	0.98	0.99	0.99
2.0	0.79	0.91	0.97	0.98	0.96
4.0	0.78	0.89	0.96	0.94	0.94
8.0	0.71	0.82	0.93	0.92	0.91
16.0	0.60	0.77	0.91	0.90	0.88
24.0	0.57	0.73	0.92	0.86	0.84

Conditions: 0.5×10^{-4} M alkali metal DPA + 0.5×10^{-4} M alkali metal hydroxide, 0.050 g powdered polyether foam, 100 mL solution, pH = 9.0.

Figure 39   Plot of % cation extraction as a function of time for the extraction of alkali

metal DPAs with polyether foam.

Time (h)
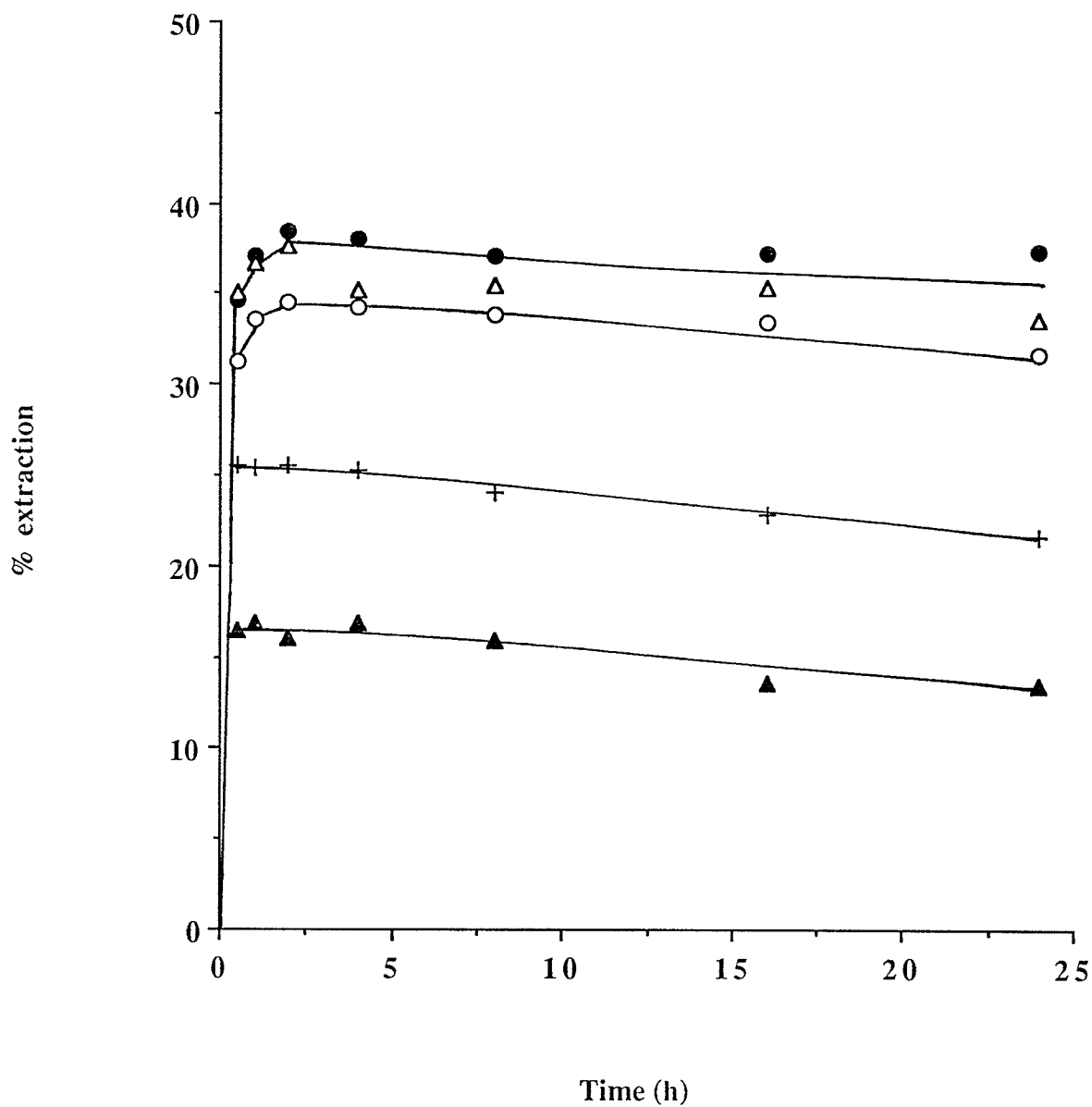
Conditions: 0.5 x 10^{-4} *M* alkali metal DPA + 0.5 x 10^{-4} *M* alkali metal hydroxide,

0.050 g powdered polyether foam, 100 mL solution, pH = 9.0, ($\blacktriangle$) Li^+,

(+) Na^+, ($\bullet$) K^+, ($\triangle$) Rb^+, (o) Cs^+.

Figure 40   Plot of % DPA⁻ extraction as a function of time for the extraction of alkali
metal DPAs with polyether foam.

Time (h)
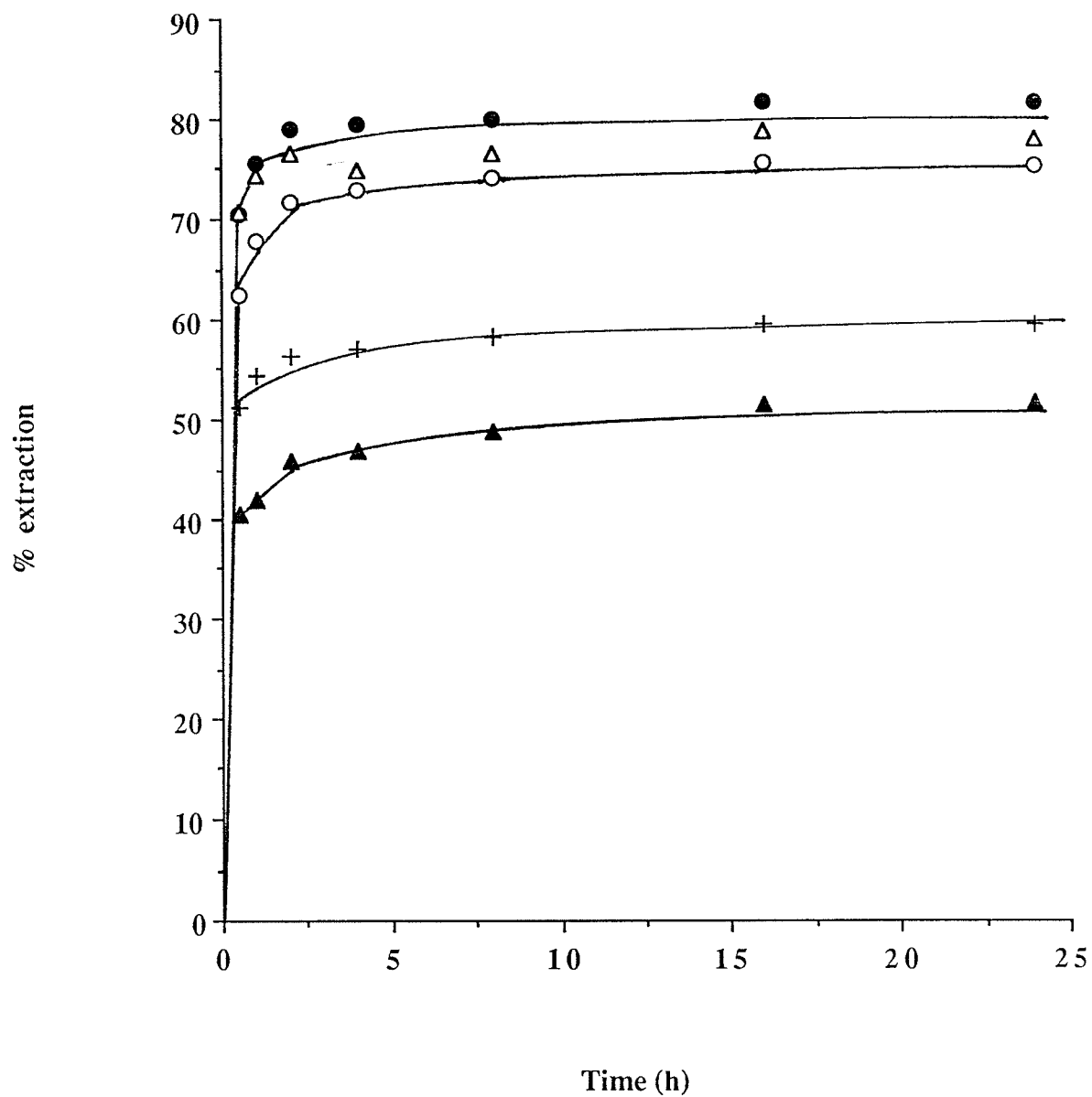
Conditions: 0.5×10^{-4} M alkali metal DPA + 0.5×10^{-4} M alkali metal hydroxide,

0.050 g powdered polyether foam, 100 mL solution, pH = 9.0, (▲) Li⁺,

(+) Na⁺, (●) K⁺, (Δ) Rb⁺, (o) Cs⁺.

Table 31   Distribution coefficient and % extraction of alkali metal ions and DPA^- at cation extracted / DPA^- extracted $\approx$ 1 for the extraction of alkali metal DPAs with polyether foam

DPA salt	Cation		DPA^-	
	% extraction	Distribution coefficient (L/kg)	% extraction	Distribution coefficient (L/kg)
Li	16.8	405	41.9	1450
Na	25.6	691	56.4	2590
K	38.4	1300	79.0	7530
Rb	37.6	1210	76.5	6480
Cs	34.5	1050	71.7	5070

Conditions: 0.5×10^{-4} M alkali metal DPA + 0.5×10^{-4} M alkali metal hydroxide, 0.050 g powdered polyether foam, 100 mL solution, pH = 9.0.

4.3.2.2 Alkylammonium DPA

As mentioned above, some alkylammonium salts could not be prepared, and moreover, alkali metal hydroxide has to be added to adjust the pH of the solution to 9. Therefore, the extraction of the alkylammonium with DPA^- could not be studied in the absence of other cations as opposed to the extraction of alkali metal DPAs. It was decided to use LiDPA as the source of DPA^- for the extraction of the alkylammoniums because Li^+ has the lowest extractability among the alkali metal ions and should compete less with alkylammonium cations for extraction. For this study, 0.5×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH + 0.5×10^{-4} M alkylammonium chloride solutions (100 mL) were extracted with 0.050 g foam.

4.3.2.2.1 Time Dependence of the Extraction

Figure 41 shows the extraction of 0.5×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH + 0.5×10^{-4} M t-butylammonium chloride as a function of time. DPA^- extraction increases rapidly to 55% after 1/2 h and slowly to 66% after 24 h. The cation extraction reaches a maximum of 35% after 1 h and then decreases with increasing extraction time. The extraction of other alkylammonium DPAs shows similar extraction characteristics. Table 32 gives the ratios of total cations (Li^+ + alkylammonium) extracted / anion extracted against varied extraction times. The ratio is generally close to 1 for the first hour of extraction.

Figure 41   Extraction of LiDPA and *t*-butylammonium chloride with polyether foam as a function of time.
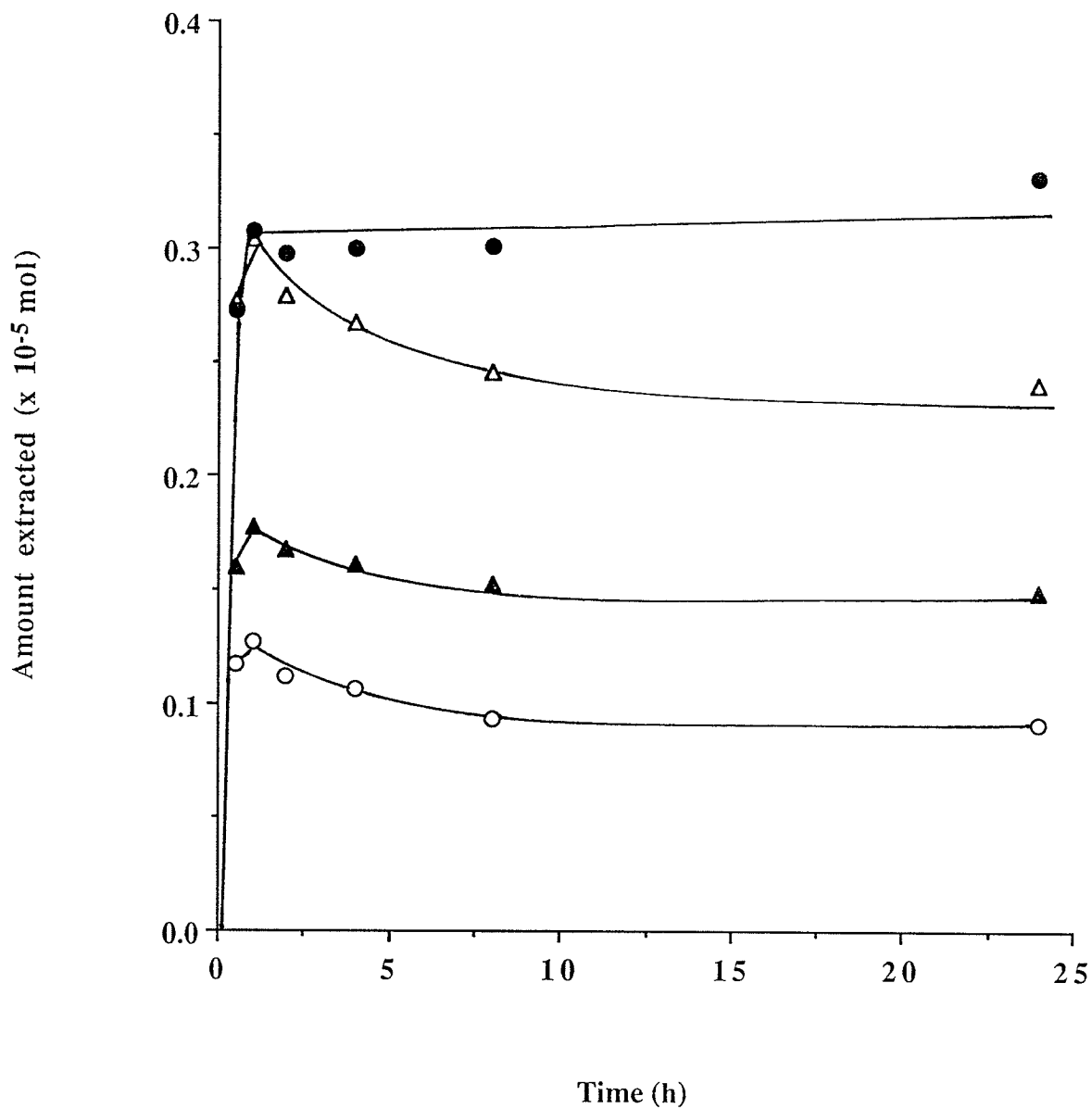
Conditions: $0.5 \times 10^{-4}\ M$ LiDPA + $0.5 \times 10^{-4}\ M$ LiOH + $0.5 \times 10^{-4}\ M$ *t*-butylammonium chloride, 0.050 g powdered polyether foam, 100 mL solution, pH = 9.0, (●) DPA⁻, (o) Li⁺, (▲) *t*-butylammonium, (Δ) total cations (Li⁺ + *t*-butylammonium).

Table 32   Ratio of total cations extracted / DPA⁻ extracted for the extraction of LiDPA, and alkylammonium, potassium and ammonium chlorides with polyether foam as a function of time

DPA salt	Time (h)					
	0.5	1.0	2.0	4.0	8.0	24.0
n-butylammonium	0.92	0.92	0.78	0.80	0.77	0.74
isobutylammonium	0.92	0.97	0.85	0.90	0.77	0.65
potassium	1.00	0.99	0.98	0.90	0.82	0.77
n-propylammonium	1.01	1.00	0.94	0.94	0.86	0.76
ammonium	0.99	0.92	0.91	0.89	0.82	0.76
t-butylammonium	1.02	0.98	0.94	0.89	0.82	0.73
isopropylammonium	1.02	0.97	0.92	0.80	0.82	0.68
diethylammonium	0.99	1.00	0.92	0.83	0.81	0.73
ethylammonium	1.06	1.01	0.99	0.93	0.82	0.70
methylammonium	0.98	1.00	1.00	0.94	0.90	0.67
dimethylammonium	0.98	0.99	0.97	0.80	0.74	0.62
trimethylammonium	0.94	0.97	0.89	0.83	0.72	0.54

Conditions: 0.5×10^{-4} *M* LiDPA + 0.5×10^{-4} *M* LiOH + 0.5×10^{-4} *M* alkylammonium, potassium or ammonium chloride, 0.050 g powdered polyether foam, 100 mL solution, pH = 9.0.

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4.3.2.2.2   Selectivity for Alkylammonium Ions

Although no equilibrium for the cation was obtained from time dependence studies, the maximum for cation extraction generally occurs after 1 h of extraction and the ratio of total cations extracted / DPA⁻ extracted is about 1 indicating no imbalance of the cation and the anion extracted. Thus, the maximum values of the cation extracted can be used to compare the extractability of the various alkylammonium cations and are listed in Table 33 and 34. Table 35 compares the maximum distribution coefficient of the cations in the extractions with TPB⁻ and with DPA⁻. The distribution coefficients with DPA⁻ are higher than those with TPB⁻ as observed in the extraction of alkali metal salts. However, the extractability sequence of the alkylammonium cations is the same as that for the extraction with TPB⁻. Thus, the results can be explained by the steric effect, hydrophobic interaction and the inductive effect as discussed previously.

4.3.3   Extraction by Polyester Foam

4.3.3.1   Alkali Metal DPA

Solutions (100 mL) of 0.2×10^{-4} M alkali metal DPA + 0.5×10^{-4} M alkali metal hydroxide were extracted with 0.100 g polyester foam.

4.3.3.1.1   Time Dependence of the Extraction

Figures 42-46 show the extraction of 0.2×10^{-4} M alkali metal DPA + 0.5×10^{-4} M alkali metal hydroxide as a function of time. Table 36 gives the ratio of cation extracted / DPA⁻ extracted versus time. There is no apparent imbalance of the cation and the anion

Table 33 Maximum distribution coefficient and % extraction of the cations at total cations extracted / DPA^- extracted ≈ 1 for the extraction of LiDPA, and alkylammonium, potassium and ammonium chlorides with polyether foam

Cation	% extraction	Distribution coefficient (L/kg)
n-butylammonium	54.3	2380
isobutylammonium	48.6	1880
potassium	48.1	1850
n-propylammonium	46.0	1700
ammonium	33.9	1610
t-butylammonium	35.5	1100
isopropylammonium	30.8	880
diethylammonium	28.7	810
ethylammonium	26.0	698
methylammonium	25.2	674
dimethylammonium	15.2	359
trimethylammonium	11.8	267

Conditions: 0.5×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH + 0.5×10^{-4} M alkylammonium, potassium or ammonium chloride, 0.050 g powdered polyether foam, 100 mL solution, pH = 9.0.

Table 34   Maximum distribution coefficient of the cations and DPA⁻ at the ratio total cations extracted / DPA⁻ extracted ≈ 1 for the extraction of LiDPA, and alkylammonium, potassium and ammonium chlorides with polyether foam

DPA salt	Distribution coefficient (L/kg)		
	Cation	Li$^+$	DPA$^-$
n-butylammonium	2380	145	4600
isobutylammonium	1880	202	4520
potassium	1850	211	4320
n-propylammonium	1700	222	3880
ammonium	1610	288	3600
t-butylammonium	1100	290	3200
isopropylammonium	880	237	2590
diethylammonium	810	308	2500
ethylammonium	698	328	2330
methylammonium	674	347	2420
dimethylammonium	359	399	2020
trimethylammonium	267	401	1720

Conditions: 0.5×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH + 0.5×10^{-4} M alkylammonium, potassium or ammonium chloride, 0.050 g powdered polyether foam, 100 mL solution, pH = 9.0.

Table 35 Comparison of the maximum distribution coefficient of the cations at the ratio of total cations extracted / anion extracted $\approx$ 1 for the extraction of LiDPA + alkylammonium, potassium and ammonium chlorides; and NaTPB + alkylammonium, potassium and ammonium chlorides with polyether foam

	Distribution coefficient (L/kg)	
Cation	DPA	TPB
n-butylammonium	2380	481
isobutylammonium	1880	not determined
potassium	1850	310
n-propylammonium	1700	369
ammonium	1610	294
t-butylammonium	1100	235
isopropylammonium	880	235
diethylammonium	810	not determined
ethylammonium	698	232
methylammonium	674	176
dimethylammonium	359	104
trimethylammonium	267	61

Conditions: DPA: $0.5 \times 10^{-4}\,M$ LiDPA + $0.5 \times 10^{-4}\,M$ LiOH + $0.5 \times 10^{-4}\,M$ alkylammonium, potassium or ammonium chloride, 0.050 g powdered polyether foam, 100 mL solution, pH = 9.0.
TPB: $1.0 \times 10^{-4}\,M$ NaTPB + $1.0 \times 10^{-4}\,M$ NaOH + $1.0 \times 10^{-4}\,M$ alkylammonium, potassium or ammonium chloride, 0.300 g powdered polyether foam, 100 mL solution, pH = 9.0.

**Figure 42**   Extraction of LiDPA with polyester foam as a function of time.
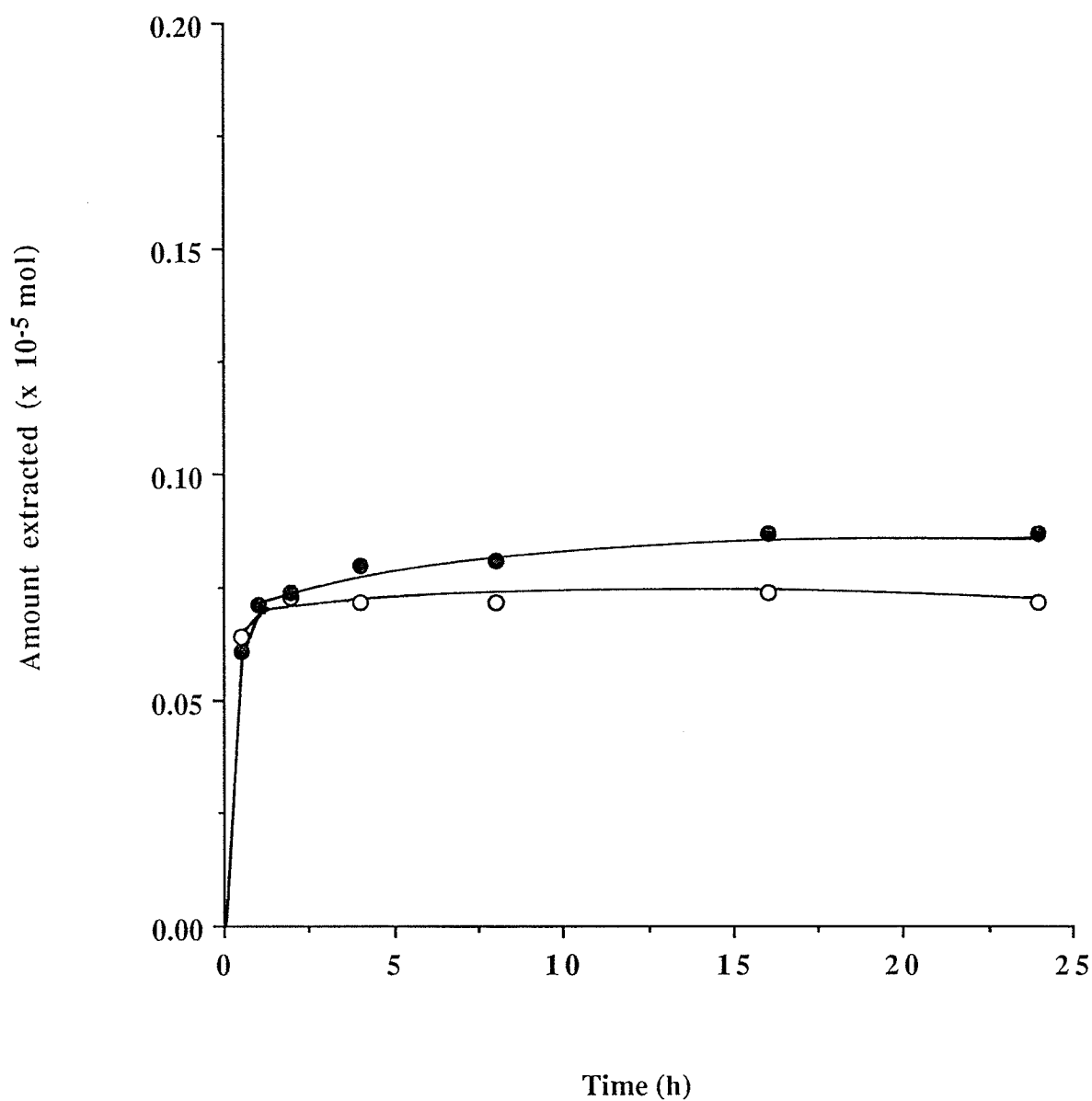
Conditions: 0.2×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH, 0.100 g powdered polyester foam, 100 mL solution, pH = 9.0, (●) DPA⁻, (o) Li⁺.

Figure 43   Extraction of NaDPA with polyester foam as a function of time.
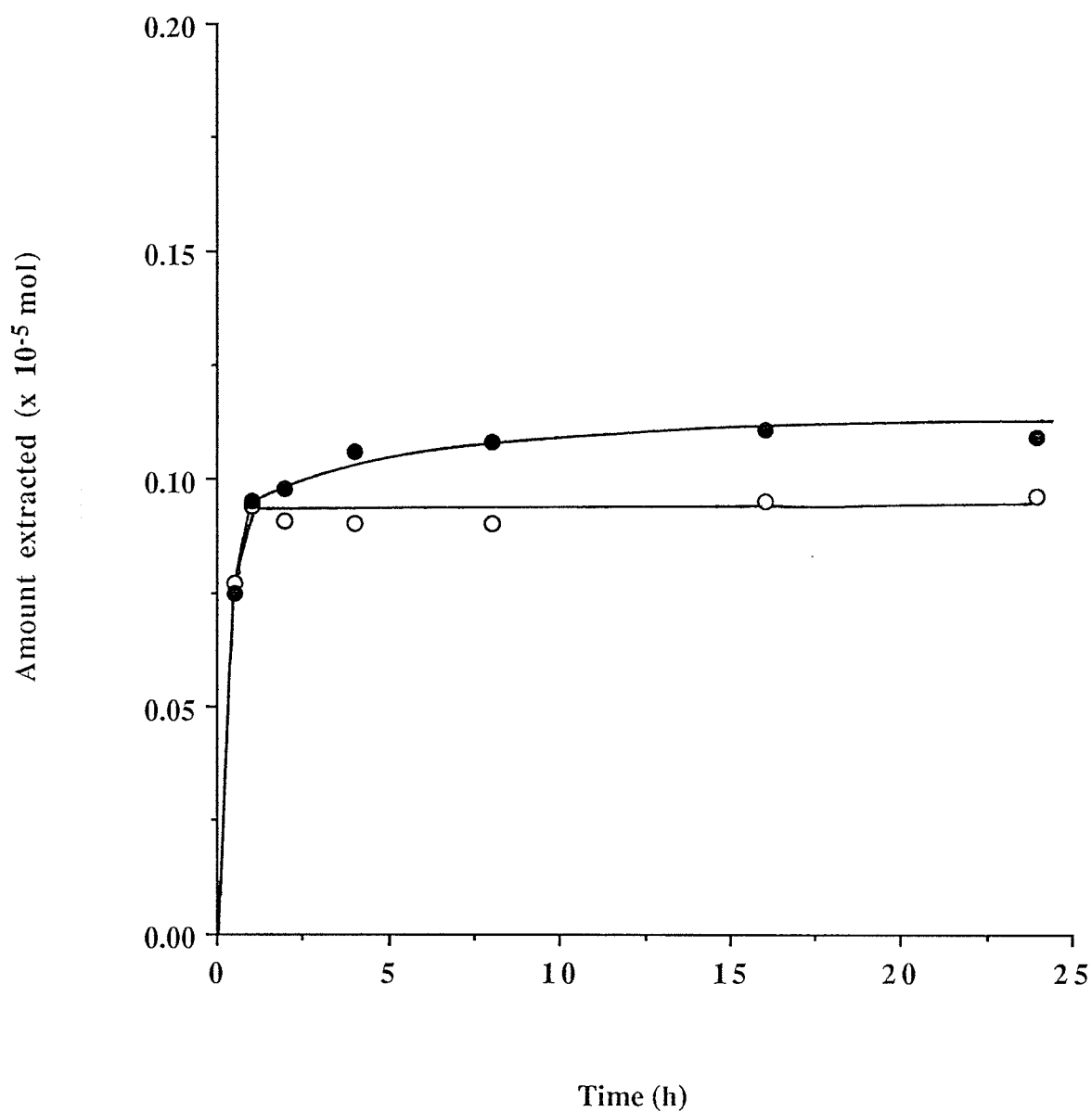
Conditions: $0.2 \times 10^{-4}\ M$ NaDPA $+ 0.5 \times 10^{-4}\ M$ NaOH, 0.100 g powdered polyester

foam, 100 mL solution, pH = 9.0, (●) DPA⁻, (o) Na⁺.

Figure 44   Extraction of KDPA with polyester foam as a function of time.
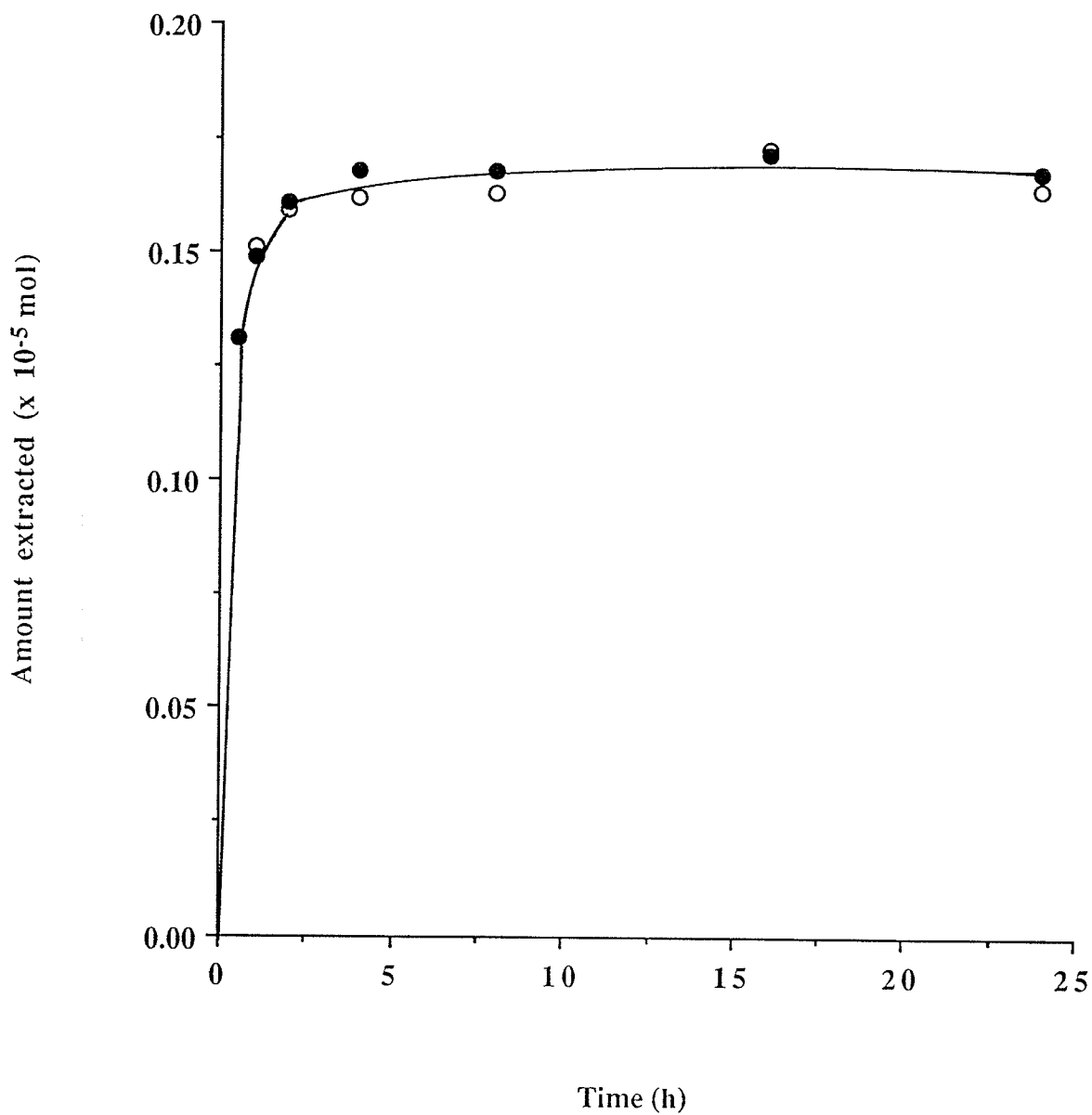
Conditions: 0.2×10^{-4} M KDPA + 0.5×10^{-4} M KOH, 0.100 g powdered polyester

foam, 100 mL solution, pH = 9.0, ($\bullet$) DPA$^-$, (o) K$^+$.

Figure 45   Extraction of RbDPA with polyester foam as a function of time.
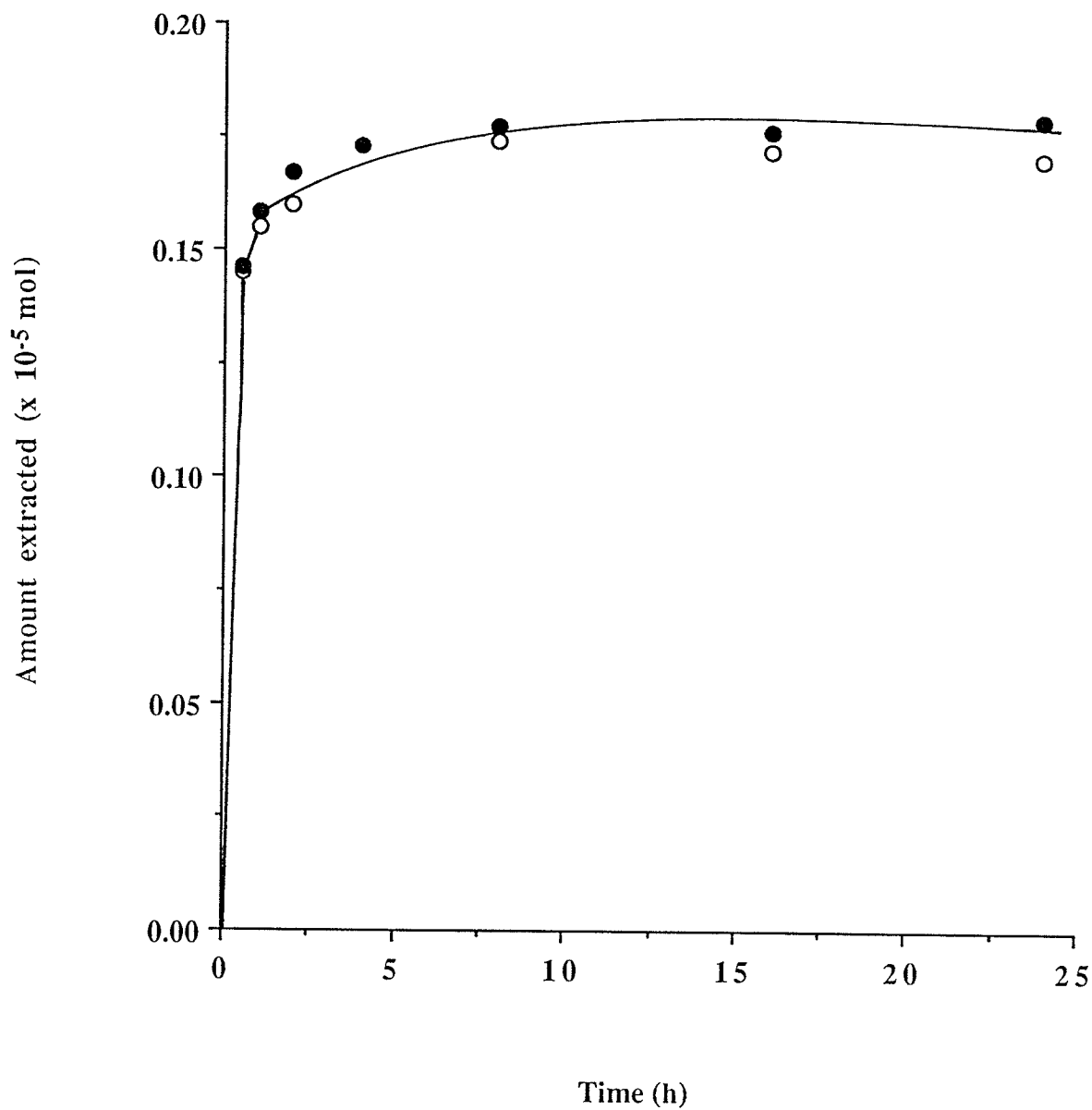
Conditions: $0.2 \times 10^{-4}\ M$ RbDPA + $0.5 \times 10^{-4}\ M$ RbOH, 0.100 g powdered polyester foam, 100 mL solution, pH = 9.0, (●) DPA$^-$, (o) Rb$^+$.

Figure 46   Extraction of CsDPA with polyester foam as a function of time.
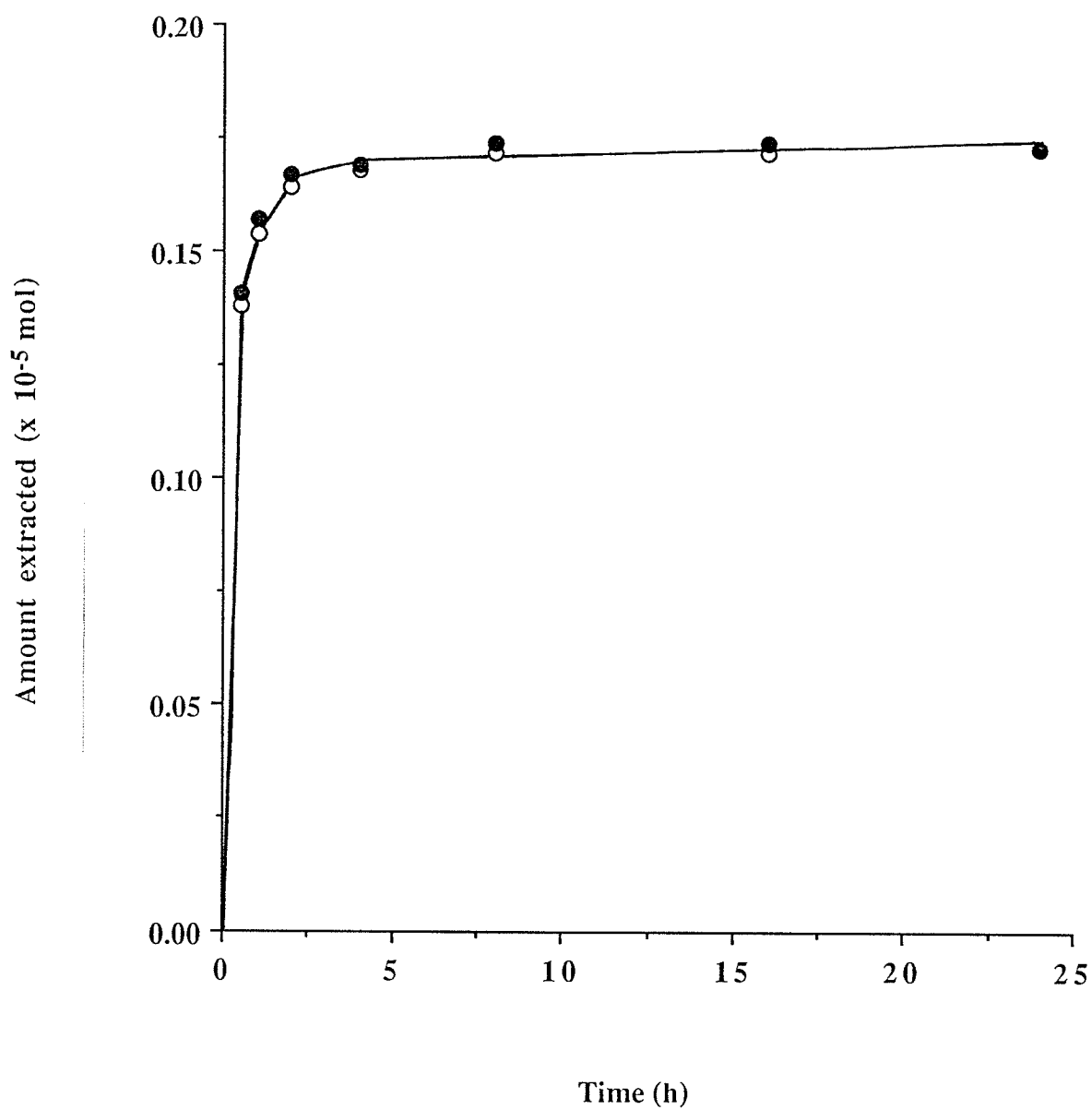
Conditions: 0.2 x 10^{-4} M CsDPA + 0.5 x 10^{-4} M CsOH, 0.100 g powdered polyester

foam, 100 mL solution, pH = 9.0, (●) DPA^{-}, (o) Cs^{+}.

Table 36   Ratio of cation extracted / DPA⁻ extracted as a function of time for the extraction of alkali metal DPAs with polyester foam

Time (h)	Cation extracted / DPA⁻ extracted				
	LiDPA	NaDPA	KDPA	RbDPA	CsDPA
0.5	1.05	1.03	1.00	0.99	0.98
1.0	0.99	0.99	1.01	0.98	0.98
2.0	0.99	0.93	0.99	0.96	0.98
4.0	0.88	0.85	0.96	1.00	0.99
8.0	0.89	0.83	0.97	0.98	0.99
16.0	0.83	0.86	1.01	0.98	0.99
24.0	0.81	0.88	0.98	0.95	1.00

Conditions: $0.2 \times 10^{-4}\ M$ alkali metal DPA + $0.5 \times 10^{-4}\ M$ alkali metal hydroxide, 0.100 g powdered polyester foam, 100 mL solution, pH = 9.0.

extracted for the extraction with potassium, rubidium and cesium DPAs, but there is a slight imbalance of the cation and the anion extracted for the extraction with lithium and sodium DPAs. The ratio of cation extracted / DPA$^-$ extracted is close to 1 after 24 h. The pH of the solution remained at 9.0 as opposed to 8.4 for the extraction with TPB$^-$. It should be noted that only 0.100 g of foam was used for the extraction with DPA$^-$, whereas 0.800 g was used for the extraction with TPB$^-$. This result suggests there is a residual amount of H_3O^+ present in the foam which is proportional to foam weight. It appears that with 0.100 g foam used for this study, the small amount of residual H_3O^+ in the foam may give rise to the small or no imbalance of the cation and the anion extracted.

4.3.3.1.2   Selectivity for Alkali Metal Ions

Figures 47 and 48 show the extraction of the cations and the anion as a function of time for the extraction of alkali metal DPAs. Table 37 gives the maximum extraction and distribution coefficient of the cations and DPA$^-$. The extractability of the cations follows the order: $K^+ \approx Rb^+ \approx Cs^+ > Na^+ > Li^+$. The same order was obtained for the extraction of alkali metal TPBs with polyester foam. These results are consistent with the cation chelation mechanism.

4.3.3.2   Alkylammonium DPA

Solutions (100 mL) containing 0.2×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH + 0.2×10^{-4} M alkylammonium chloride were extracted with 0.100 g polyester foam.

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Figure 47 Plot of % cation extraction as a function of time for the extraction of alkali metal DPAs with polyester foam.
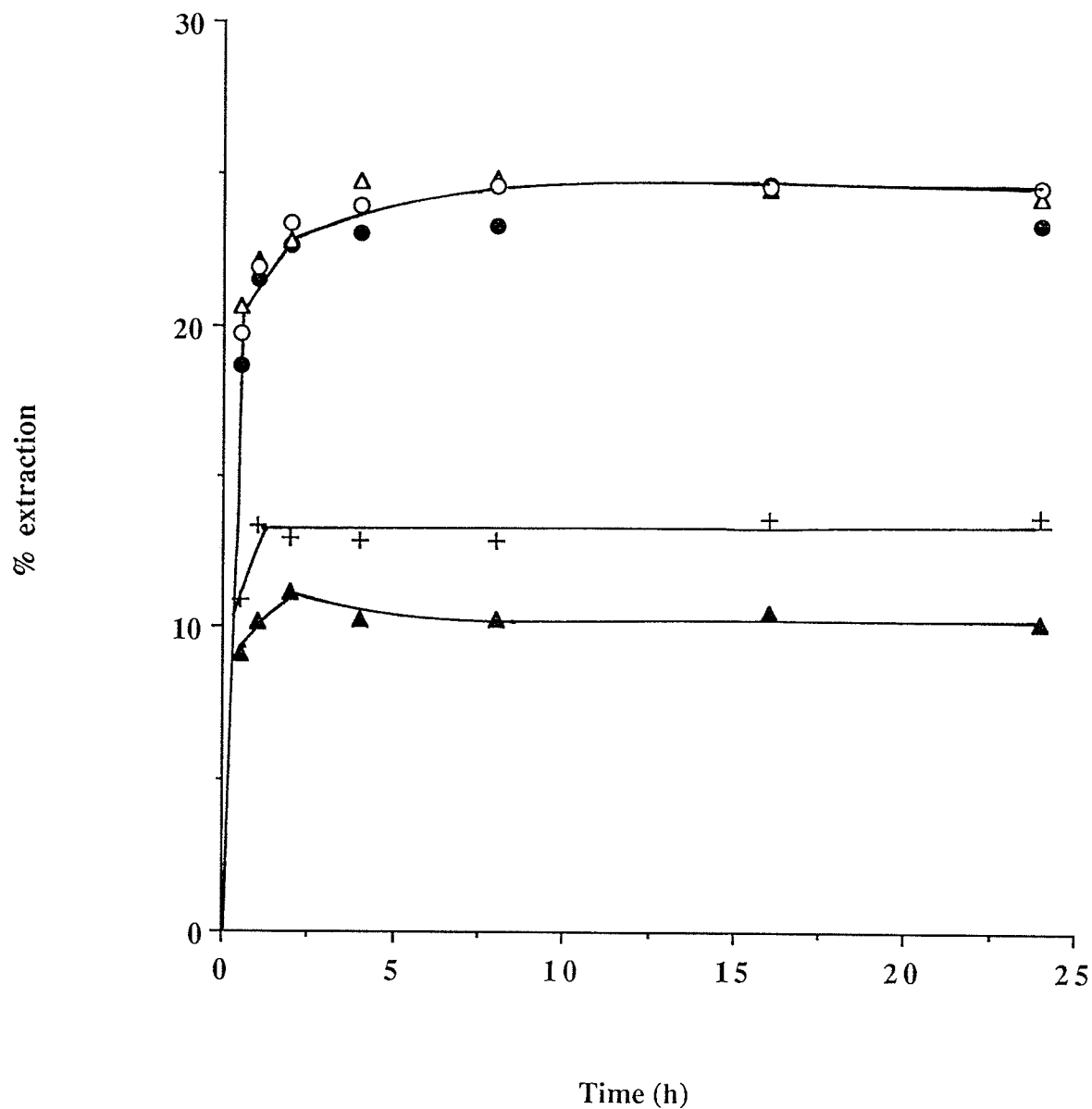
Conditions: 0.2×10^{-4} M alkali metal DPA + 0.5×10^{-4} M alkali metal hydroxide, 0.100 g powdered polyester foam, 100 mL solution, pH = 9.0, (▲) Li^+, (+) Na^+, (●) K^+, (Δ) Rb^+, (o) Cs^+.

Figure 48   Plot of % DPA⁻ extraction as a function of time for the extraction of alkali

metal DPAs with polyester foam.

% extraction

Time (h)
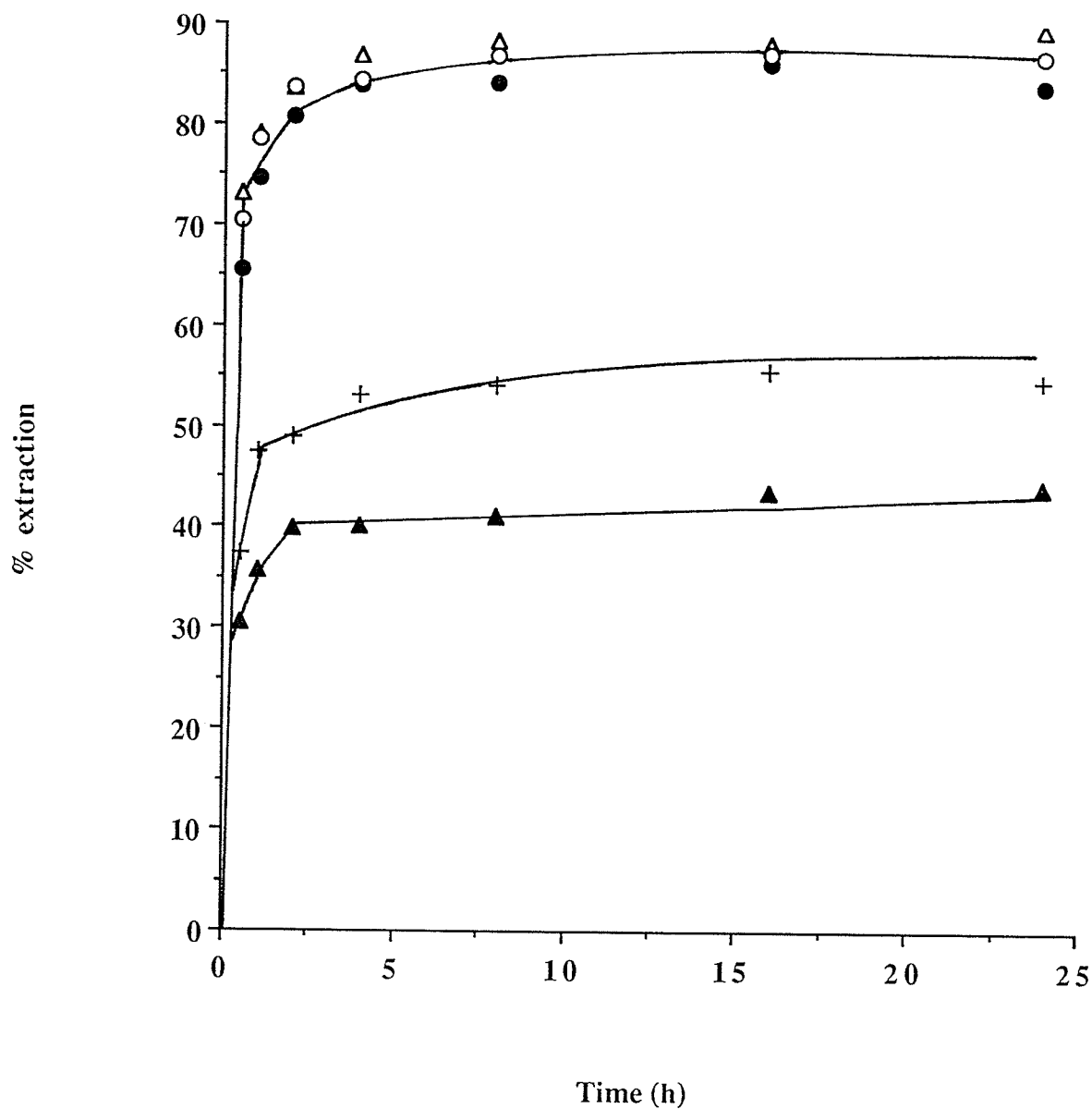
Conditions: $0.2 \times 10^{-4}\,M$ alkali metal DPA + $0.5 \times 10^{-4}\,M$ alkali metal hydroxide,

0.100 g powdered polyester foam, 100 mL solution, pH = 9.0, (▲) Li^+,

(+) Na^+, (●) K^+, (Δ) Rb^+, (o) Cs^+.

Table 37   Maximum distribution coefficient and % extraction of alkali metal ions and DPA⁻ for the extraction of alkali metal DPAs with polyester foam

DPA salt	Cation		DPA⁻	
	% extraction	Distribution coefficient (L/kg)	% extraction	Distribution coefficient (L/kg)
Li	10.2	114	44.1	790
Na	13.7	159	54.6	1200
K	23.4	306	84.0	5240
Rb	24.3	313	89.4	8370
Cs	24.6	328	86.7	6520

Conditions: 0.2×10^{-4} M alkali metal DPA + 0.5×10^{-4} M alkali metal hydroxide, 0.100 g powdered polyester foam, 100 mL solution, pH = 9.0, 24 h extraction time.

4.3.3.2.1 Time Dependence of the Extraction

Figure 49 shows the extraction of 0.2×10^{-4} M LiDPA $+ 0.5 \times 10^{-4}$ M LiOH $+ 0.2 \times 10^{-4}$ M methylammonium chloride as a function of time. The ratio of total cations (Li^+ + alkylammonium ion) extracted / DPA^- extracted versus time (Table 38) is close to 1 after 24 h extraction indicating no imbalance of the cationand the anion extracted. Thus, the extraction of other alkylammoniums was studied with 24 h extraction time.

4.3.3.2.2 Selectivity for Alkylammonium Ions

Tables 39 and 40 give the extraction and distribution coefficient of the cations and DPA^-. Each value of the cation extracted and DPA^- extracted in Tables 39 and 40 were determined from three separate extractions. By combining all the % deviations for the cation extracted and DPA^- extracted, the deviations were found to be 5.0 % and 2.4 % of the % extraction for the cation and the anion respectively. It is reasonable to use these % deviations for the cation and the anion as an estimate for the other extractions since they were carried out under similar conditions using similar analytical procedure. Table 41 compares the maximum distribution coefficients of the alkylammoniums for the extraction with TPB^- and DPA^-. Again the values for the extraction with DPA^- are higher than those with TPB^-, but nevertheless, the extractability sequence of the alkylammoniums are the same. This can be explained by the steric effect, hydrophobic interaction and the inductive effect as discussed in Section 3.3.2.2.2..

Table 42 compares the maximum distribution coefficients of the alkylammoniums for the extractions with polyether and polyester foam. The distribution coefficients are lower for polyester foam than for polyether foam. DPA^- concentrations were 0.2×10^{-4} M

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Figure 49   Extraction of LiDPA and methylammonium chloride with polyester foam as a function of time.
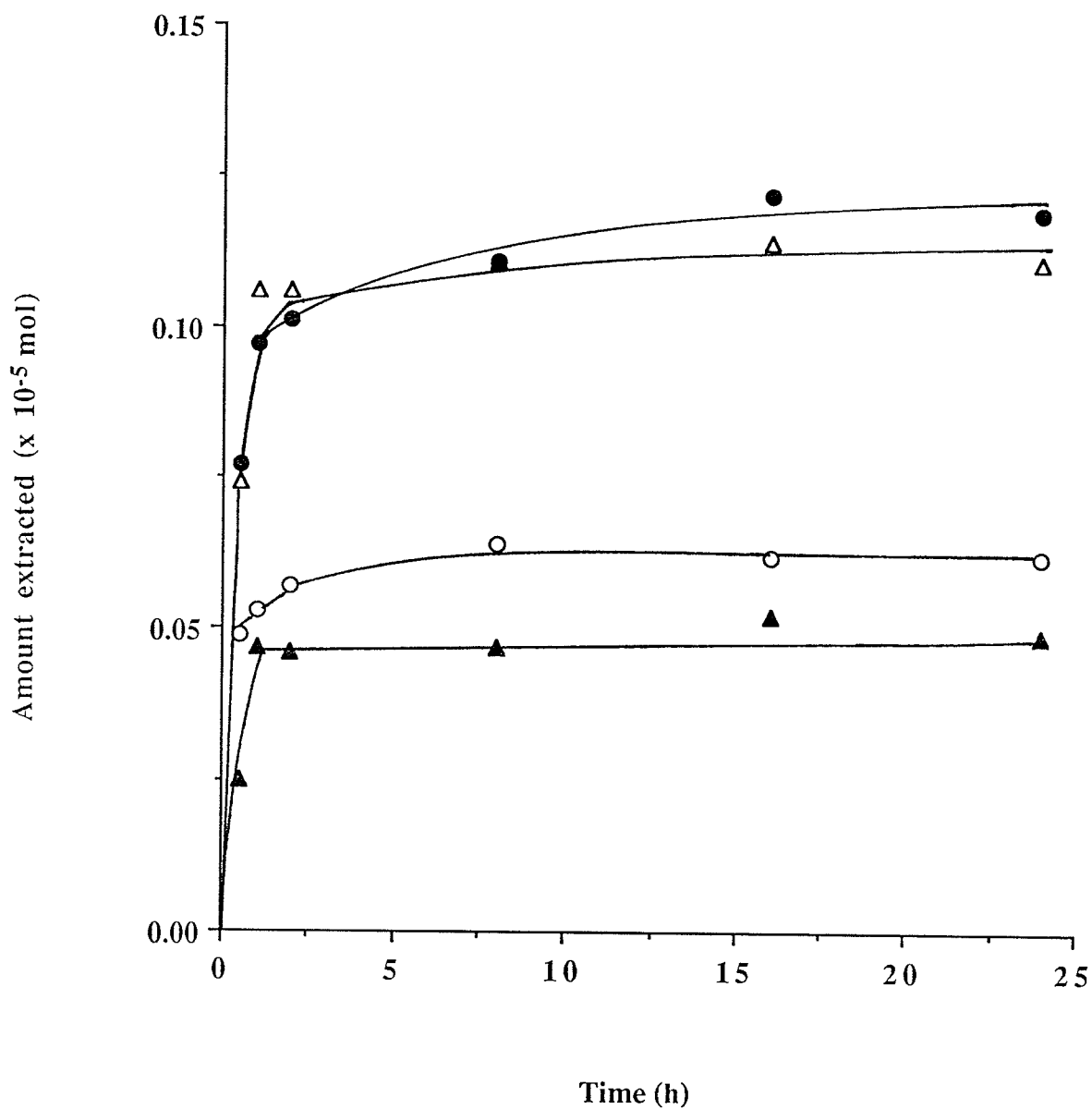
Conditions: $0.2 \times 10^{-4}\ M$ LiDPA + $0.5 \times 10^{-4}\ M$ LiOH + $0.2 \times 10^{-4}\ M$ methylammonium chloride, 0.100 g powdered polyether foam, 100 mL solution, pH = 9.0, (●) DPA⁻, (o) Li⁺, (▲) methylammonium, (Δ) total cations (Li⁺ + methylammonium).

Table 38   Ratio of total cations extracted / DPA⁻ extracted as a function of time for the extraction of LiDPA and methylammonium chloride with polyester foam

Time (h)	Total cations extracted / DPA⁻ extracted
0.5	0.96
1.0	1.03
2.0	1.02
8.0	1.00
16.0	0.93
24.0	0.93

Conditions: $0.2 \times 10^{-4}\ M$ LiDPA + $0.5 \times 10^{-4}\ M$ LiOH + $0.2 \times 10^{-4}\ M$ methylammonium chloride, 0.100 g powdered polyester foam, 100 mL solution, pH = 9.0.

Table 39   Distribution coefficient and % extraction of the cations for the extraction of LiDPA, and alkylammonium, potassium and ammonium chlorides with polyester foam

Cation	% extraction ± s	Distribution coefficient (L/kg ± s)
n-butylammonium	60.4 ± 5.4	1560 ± 350
potassium	55.5 ± 3.1	1260 ± 150
isobutylammonium	53.9 ± 1.3	1150 ± 63
n-propylammonium	47.0 ± 0.5	886 ± 15
isopropylammonium	40.4 ± 0.9	681 ± 23
t-butylammonium	39.9 ± 2.2	668 ± 62
ammonium	25.4 ± 1.1	536 ± 31
diethylammonium	33.7 ± 1.7	536 ± 31
ethylammonium	30.6 ± 1.0	442 ± 21
methylammonium	23.7 ± 0.7	310 ± 12
dimethylammonium	21.8 ± 1.0	278 ± 16
trimethylammonium	18.9 ± 1.9	232 ± 29

Conditions: 0.2×10^{-4} *M* LiDPA + 0.5×10^{-4} *M* LiOH + 0.2×10^{-4} *M* alkylammonium, potassium or ammonium chloride, 0.100 g powdered polyester foam, 100 mL solution, pH = 9.0, 24 h extraction time, three trials for each value, s = standard deviation.

Table 40   Distribution coefficients of the cations and DPA⁻ for the extraction of LiDPA, and alkylammonium, potassium and ammonium chlorides with polyester foam

DPA salt	Distribution coefficient (L/kg ± s)		
	Cation	Li^+	DPA^-
n-butylammonium	1560 ± 350	36.3 ± 11.1	3080 ± 360
potassium	1260 ± 150	55.2 ± 5.6	2160 ± 250
isobutylammonium	1150 ± 63	52.8 ± 5.6	2370 ± 40
n-propylammonium	886 ± 15	62.0 ± 9.9	2270 ± 170
isopropylammonium	681 ± 23	79.5 ± 6.6	1780 ± 180
t-butylammonium	668 ± 62	72.9 ± 5.9	2000 ± 50
ammonium	536 ± 31	96.6 ± 1.1	1490 ± 60
diethylammonium	509 ± 38	68.7 ± 1.7	1710 ± 20
ethylammonium	442 ± 21	74.7 ± 7.9	1490 ± 60
methylammonium	310 ± 12	97.2 ± 2.3	1310 ± 140
dimethylammonium	278 ± 16	83.6 ± 5.6	1420 ± 90
trimethylammonium	232 ± 29	92.4 ± 2.9	1230 ± 10

Conditions: 0.2×10^{-4} *M* LiDPA + 0.5×10^{-4} *M* LiOH + 0.2×10^{-4} *M* alkylammonium, potassium or ammonium chloride, 0.100 g powdered polyester foam, 100 mL solution, pH = 9.0, 24 h extraction time, three trials for each value, s = standard deviation.

Table 41 Comparison of the maximum distribution coefficients of the cations for the extraction of LiDPA + alkylammonium, potassium and ammonium chlorides; and NaTPB + alkylammonium, potassium and ammonium chlorides with polyester foam

Cation	Distribution coefficient (L/kg)	
	DPA	TPB
n-butylammonium	1560 ± 350	144
potassium	1260 ± 150	89.2
isobutylammonium	1150 ± 60	not determined
n-propylammonium	886 ± 23	89.6
isopropylammonium	681 ± 23	76.1
t-butylammonium	668 ± 62	77.6
ammonium	536 ± 31	71.3
diethylammonium	509 ± 38	not determined
ethylammonium	442 ± 21	67.9
methylammonium	310 ± 12	54.9
dimethylammonium	278 ± 16	50.0
trimethylammonium	232 ± 29	24.8

Conditions: Extraction with DPA: 0.2×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH + 0.2×10^{-4} M alkylammonium, potassium or ammonium chloride, 0.100 g powdered polyester foam, 100 mL solution, pH = 9.0, 24 h extraction time, three trials for each value, s = standard deviation.

Extraction with TPB: 1.0×10^{-4} M NaTPB + 1.0×10^{-4} M NaOH + 1.0×10^{-4} M alkylammonium, potassium or ammonium chloride, 0.800 g powdered polyester foam, 50 mL solution, pH = 9.0, values at total cations extracted / TPB$^-$ extracted $\approx$ 1.

Table 42 Comparison of the maximum distribution coefficients of the cations for the extraction of LiDPA, and alkylammonium, potassium and ammonium chlorides with polyether and polyester foams

Cation	Distribution coefficient (L/kg)	
	Polyester	Polyether
n-butylammonium	1560 ± 350	2380
potassium	1260 ± 150	1850
isobutylammonium	1150 ± 60	1880
n-propylammonium	886 ± 23	1700
isopropylammonium	681 ± 23	880
t-butylammonium	668 ± 62	1100
ammonium	536 ± 31	1610
diethylammonium	509 ± 38	810
ethylammonium	442 ± 21	698
methylammonium	310 ± 12	674
dimethylammonium	278 ± 16	359
trimethylammonium	232 ± 29	267

Conditions: Extraction with polyester foam: 0.2×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH + 0.2×10^{-4} M alkylammonium, potassium or ammonium chloride, 0.100 g powdered polyester foam, 100 mL solution, pH = 9.0, 24 h extraction time, three trials for each value, s = standard deviation.

Extraction with polyether foam: 0.5×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH + 0.5×10^{-4} M alkylammonium, potassium or ammonium chloride, 0.050 g powdered polyether foam, 100 mL solution, pH = 9.0, values at total cations extracted / DPA⁻ extracted ≈ 1.

and 0.5×10^{-4} M for the extraction with polyester and polyether foam respectively. The higher extraction of DPA$^-$ with polyether foam than polyester foam may arise from the different initial concentrations in solution. It may also be due to the inability of the ester oxygens to provide an optimal arrangement for hydrogen bonding with the protonated amine group. However, the difference of distribution coefficients between the extraction with polyether and that with polyester foam is smaller for the extraction with DPA$^-$ than with TPB$^-$ (Tables 26 and 42). The ether oxygens of polyether foam are prevented from interaction with the anions, TPB$^-$ or DPA$^-$, due to the helical structure of the polyethylene oxide portion of the foam as discussed in Section 4.3.1. Thus, the anions interact with the hydrophobic portion of the foam mainly due to their hydrophobicity. However, the ester oxygens of polyester foam are available to interact with the anions because the polyester portion of the foam assumes a zig-zag structure. The ester oxygens can have dipole-dipole interaction with the slightly positively charged nitrogen of the nitro group of DPA$^-$ in addition to hydrophobic interaction. This effect would increase the extractability of DPA$^-$ with polyester foam. On the other hand, the additional stabilizing effect on DPA$^-$ does not occur for TPB$^-$ extraction because TPB$^-$ contains only phenyl groups. As a result of this, the difference of distribution coefficients between the extraction with polyether and that with polyester foam is smaller for DPA$^-$ extraction relative to that for TPB$^-$ extraction. It should be pointed out that potassium extraction is higher than n-propylammonium with polyester foam but they have similar extraction with polyether foam (Table 42). The reason for this phenomenon is not understood.

4.3.4 Extraction by 100% Polypropylene Oxide Polyether Foam

The extraction of alkali metal DPAs and TPBs with polyether foam follows the order $K^+ \approx Rb^+ > Cs^+ > Na^+ > Li^+$. These results can be explained by the cation chelation

mechanism. The high extractability of K^+ is attributed to the good fit of K^+ in the cavity formed by the polyethylene oxide portion of the polyether foam. The lesser solvation of Rb^+ than K^+ in solution may result in the approximately equal extraction of K^+ and Rb^+. The polyether foam used consists of a mixture of polyethylene oxide and polypropylene oxide of unknown composition. Polyether foam containing only polypropylene oxide cannot readily assume a helical structure, and hence no such cavities are present to interact with the extracted cations. It was anticipated that the extractability sequence of alkali metals with 100% polypropylene oxide polyether foam would not be the same as that with polyether with polyethylene oxide. Thus, the extraction of alkali metal DPAs containing 100% polypropylene oxide polyether foam was studied.

4.3.4.1 Time Dependence of the Extraction

Solutions (100 mL) containing 0.5×10^{-4} M alkali metal DPA $+ 0.5 \times 10^{-4}$ M alkali metal hydroxide were extracted with 0.050 g powdered 100% polypropylene polyether foam. The results are given in Figures 50-54. Table 43 lists the ratio of cation extracted / DPA^- extracted as a function of time. The ratio is about 1 after 24 h extraction indicating that there is no imbalance of the cation and the anion extracted, with the exception of the LiDPA extraction. The extraction of cations and anions increases rapidly after 1/2 h extraction and levels off after 4 h extraction.

4.3.4.2 Selectivity for Alkali Metal Ions

Figures 55 and 56 show the extraction of the cations and DPA^- as a function of time. Table 44 gives the maximum distribution coefficients of the cations and DPA^-. The

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Figure 50   Extraction of LiDPA with 100% polypropylene oxide polyether foam as a
function of time.
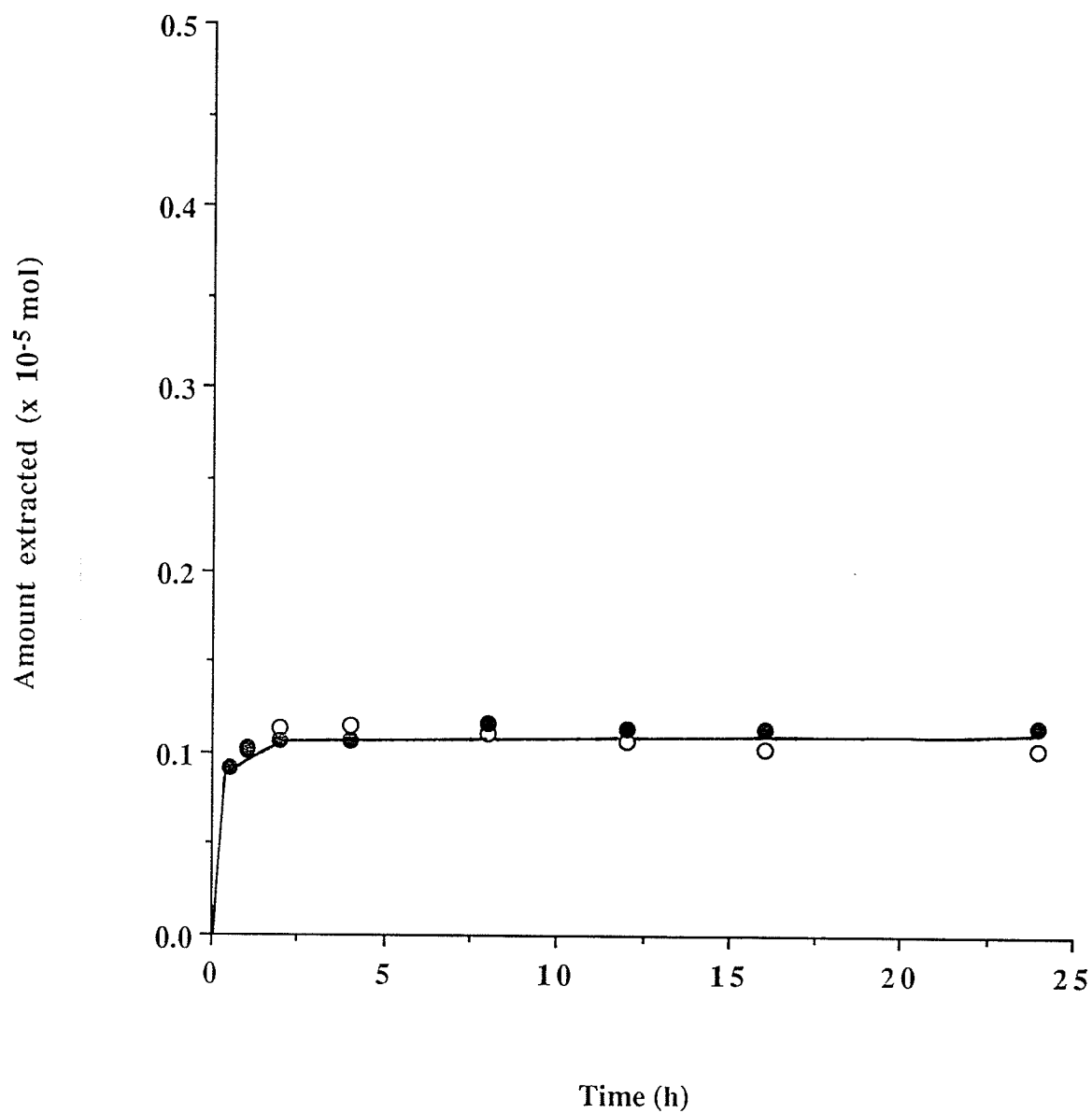
Time (h)

Conditions: 0.5×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH, 0.050 g powdered 100%
polypropylene oxide polyether foam, 100 mL solution, pH = 9.0, (●) DPA$^-$,
(o) Li$^+$.

Figure 51 Extraction of NaDPA with 100% polypropylene oxide polyether foam as a function of time.
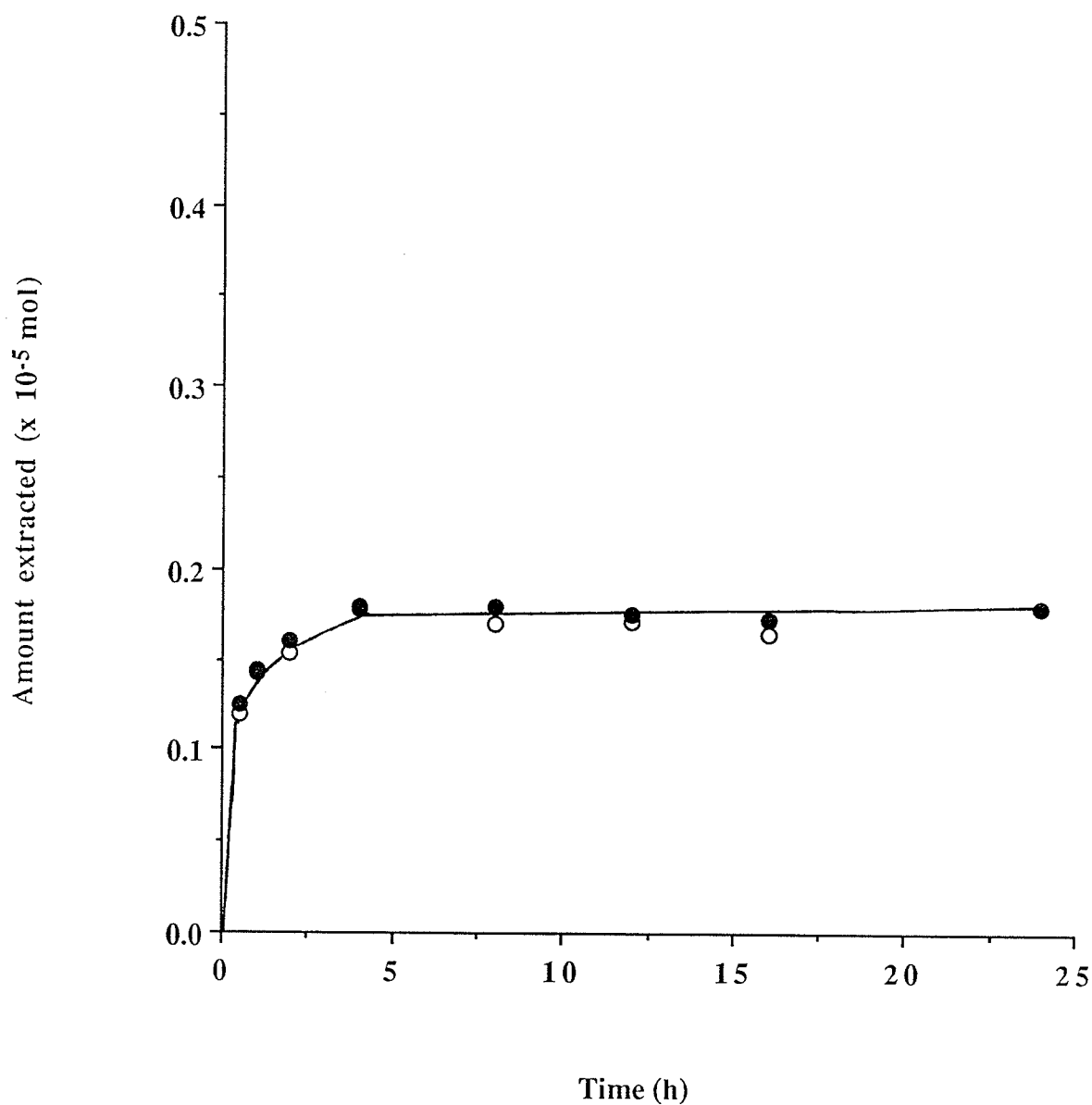
Conditions: 0.5 x 10^{-4} M NaDPA + 0.5 x 10^{-4} M NaOH, 0.050 g powdered 100% polypropylene oxide polyether foam, 100 mL solution, pH = 9.0, (●) DPA^{-}, (o) Na^{+}.

Figure 52   Extraction of KDPA with 100% polypropylene oxide polyether foam as a
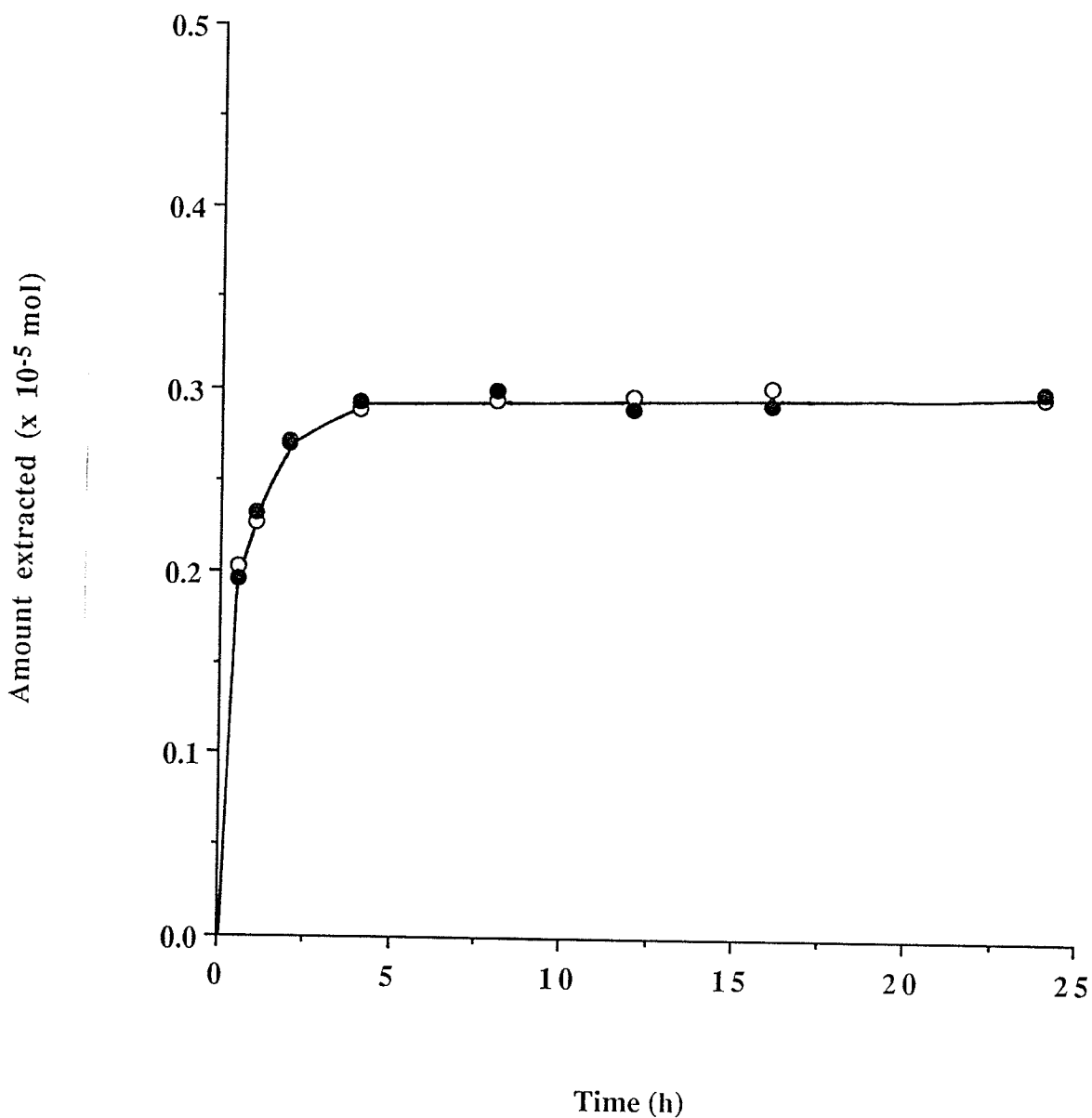
function of time.

Conditions: $0.5 \times 10^{-4}\ M$ KDPA + $0.5 \times 10^{-4}\ M$ KOH, 0.050 g powdered 100%

polypropylene oxide polyether foam, 100 mL solution, pH = 9.0, (●) DPA⁻,

(o) K⁺.

Figure 53   Extraction of RbDPA with 100% polypropylene oxide polyether foam as a function of time.
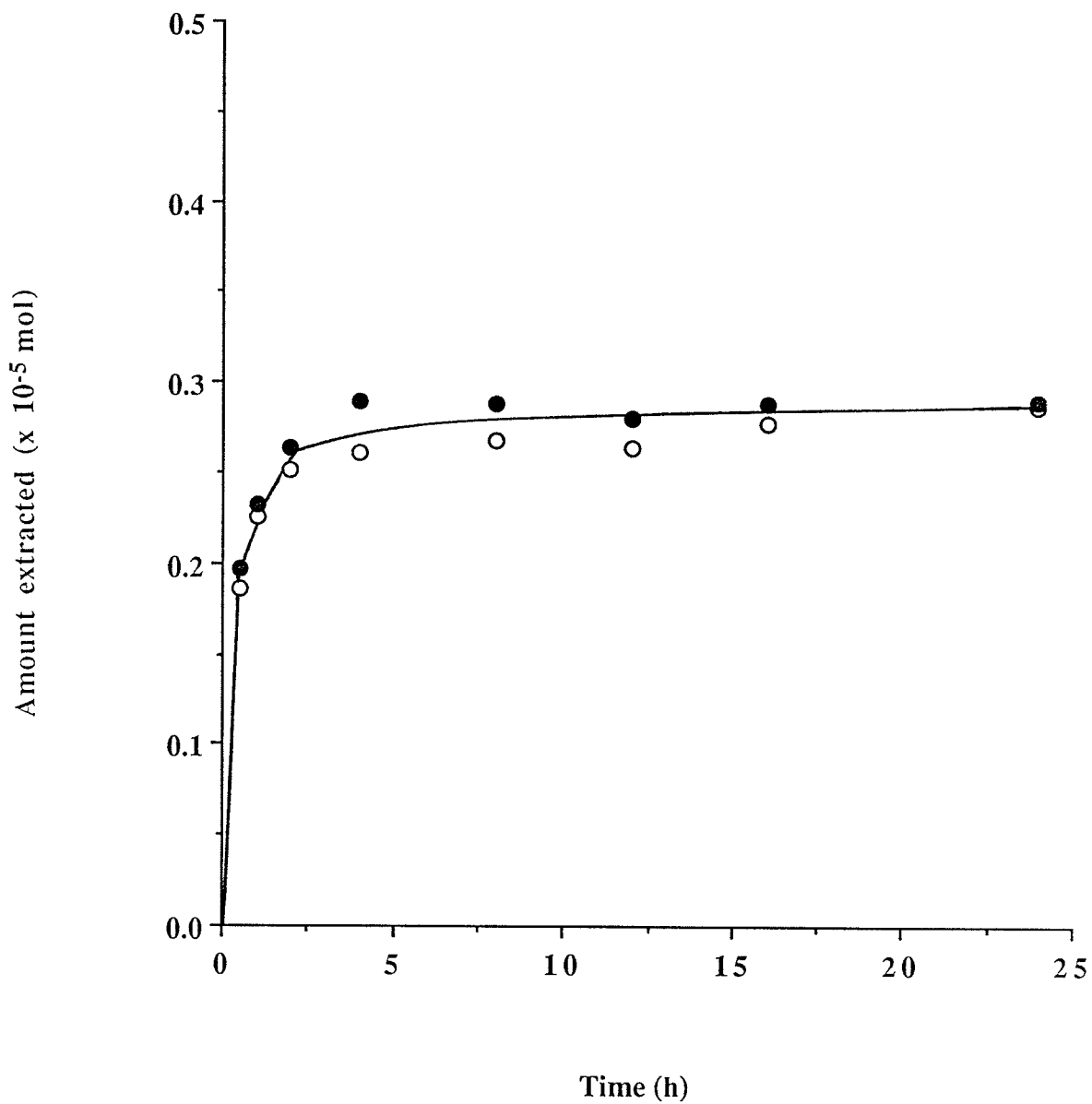
Conditions: 0.5 x 10^{-4} M RbDPA + 0.5 x 10^{-4} M RbOH, 0.050 g powdered 100% polypropylene oxide polyether foam, 100 mL solution, pH = 9.0, (•) DPA$^-$, (o) Rb$^+$.

Figure 54   Extraction of CsDPA with 100% polypropylene oxide polyether foam as a function of time.
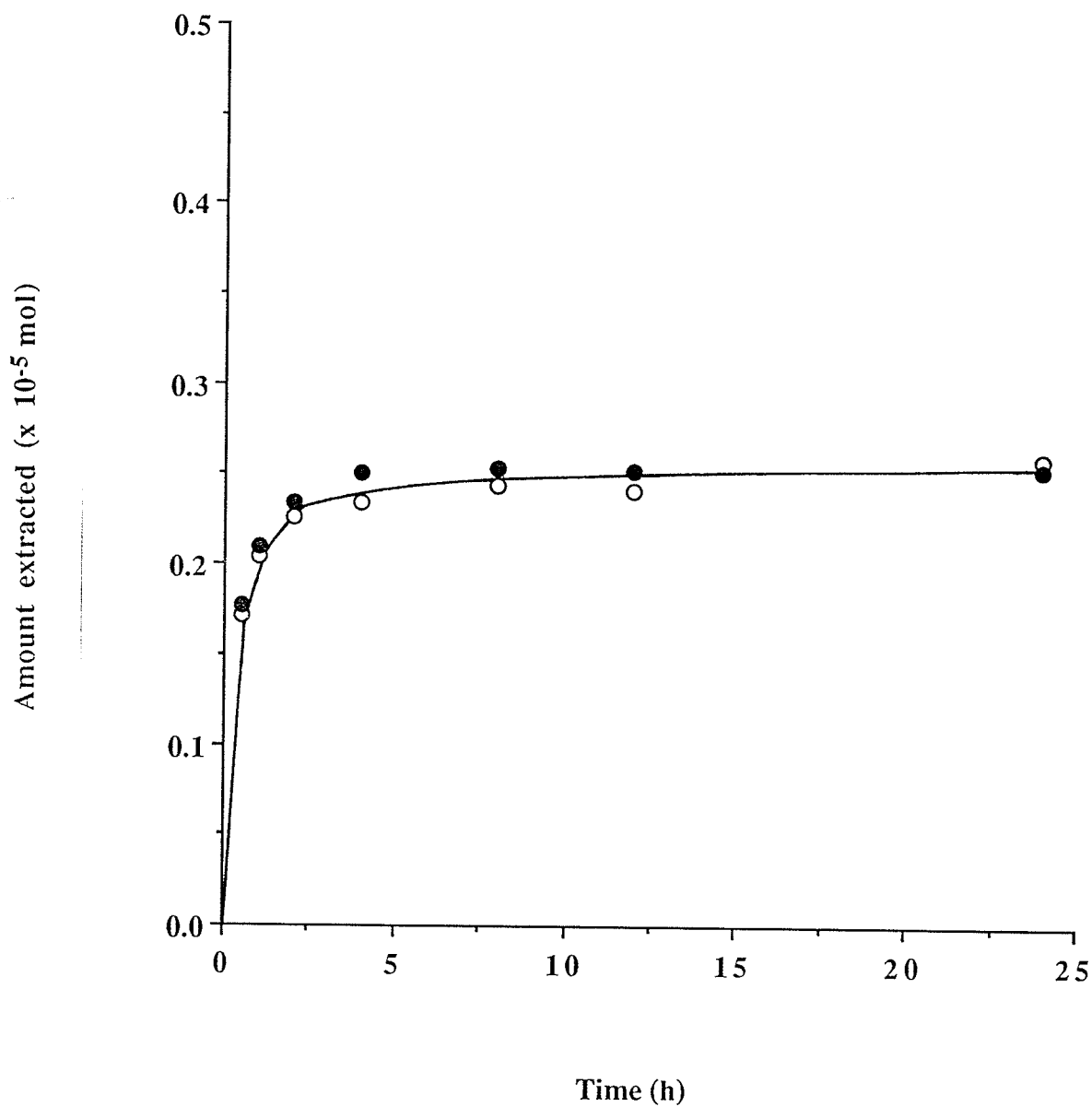
Conditions: 0.5×10^{-4} M CsDPA + 0.5×10^{-4} M CsOH, 0.050 g powdered 100% polypropylene oxide polyether foam, 100 mL solution, pH = 9.0, (●) DPA⁻, (o) Cs⁺.

Table 43   Ratio of cation extracted / DPA⁻ extracted as a function of time for the extraction of alkali metal DPAs with 100% polypropylene oxide polyether foam

		Cation extracted / DPA⁻ extracted			
Time (h)	LiDPA	NaDPA	KDPA	RbDPA	CsDPA
0.5	0.99	0.95	1.04	0.94	0.97
1.0	0.98	0.99	0.97	0.97	0.98
2.0	0.97	0.96	0.99	0.99	0.97
4.0	0.98	1.01	0.99	0.94	0.94
8.0	0.96	0.94	0.98	0.96	0.96
12.0	0.95	0.98	1.02	0.98	0.96
16.0	0.91	0.95	1.03	0.98	not determined
24.0	0.90	1.00	0.99	0.99	0.98

Conditions: 0.5×10^{-4} M alkali metal DPA + 0.5×10^{-4} M alkali metal hydroxide, 0.050 g powdered 100% polypropylene oxide polyether foam, 100 mL solution, pH = 9.0.

Figure 55 Plot of % cation extraction as a function of time for the extraction of alkali metal DPAs with 100% polypropylene oxide polyether foam.

Time (h)
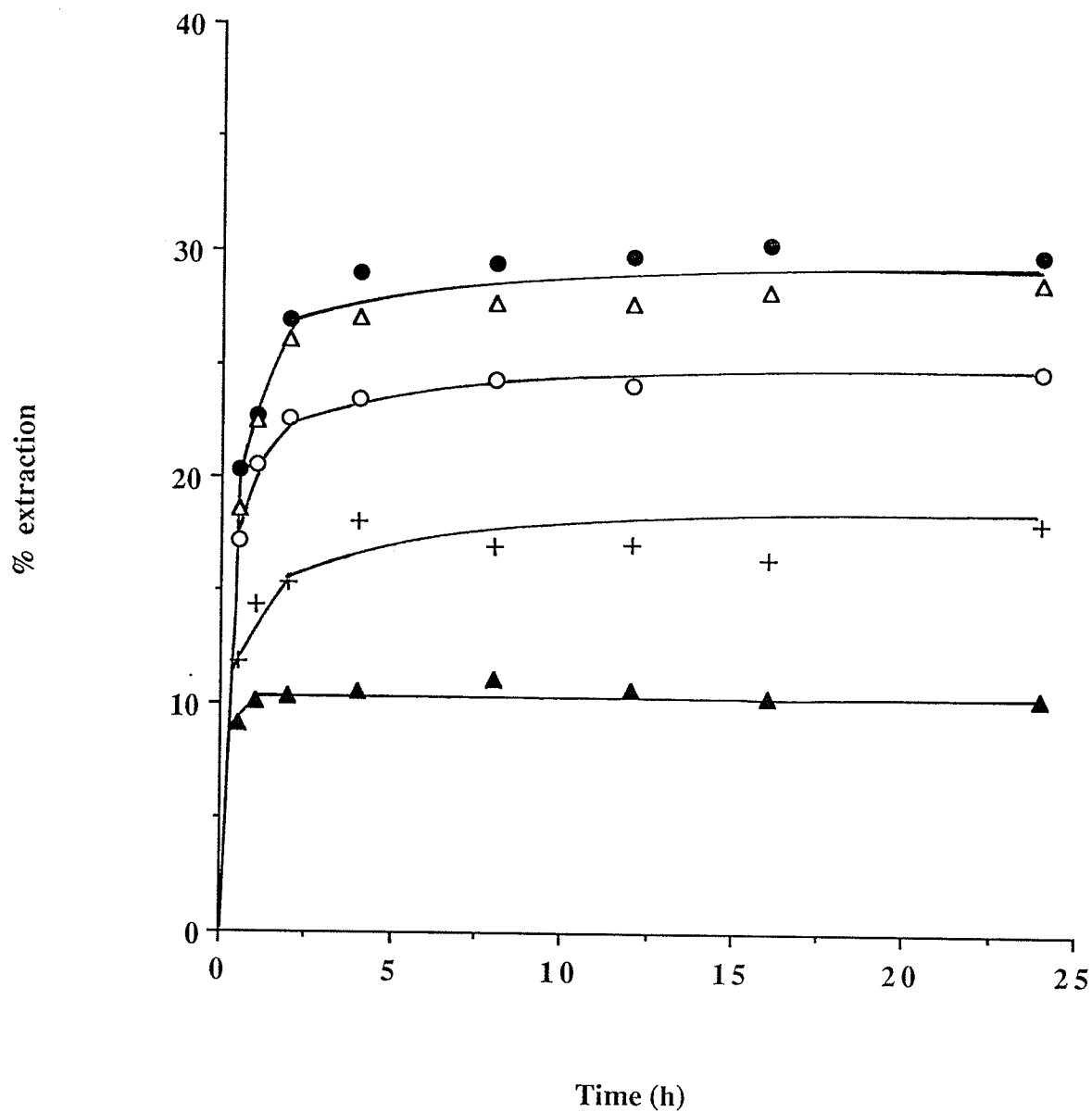
Conditions: 0.5 x 10^{-4} *M* alkali metal DPA + 0.5 x 10^{-4} *M* alkali metal hydroxide, 0.050 g powdered 100% polypropylene oxide polyether foam, pH = 9.0, (▲) Li^+, (+) Na^+, (●) K^+, (△) Rb^+, (o) Cs^+.

Figure 56 Plot of % DPA$^-$ extraction as a function of time for the extraction of alkali metal DPAs with 100% polypropylene oxide polyether foam.

Time (h)
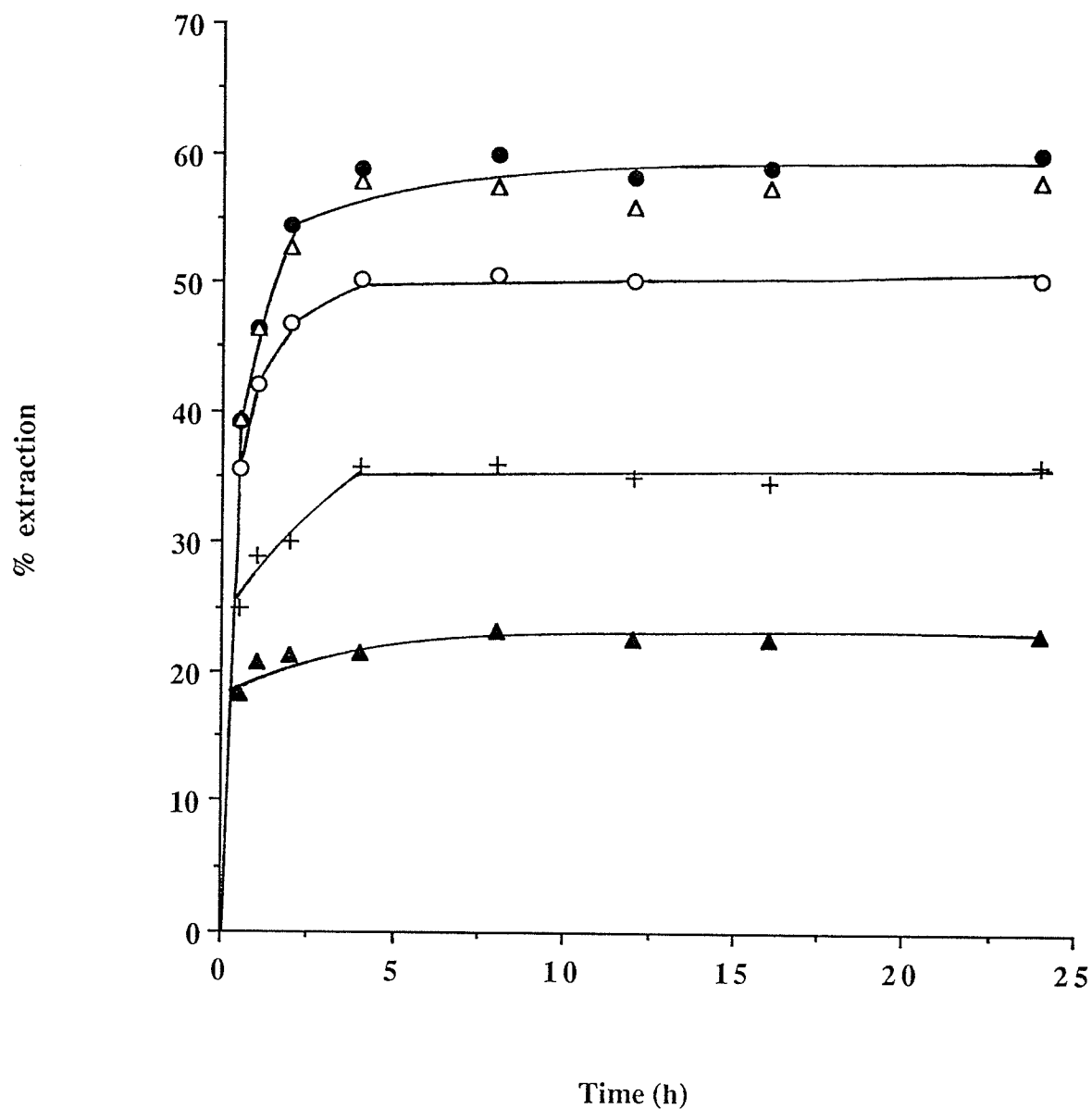
Conditions: 0.5 x 10^{-4} *M* alkali metal DPA + 0.5 x 10^{-4} *M* alkali metal hydroxide, 0.050 g powdered 100% polypropylene oxide polyether foam, pH = 9.0, (▲) Li$^+$, (+) Na$^+$, (●) K$^+$, (△) Rb$^+$, (o) Cs$^+$.

Table 44   Distribution coefficient and % extraction of alkali metal ions and DPA$^-$ for the extraction of alkali metal DPAs with 100% polypropylene oxide polyether foam

DPA salt	Cation		DPA$^-$	
	%extraction	Distribution coefficient (L/kg)	% extraction	Distribution coefficient (L/kg)
Li	10.3	232	23.1	604
Na	18.0	439	36.0	1130
K	29.9	860	60.1	3010
Rb	28.7	803	58.0	2760
Cs	24.8	660	50.5	2020

Conditions: 0.5 x 10^{-4} M alkali metal DPA + 0.5 x 10^{-4} M alkali metal hydroxide, 0.050 g powdered 100% polypropylene oxide polyether foam, 100 mL solution, pH = 9.0, 24 h extraction time.

extractability sequence of the alkali metals is $K^+ \approx Rb^+ > Cs^+ > Na^+ > Li^+$, which is the same as that for the extraction with the polyether foam containing polyethylene oxide. These results suggest that the high extractability of K^+ may not necessarily be due to a hole-size / cation-diameter relationship.

Some studies have been reported that the selectivity for alkali metals does not correlate with the hole size of crown ethers. For example, 15-crown-5 has a cavity in which Na^+ can be nicely fitted[106]. However, the stability constant of the Na^+ complex with 15-crown-5 in various solvents is about equal to or smaller than that of the K^+ complex[168,169]. Yamabe *et al.*[170] used CNDO/2 method to calculate the destabilization energy ΔE_{destab} due to conformational change for the complex formation and the complexation energy ΔE_{comp} for the interaction of K^+ and Na^+ with 18-crown-6 and 12-crown-4 in aqueous solution. It was found that the destabilization energy is relatively small compared with the complexation energy indicating that conformational change is not responsible for the selectivity of crown ethers. To form the complex, the ion has to be desolvated, and hence the stabilization energy ΔE_{stab} can be expressed as

$$\Delta E_{stab} = \Delta E_{comp} - \Delta E_{hyd} \qquad (48)$$

where ΔE_{hyd} is the hydration energy of the ion. The calculation shows that ΔE_{comp} for Na^+ is higher than that for K^+ suggesting stronger interaction of Na^+ with the crown ether than of K^+. On the other hand, ΔE_{hyd} for Na^+ is higher than that for K^+. As a result of this, ΔE_{stab} for K^+ is higher than for Na^+ and the K^+ complex is more stable than the Na^+ complex. This study demonstrates that although Na^+ can interact more strongly with crown ethers than K^+, the higher energy required to desolvate the Na^+ ion makes the K^+ complex formation more favourable. It was concluded that the solvent effect seems to have

the largest contribution to the selectivity of 18-crown-6 regarding the complexation with cations.

Michaux and Reisse[171] studied the interactions of 18-crown-6, 15-crown-5 and 12-crown-4 with Na^+ and K^+ in methanol and water. ΔG^o, ΔH^o and ΔS^o for the complex formation were determined by potentiometric titrations. It was found that the crown ether interactions are stronger with Na^+ than with K^+ and the selectivity for K^+ is due to the lower desolvation energy for K^+. The results illustrate that the interactions of crown ethers with cations do not correlate with size of the hole in the crown ether or with cation size. Wipff et al.[172] reached the same conclusion with the study of 18-crown-6 and its alkali metal complexes by molecular mechanics calculation.

Gokel et al.[173] determined the stability constants for the homologous series of crown ethers ranging from 12-crown-4 to 24-crown-8 with Na^+, K^+, NH_4^+ and Ca^{2+} in anhydrous methanol solution by potentiometric methods. It was found that for this series of crown ethers and cations, K^+ is bound more strongly than Na^+, Ca^{2+} or NH_4^+ by all of the crown ethers irrespective of hole size and the strongest binding is obtained with 18-crown-6 irrespective of cation size or geometry. It was pointed out that there are four factors making major contributions to the complexation of cations with crown ethers as follows: (1) the hole-size / cation-diameter relationship, (2) the solvation energy of the cations, (3) the number of donor atoms participating in binding, (4) the conformation of the complexed and uncomplexed crown ether.

The above studies illustrate the importance of the solvent effect in determining the selectivity of crown ethers for alkali metals. A hole-size / cation-diameter relationship is not imperative for the selectivity for alkali metals. Similarly, the existence of a hole-size / cation-diameter relationship is not necessary to explain the high extractability of K^+ for the extraction with 100% polypropylene polyether foam.

4.3.5　Solvent Effect

4.3.5.1　Alkali Metal DPA

Studies[170-173] have shown the significance of the solvent effect on the selectivity for alkali metals. It was decided to study the extraction of alkali metal DPAs from methanol. It was found that the DPAs were almost nonextractable with 0.050 g polyether foam. It was necessary to increase the foam weight to 0.500 g and to decrease the volume of solution to 50 mL for any observable extraction of DPA$^-$. Figure 57 shows the extractions of 0.5 M NaDPA (50 mL) with 0.500 g powdered polyether foam as a function of time. The extraction of Na$^+$ and DPA$^-$ increases rapidly up to 1 h and then levels off with increasing extraction times. The extraction of Na$^+$ is much lower than that of DPA$^-$ and this could be because of the large amount of residual H$^+$ present in the foam since 0.500 g foam was used rather than 0.100 g for the extraction from aqueous solution, resulting in the competitive extraction of HDPA. Table 45 gives the extraction and distribution coefficient of the cations and DPA$^-$ for the extraction of the alkali metal DPAs with polyether foam. The selectivity for alkali metals follows the order: K$^+$ $\approx$ Rb$^+$ > Cs$^+$ > Na$^+$ > Li$^+$, which is the same as that obtained for the extraction from water.

Table 46 compares the distribution coefficients of the cations and DPA$^-$ for the extraction of alkali metal DPAs with polyether foam from water and methanol. The values for the extraction from water are much higher than those from methanol. A similar phenomenon has been reported for the extraction of alkali metal DPAs from aqueous-organic solutions into nitrobenzene[144]. These effects may be due to the higher solubility of DPA$^-$ in organic solvents than in water. Alternatively, it may be caused by the water structure-enforced ion-pairing (WSEIP)[174]. Interactions between the dipoles of water molecules and associations of these molecules through hydrogen bonds result in clusters of

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Figure 57   Extraction of NaDPA with polyether foam from methanol as a function of time.
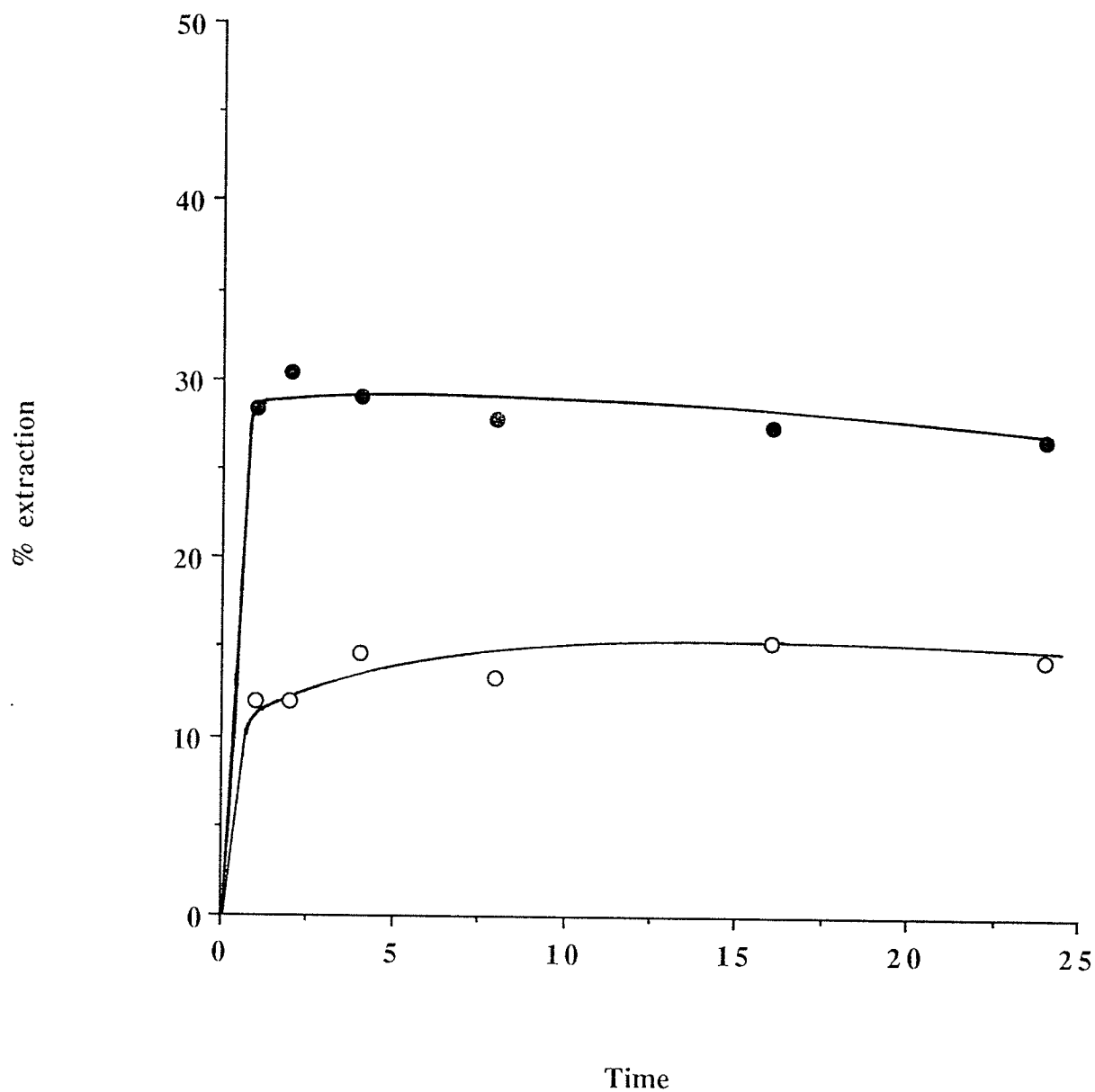
Conditions: $0.5 \times 10^{-4}\ M$ NaDPA, 0.500 g powdered polyether foam, 50 mL solution,

(●) DPA⁻, (o) Na⁺.

Table 45   Distribution coefficient and % extraction of alkali metal ions and DPA^- for the extraction of alkali metal DPAs with polyether foam from methanol

DPA salt	Cation		DPA^-	
	$\% \pm s$	Distribution coefficient $(L/kg \pm s)$	$\% \pm s$	Distribution coefficient $(L/kg \pm s)$
Li	0	0	25.3	33.6
Na	11.9	13.4	30.4	43.6
K	35.5 ± 2.7	55.1 ± 6.5	36.5 ± 2.4	57.5 ± 5.9
Rb	32.7 ± 2.2	48.6 ± 3.7	37.0 ± 1.2	58.9 ± 2.9
Cs	30.1 ± 1.1	42.9 ± 2.2	35.5 ± 0.5	55.0 ± 1.2

Conditions: 0.5×10^{-4} M alkali metal DPA, 0.500 g powdered polyether foam, 50 mL solution, 2 h extraction time, three trials for each value, s = standard deviation.

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Table 46   Comparison of the distribution coefficients of the cations and DPA⁻ for the extraction of alkali metal DPAs with polyether foam from water and methanol

	Distribution coefficient (L/kg)			
	Water		Methanol	
DPA salt	Cation	DPA⁻	Cation	DPA⁻
Li	405	1450	0	33.6
Na	691	2590	13.4	43.6
K	1300	7530	55.1 ± 6.5	57.5 ± 5.9
Rb	1210	6480	48.6 ± 3.7	58.9 ± 2.9
Cs	1050	5070	42.9 ± 2.2	55.0 ± 1.2

Conditions: Extraction from water:

$0.5 \times 10^{-4}\ M$ alkali metal DPA + $0.5 \times 10^{-4}\ M$ alkali metal hydroxide, 0.050 g powdered polyether foam, 100 mL solution, pH = 9.0, cation extracted / DPA⁻ extracted ≈ 1.

Extraction from methanol:

$0.5 \times 10^{-4}\ M$ alkali metal DPA, 0.500 g powdered polyether foam, 50 mL solution, 2 h extraction time, three trials for each value, s = standard deviation.

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water molecules which are reminiscent of the hexagonal structure of ice (Figure 58)[175]. In WSEIP, the hydrogen-bonded water structure forces the bulky hydrophobic ions together to form ion-pairs rather than placing the ions separately. This effect maximizes the water-water interactions and minimizes the disturbance to the water structure. Methanol molecules can also be hydrogen-bonded and form clusters, but it is not so highly structured as in water. Thus, methanol with a lower dielectric constant than water which normally favours ion-pair formation is less effective to effect ion-pairing because of the absent or lower WSEIP. This results in the lower extraction of alkali metal DPA from methanol than from water. Although the lower extraction of alkali metal DPA can be explained by the higher solubility of DPA^- in methanol, it is likely that the WSEIP effect of water to promote the ion-pair formation is the driving force for the extraction of alkali metal DPA from water because less bulky and hydrophobic anions such as salicylate, 1-amino-2-naphthol-4-sulfonate and cinnamate are not extractable from water.

4.3.5.2 Alkali Metal Hydroxide

From Table 45, it can be seen that DPA^- is extractable, but Li^+ is nonextractable. It was thought that this is because of the presence of a residual amount of H^+ in the foam causing the competitive extraction of HDPA. Thus, polyether foam was washed with 0.02 M LiOH and was used to extract 50 mL 0.5 x 10^{-4} M LiDPA. The extraction of DPA^- lowered to 11% from 25%, but Li^+ was still not extractable. The extraction of 0.5 x 10^{-4} M NaDPA (50 mL) with the LiOH-treated foam (0.500 g) was carried out to determine whether NaDPA is extractable from methanol. DPA^- extraction decreased to 13% and Na^+ extraction was 39%. The higher extraction of Na^+ than DPA^- indicates that NaOH is extractable.

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Figure 58   Structure of ice[175].
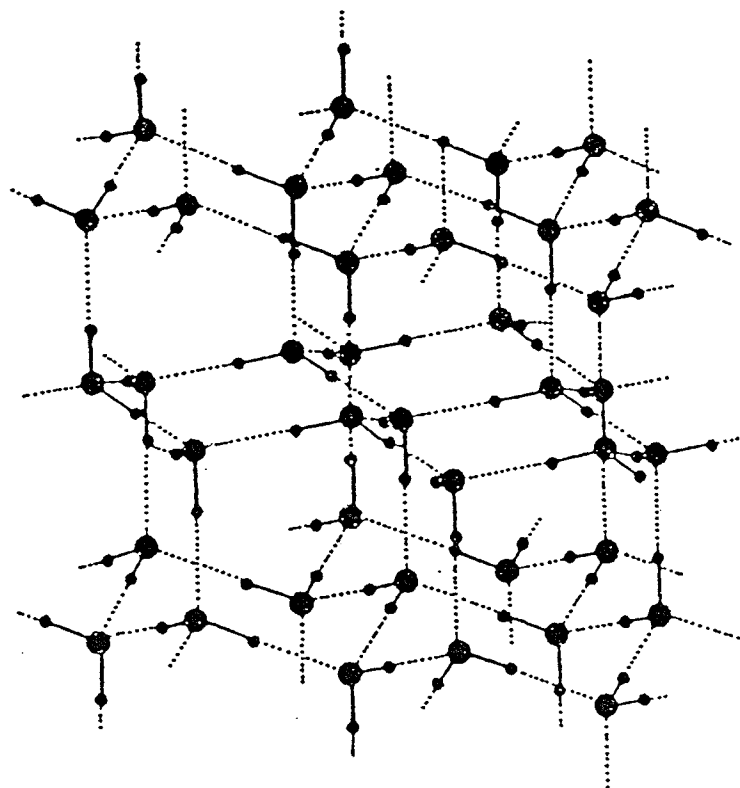
The large circles are oxygen atoms and the smaller ones are hydrogen atoms.

Therefore, the extraction of 0.5×10^{-4} *M* alkali metal hydroxide (50 mL) with 0.500 g polyether foam was studied. Table 47 shows the extractions and distribution coefficients of the cations. The extractability sequence of alkali metals is $Cs^+ \approx Rb^+ > K^+ > Na^+ > Li^+$. This order is different from that obtained for the extraction of alkali metal DPAs which is $K^+ \approx Rb^+ > Cs^+ > Na^+ > Li^+$. It should be noted that OH^- is very hydrophilic and the ion-pairing process is different from that with DPA^-. The ion-pairing for alkali metal hydroxides is governed by electrostatic attraction between the cation and the anion as shown in Equation (49)[176].

$$u_{12} = z_1 z_2 e^2 / \varepsilon_0 \varepsilon r \qquad\qquad (49)$$

where u = potential energy of the ion-pairing

   r = distance apart of the ions

   z_1 = charge number of the cation

   z_2 = charge number of the anion

   e = elementary charge

   ε_0 = absolute permittivity of free space

   ε = relative permittivity of the medium

The solvated ionic radii of alkali metals decrease in the order $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$, and hence the association constants of alkali metal salts should follow the order $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. However, the extractability of the cations is also dependent on the magnitude of the interaction of the cation with foam. Results of the extraction of alkali metal DPAs from water suggest that K^+ has the strongest interaction with foam. If this interaction of K^+ with foam is able to offset the high association of CsOH and RbOH, the sequence of extractability may not be the same as $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. It appears that the interaction of K^+ with polyether foam is not strong enough to compensate

Table 47   Distribution coefficient and % extraction of alkali metal ions for the extraction of alkali metal hydroxides with polyether foam from methanol

Cation	% extraction	Distribution coefficient (L/kg)
Li^+	7.1	7.7
Na^+	34.6	53.2
K^+	47.2	89.1
Rb^+	51.8	108
Cs^+	53.5	114

Conditions: $0.5 \times 10^{-4}\ M$ alkali metal hydroxide, 0.500 g powdered polyether foam, 50 mL solution, 2 h extraction time.

for the lower association of KOH in methanol relative to Cs^+ and Rb^+, and hence the extractability sequence of $Cs^+ \approx Rb^+ > K^+ > Na^+ > Li^+$ was obtained. Nevertheless, these results demonstrate the importance of the solvent effect on the selectivity for the cations.

DPA^- is very hydrophobic and ion-pairing in methanol is not based mainly on electrostatic interaction as for alkali metal hydroxides. The ion-pairing process is likely to be more similar to the water structure-enforced ion-pairing (WSEIP) even though methanol is not so structured as water. Although the trend of ion-pairing should be the same as for alkali metal hydroxides, the difference of association constants between alkali metal DPAs may be lower than that for alkali metal hydroxides. Jawaid and Ingman[166] studied the extraction of ion-pairs between the Na^+ and K^+ complexes of dicyclohexyl-18-crown-6 and picric acid and dipicrylamine from aqueous solution into dichloromethane. It was found that the selectivity for cations decreases with increasing hydrophobicity of the anions. As the anion becomes more hydrophobic, it promotes ion-pairing with the less hydrophobic cations due to the WSEIP effect. In effect, this would narrow the difference of ion-pairings between a series of cations of different hydrophobicities and the anion. DPA^- is much more hydrophobic than OH^-, it is likely that the difference of ion-pairings between alkali metal DPAs is lower than for alkali metal hydroxides. The high interaction of K^+ with polyether foam may overcome the lower ion-pairing of KDPA compared with Rb and CsDPAs, and hence the extractability sequence of $K^+ \approx Rb^+ > Cs^+ > Na^+ > Li^+$ was observed.

The extraction of 0.5×10^{-4} M alkali metal hydroxide with 0.500 g polyester foam was also studied. Table 48 shows the extraction and distribution coefficient of the cations. The extractability sequence is $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ which is the same as that for the extraction of alkali metal DPAs from water into nitrobenzene[165]. This result is indicative of the increasing importance of the solvent effect. The extractions of the cations are lower than those for polyether foam; however, the difference of the extractions between

Table 48   Distribution coefficient and % extraction of alkali metal ions for the extraction of alkali metal hydroxides with polyester foam from methanol

Cation	% extraction	Distribution coefficient (L/kg)
Li$^+$	0	0
Na$^+$	0	0
K$^+$	12.6	7.2
Rb$^+$	22.6	14.6
Cs$^+$	27.7	19.1

Conditions: 0.5 x 10^{-4} M alkali metal hydroxide, 0.500 g powdered polyester foam, 50 mL solution, 2 h extraction time.

the cations is higher than for polyether foam. Since the selectivity for the cations is determined by the overall effect of ion-pairing in methanol and interaction of the cation with foam, a lower interaction between the cation and polyester foam would cause the solvent effect to become more significant. The results have shown that the interaction of the cation with polyester foam is weaker than with polyether foam because of the lower extraction of alkali metal DPAs with polyester foam. Thus, the larger difference of the extractabilities of the cations is a result of the lower interaction of the cations with polyester foam.

4.3.6   Extraction Mechanism

Many inorganic extraction systems can be explained by the cation chelation mechanism[34,35,37,38,42,48,131]. It is considered that the strong cation chelation of M^+ by the polyether is the driving force for the extraction of the anionic metal complex MeX_n^{m-}. An anion-exchange process may be operating if another extractable anion A^- is present (Equations 48-50).

$$M^+_{(aq)} \rightleftharpoons M^+_{(foam)} \qquad (50)$$

$$M^+_{(foam)} + MeX_n^{m-}{}_{(aq)} \rightleftharpoons M^+.MeX_n^{m-}{}_{(foam)} \qquad (51)$$

$$M^+.MeX_n^{m-}{}_{(foam)} + A^-_{(aq)} \rightleftharpoons M^+.A^-_{(foam)} + MeX_n^{m-}{}_{(aq)} \qquad (52)$$
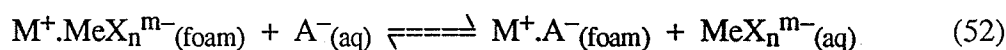
Adams[131] studied the extraction of aurocyanide ion-pairs with alkali metal ions into organic solvents with long-chain polyethers. It was found that at high KCl concentrations as a background electrolyte, the extraction of $Au(CN)_2^-$ decreases because of the competitive extraction of Cl^- (Equation 51).

$$M^+.Au(CN)_2^-{}_{(foam)} + Cl^-_{(aq)} \rightleftharpoons M^+.Cl^-_{(foam)} + Au(CN)_2^-{}_{(aq)} \qquad (53)$$
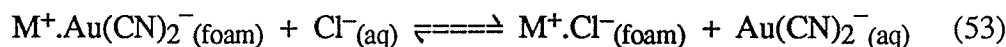
A similar anion-exchange phenomenon has been reported by Al-Bazi and Chow[35] on the extraction of palladium(II) thiocyanate complex with polyether foam. For the present study, the concentrations of the cations and the anion varied from 0.2 to 1.0 x 10^{-4} M as opposed to 1 to 2 M in the other studies. No displacement of the anions was observed. Experiments were carried out to determine whether KCl is extractable by extracting 0.5 x 10^{-4} M KCl solution (100 mL) with 0.500 g polyether and polyester foam. It was found that KCl is nonextractable. The cations are also nonextractable using salicylates and cinnamates as counter ions (Chapter 2). Only in the presence of very hydrophobic anions such as TPB^- and DPA^- are alkali metals ions extractable from water. The results suggest that the hydrophobicity of the anions is a determining factor on the extraction of alkali metals from water by polyether and polyester foams. It appears that the water structure-enforced ion-pairing (WSEIP) is the driving force for the extraction of the alkali metal salts.

With respect to the selectivity for alkali metals, two factors play an important role:

(1) ion-pairing in the aqueous phase

(2) interaction of the cation with foam

For ion-pairing in the aqueous phase, the trend is $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ because of the increasing solvation of the cation from Cs^+ to Li^+. If this is the major contributor, the extractability of alkali metals should be $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. In fact, this order has been reported on the extraction of alkali metal DPAs[165] and picrates[177] from water into nitrobenzene. However, the effect of interaction of the cation with foam has to be considered. If the interaction with foam is strong, the extractability sequence can be changed. According to the cation chelation mechanism the polyethylene oxide portion of the foam can form a cavity which has a good fit with K^+ and this results in the high extractability of K^+. It appears that the cation chelation mechanism can explain the results of alkali metal DPAs and TPBs with polyether foam because the extractability sequence is $K^+ \approx Rb^+ > Cs^+ > Na^+ > Li^+$. However, the results from the extraction of alkali metal

DPAs with 100% polypropylene oxide polyether foam also have the highest extraction for K^+. Polypropylene oxide does not normally assume a helical structure, and therefore is not able to form an oxygen-rich cavity as easily or as effectively as polyethylene oxide. This suggests that a hole-size / cation-diameter relationship is not necessary for the strong interaction of K^+ with the foam. It should be noted that the interaction of the cation with foam is dependent on the properties of the foam as follows:

(1)   the number of oxygen atoms present

(2)   the distance between successive oxygen atoms in the polymer

(3)   the nature of the oxygen-containing groups

(4)   the ftraction of oxygen atoms which are available to interact with cations

On the basis of electrostatic attraction, Li^+ should have the strongest interaction with the oxygens in the foam because of the smallest ionic radius relative to the other alkali metal ions if it is assumed that the ions are completely desolvated. Motomizu and Toei[160] reported that the association constants of alkali metal DPAs in nitrobenzene saturated with water are smaller than those in dry nitrobenzene indicating that the alkali metal ions are solvated. Rais *et al.*[164] determined the number of water molecules coextracted with alkali metal DPAs from water into nitrobenzene and the values are 4.2, 3.6 and 1.0 for Li^+, Na^+ and K^+ respectively. These results show that the alkali metal ions are not completely desolvated in nitrobenzene. Similarly, it would be expected that the alkali metal ions are partially solvated by water in the extraction with foam. The cations are displaced in the extraction of alkali metal DPAs with polyether foam. The degree of displacement is indicative of how strongly the cations interact with the foam. Table 49 shows the amount of the cations displaced at 24 h for the extraction of alkali metal DPAs with polyether foam from water. The amount of cation displacement, Δ cation, was calculated according to Equation (54) by using the results of Figures 34-38.

Table 49   Amount of cation displacement for the extraction of alkali metal DPAs with polyether foam

Cation	Amount of displacement (x 10^{-5} mol)
Li^+	0.114
Na^+	0.082
K^+	0.034
Rb^+	0.054
Cs^+	0.061

Conditions: 0.5×10^{-4} *M* alkali metal DPA + 0.5×10^{-4} *M* alkali metal hydroxide, 0.050 g powdered polyether foam, 100 mL solution, pH = 9.0, 24 h extraction time.

$$\Delta \text{ cation } = \text{DPA}^- \text{ extraction } - \text{ cation extraction} \qquad (54)$$

The displacement follows the order of $Li^+ > Na^+ > Cs^+ > Rb^+ > K^+$. Similarly, the displacement sequence is $Li^+ > Na^+ > K^+$ for the extraction with polyester foam. Thus, K^+ has the strongest interaction with the foam. Although Li^+ should have the strongest interaction based on electrostatic consideration, the more solvated Li^+ results in the weakest interaction with the foam. These results illustrate that K^+ interacts most strongly with the foam. The strong interaction of K^+ with the foam is able to compensate for the lower association in the aqueous phase relative to Rb^+ and Cs^+ and hence the extraction sequence $K^+ \approx Rb^+ > Cs^+ > Na^+ > Li^+$ was obtained for the extraction with polyether and 100% polypropylene oxide polyether foams.

In conclusion, the interaction of the cation with foam plays an important role in determining the selectivity for alkali metals as in the cation chelation mechanism. The proposed mechanism differs from the cation chelation mechanism in that a hole-size / cation-diameter relationship is not required to explain the observed selectivity with polyether and 100% polypropylene oxide polyether foams. The strong interaction of K^+ with these foams can be a result of the strong electrostatic interaction with the foam and the low solvation of the extracted K^+.

4.4 Conclusion

This study illustrates that both polyether and polyester foams can extract alkali metal and alkylammonium cations in the presence of DPA^-. The extraction of the cations and DPA^- is higher for polyether than for polyester foam. This can be explained by the ester oxygens being farther apart resulting in a weaker interaction with the cations. The

extraction of the alkylammoniums shows that the extractability of these cations is affected by hydrophobic interaction, steric, and inductive effects.

The extractability sequences are $K^+ \approx Rb^+ > Cs^+ > Na^+ > Li^+$ for polyether and 100% polypropylene oxide polyether foam and $K^+ \approx Rb^+ \approx Cs^+ > Na^+ > Li^+$ for polyester foam. It seems that the cation chelation mechanism could account for these results. However, the extraction with 100% polypropylene oxide polyether foam suggests that a helical structure of the polyether foam is not required for a high extraction of K^+. Alternatively, the extraction order can be explained by a delicate balance of the solvent effect and the interaction of the cation with foam. The strong interaction of K^+ with foam is a result of a stronger electrostatic interaction with foam relative to Rb^+ and Cs^+ and a lower solvation of K^+ compared with Na^+ and Li^+. It agrees with the cation chelation mechanism in that there is strong solvation of the cation by the foam. However, this interpretation is different from the cation chelation mechanism in that the hole-size / cation diameter relationship is not necessarily responsible for the selectivity for alkali metals.

The study of the extraction from methanol demonstrates the importance of the solvent effect. It indicates that the water structure-enforced ion-pairing (WSEIP) may be the driving force for the extraction of the alkali metal DPAs and TPBs. The extraction of alkali metal hydroxides from methanol shows that the extent of ion-pairing is the determining factor for the selectivity for alkali metal ions when the interaction of the cation with foam is relatively weak, and produces an extractability sequence of $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$.

CHAPTER 5

IMBALANCE OF CATION
AND ANION EXTRACTIONS

5.1   Introduction

The previous results described in Chapters 3 and 4 have demonstrated that the ratio of cation extracted / anion extracted was less than 1 in many experiments. For example, for the extraction of LiDPA with polyether foam, the Li^+ extracted / DPA^- extracted ratio decreases from 0.88 after 0.5 h extraction to 0.57 after 24 h extraction (Figure 34 and Table 30). For the extraction of NaDPA with polyether foam, the Na^+ extracted / DPA^- extracted ratio decreases from 1.00 to 0.73 for 0.5 and 24 h extraction respectively (Figure 35 and Table 30). A decrease in the cation extraction after reaching a maximum with extraction time was observed for both cases. However, there is also a significant difference between the amount of Li^+ and DPA^- extracted after 0.5 h in the extraction of LiDPA. The imbalance of the cation and the anion extracted after a short extraction time can be considered to be due to some time-independent effect, whereas the steady decline of cation extraction as a function of extraction time can be regarded as a result of some time-dependent effect. The imbalance of the cation and the anion extracted was greatest for the extraction with Li^+ as the cation, therefore further investigations of the extraction of LiDPA under different conditions were conducted to determine the possible causes of the time-dependent and the time-independent effects.

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5.2 Experimental

It is the same as in Chapter 4.

5.3 Results and Discussion

5.3.1 Effect of Residual H_3O^+

For the extraction of NaTPB with 0.800 g polyester foam, the pH of the solution changes from 9.0 to 8.4 (Figure 26). The ratio of Na^+ extracted / TPB^- extracted is 0.88 after 0.5 h extraction (Table 20). When the amount of polyester foam was reduced to 0.100 g for the extraction of NaDPA, the ratio of Na^+ extracted / DPA^- extracted after 0.5 h is 1.03 and the pH of the solution remains at 9.0 (Figure 43 and Table 36). The extractions of Na^+ with TPB^- and with DPA^- were compared rather than those of Li^+ because Na^+ was always present for the extraction of alkali metal cations with TPB^-. It is reasonable that residual H_3O^+ on the foam may cause the lowering of pH of the solution. More residual H_3O^+ would be present in 0.8 g than 0.1 g foam, and hence a decrease in pH of the solution in contact with 0.8 g foam would be observed. Moreover, HDPA or HTPB can coextract with NaDPA or NaTPB and can give rise to the lower Na^+ extracted / anion extracted ratio with increasing foam weight.

To demonstrate that there is residual H_3O^+ on the foam, the pH of a solution (100 mL) containing 0.5×10^{-4} M KOH with varied amounts of polyether foam washed with 0.1 M HCl and water was studied. The sample vials were kept in a vacuum desiccator to eliminate CO_2 absorption from air. Figure 59 shows that the pH of the solution decreases as foam weight increases, indicating increasing amount of residual H_3O^+ with increasing foam weight. There is only a slight decrease in pH of the solution from 1.5 to 16.0 h of

Figure 59   Effect of foam weight on the pH of the solution
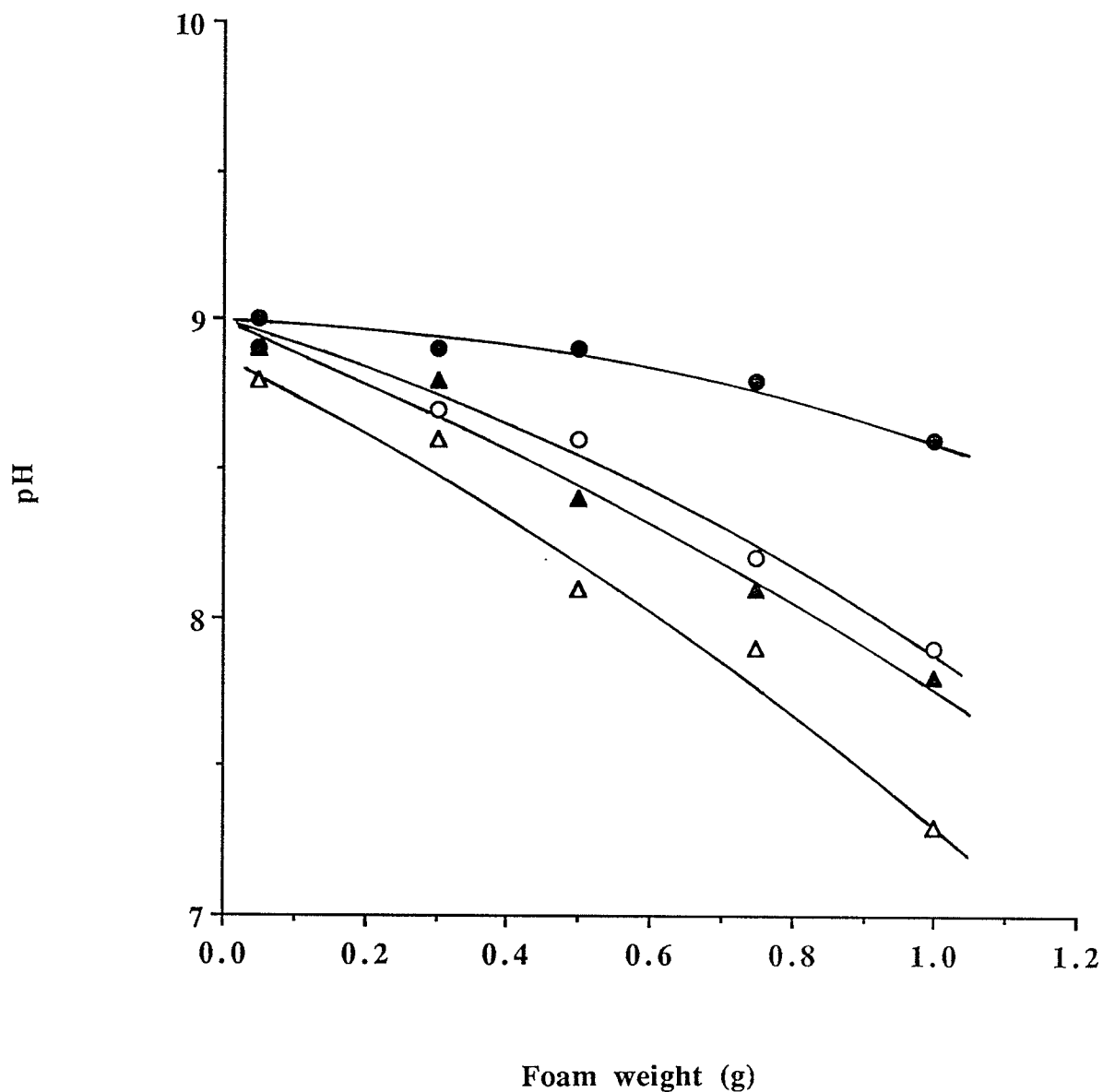
Conditions: $0.5 \times 10^{-4}\,M$ KOH, 100 mL solution, initial pH = 9.0; (●) water-washed

polyether foam, 1.5 h contact time; (▲) acid-washed polyether foam, 1.5 h

contact time; (o) water-washed polyether foam, 16.0 h contact time; (Δ)

acid-washed polyether foam, 16.0 h contact time.

contact for foam weight less than 0.3 g which is the highest polyether foam weight used in all the extractions in this study, so it can be considered that the major effect of the residual H_3O^+ takes place within 1.5 h.

Since foam washed with only water can reduce the amount of residual H_3O^+, foam washed with alkali solution should further reduce the residual H_3O^+. Therefore, the extraction of a solution (100 mL) containing 0.5×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH with 0.050 g polyether foam washed with 0.1 M KOH was investigated. The foam was soaked in 0.1 M KOH solution for 5 h. Then the foam was washed with 100 mL water twice. Not all of the KOH was removed from the foam because there was a detectable amount of K^+ in a solution of 0.5×10^{-4} M LiOH with 0.050 g foam. The difference of K^+ in a solution containing 0.5×10^{-4} M LiOH and that containing 0.5×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH was considered to be the amount of K^+ extracted as KDPA. The amount of Li^+ extraction increases from 0.16×10^{-5} mol (Figure 34) for the extraction with acid-washed foam to 0.22×10^{-5} mol (Figure 60) for the extraction with KOH-treated foam after 0.5 h extraction. The ratios of total cations ($Li^+ + K^+$) extracted / DPA^- extracted were 1.03 and 0.88 for KOH-treated foam and acid washed foam respectively. These results indicate that the removal of residual H_3O^+ could increase the extraction of Li^+ and residual H_3O^+ appears to be responsible for the time-independent decrease of the cation extraction. However, a decline of the cation extraction after reaching a maximum was still observed with increasing extraction time. Thus, some other factors must be involved in the time-dependent decrease of the cation extraction.

5.3.2 Effect of Foam Type

There are two principal methods of polyurethane foam preparation: (1) one-shot and

Figure 60   Extraction of LiDPA with KOH-treated polyether foam as a function of time
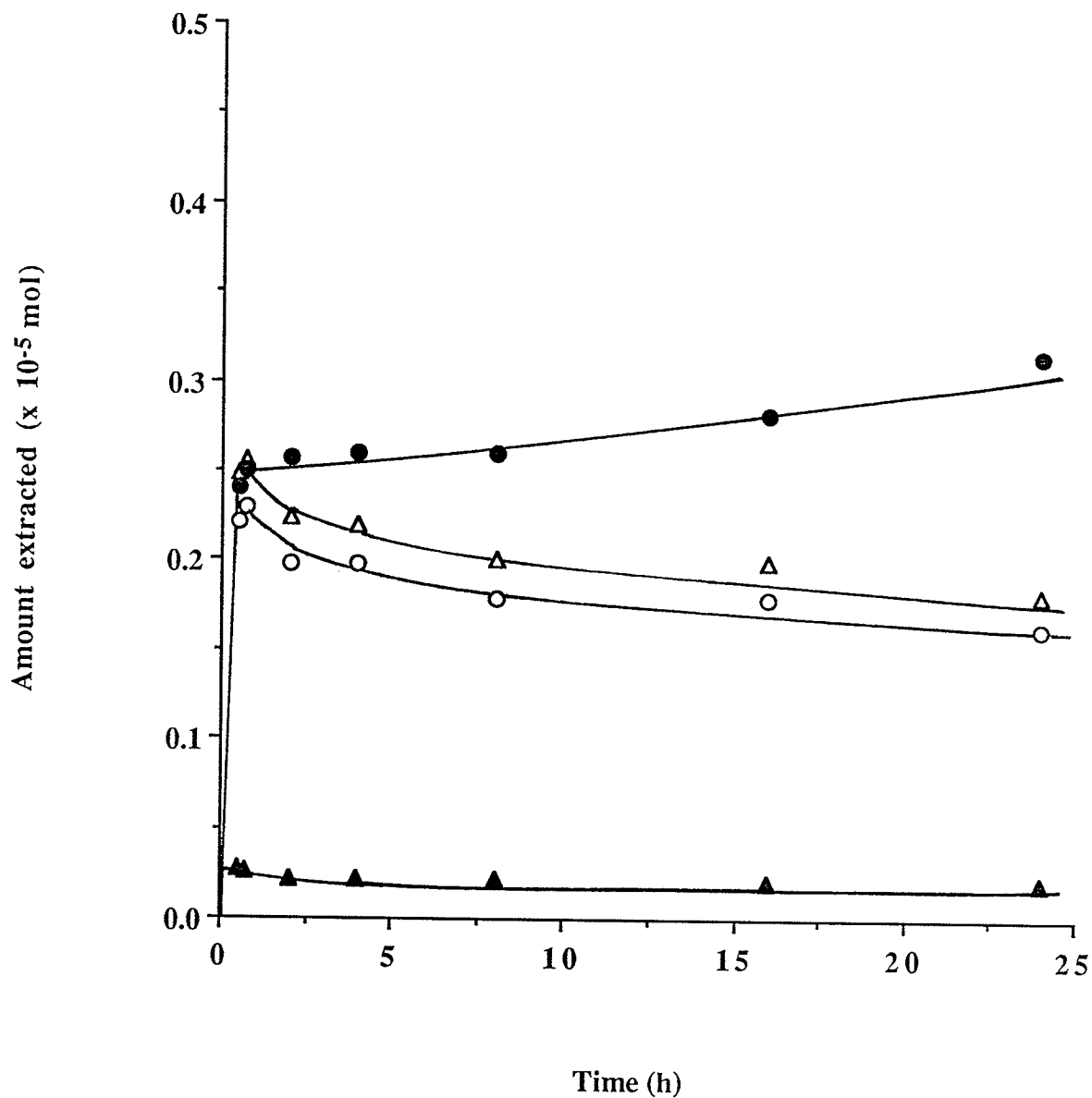
Conditions: 0.5×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH, 0.050 g KOH-treated powdered

polyether foam, 100 mL solution, pH = 9.6, (●) DPA⁻, (o) Li⁺, (▲) K⁺,

(Δ) total cations (Li⁺ + K⁺).

(2) prepolymer. Commercially available foams are generally prepared by the one-shot method. In this process, the various foam components are mixed simultaneously with the addition of catalysts. Organometallic tin compounds such as tin octanoate, dibutyltin dioctanoate and dibutyltin acetate are widely employed as catalysts to promote the isocyanate-hydroxyl reaction. Tertiary amines such as trimethylamine, N,N'-diethylpiperazine and tribenzylamine are used to catalyze the isocyanate-water reaction. In the prepolymer process, a polyether or polyester is reacted with an excess of diisocyanate prior to foaming to yield the isocyanate-terminated prepolymer. Foaming occurs by a reaction of the prepolymer with water to form urea linkages and carbon dioxide, which acts as the blowing agent. There is no catalyst added in the prepolymer method.

Braun *et al*.[96] studied the impurities present in polyurethane foam by the neutron activation method. The foams were washed with HNO_3 , water and acetone before the analysis. It was found that tin is the major impurity in polyether-type foam and that the amount of tin present in polyester-type foam is very much lower. It was concluded that tin is probably covalently bonded to the polymer and cannot be removed by the washing process.

If some cations are present in the foam as impurities, which can displace the extractable cations, and this displacement is a slow process, a decrease in the extractable cations with increasing extraction time might be observed. The cleaning procedure in this study is similar to that employed by Braun *et al*. with the exception of using HCl. Accordingly, tin should be the major impurity in the foam. It is probable that tin might cause the Li^+ displacement. It was decided to use a type of foam containing no tin for the extraction of LiDPA to determine whether there is Li^+ displacement. Foam prepared by the prepolymer method should not contain tin because no tin catalyst is used. Hypol polyether prepolymer was obtained from W. R. Grace & Co.. Hypol polymer was prepared by mixing the prepolymer with water in 1:1 weight ratio. The foam was washed with water

and then acetone. It was ground to a powder by the procedure described before. Solutions (100 mL) containing 0.5×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH were extracted with 0.050 g powdered Hypol foam. Figure 61 shows the extraction of Li^+ and DPA^- as a function of time. The ratio of Li^+ extracted / DPA^- extracted and the amount of Li^+ displacement are listed in Table 50. There is almost no displacement of Li^+ for the extraction with Hypol foam which contains no tin. These results suggest that tin present in the foam may cause the displacement of Li^+ and other cations.

To determine the amount of tin in foam, the foam was first dry ashed in a muffle furnace at 450°C for 4 h and then the ash was dissolved in 5 % v / v HNO_3 solution. The resulting solution was analyzed by graphite furnace atomic absorption spectrometry. It was found that polyether foam contains 0.73×10^{-3} mol tin / kg foam corresponding to 0.04×10^{-6} mol tin in 0.050 g polyether foam. This amount of tin is too small to account for the displacement of Li^+, 0.114×10^{-5} mol (Equation 54 and Figure 34). Therefore, it appears that tin in the foam is not a major contributor to the displacement of Li^+.

No detectable amount of tin was found in Hypol foam. Experiments of the extraction with Hypol foams coated or incorporated with tin were carried out to determine whether there is any increase in Li^+ displacement. Hypol foam was coated with a tin catalyst of unknown composition used for polyurethane foam preparation by dissolving the catalyst in dioxane and then by evaporating to dryness. The tin-incorporated Hypol foam was prepared by mixing 1:1 the prepolymer and water containing the tin catalyst. The extraction of a solution (100 mL) containing 0.5×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH with 0.050 g tin-coated and tin-incoporated Hypol foams as a function of time was studied. The results are given in Figures 62 and 63. The extraction of Li^+ and DPA^- increases slightly in the presence of tin. However, there is no displacement of Li^+ for either type of foams after 24 h extraction. The amounts of tin were found to be 25×10^{-3} mol / kg and 0.60×10^{-3} mol / kg for the tin-incorporated foam and the tin-coated foam respectively.

Figure 61   Extraction of LiDPA with Hypol foam as a function of time
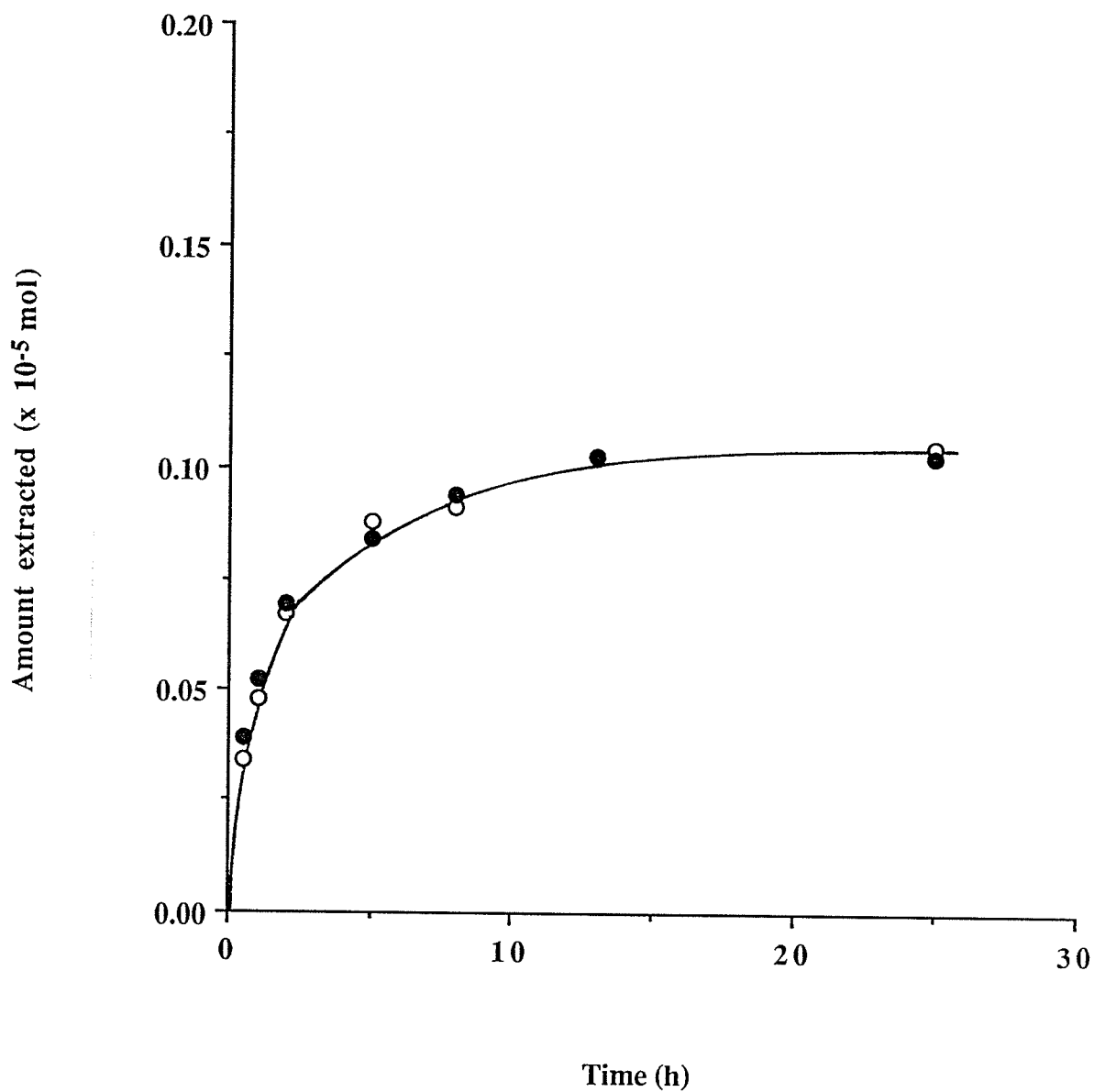
Conditions: 0.5×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH, 0.050 g powdered Hypol foam, 100 mL solution, pH = 9.0, (●) DPA⁻, (o) Li⁺.

Table 50   Ratio of Li^+ extracted / DPA^- extracted and the amount of Li^+ displacement for the extraction of LiDPA with Hypol foam as a function of time

Time (h)	Li^+ extraction / DPA^- extraction	$DPA^- - Li^+$ (x 10^{-5} mol)
0.5	0.92	0.003
1.0	0.92	0.004
2.0	0.97	0.002
5.0	1.05	−0.004
8.0	0.97	0.003
13.0	1.00	0.000
25.0	1.02	−0.002

Conditions: 0.5 x 10^{-4} M LiDPA + 0.5 x 10^{-4} M LiOH, 0.050 g powdered Hypol foam, 100 mL solution, pH = 9.0.

Figure 62   Extraction of LiDPA with tin-coated Hypol foam as a function of time
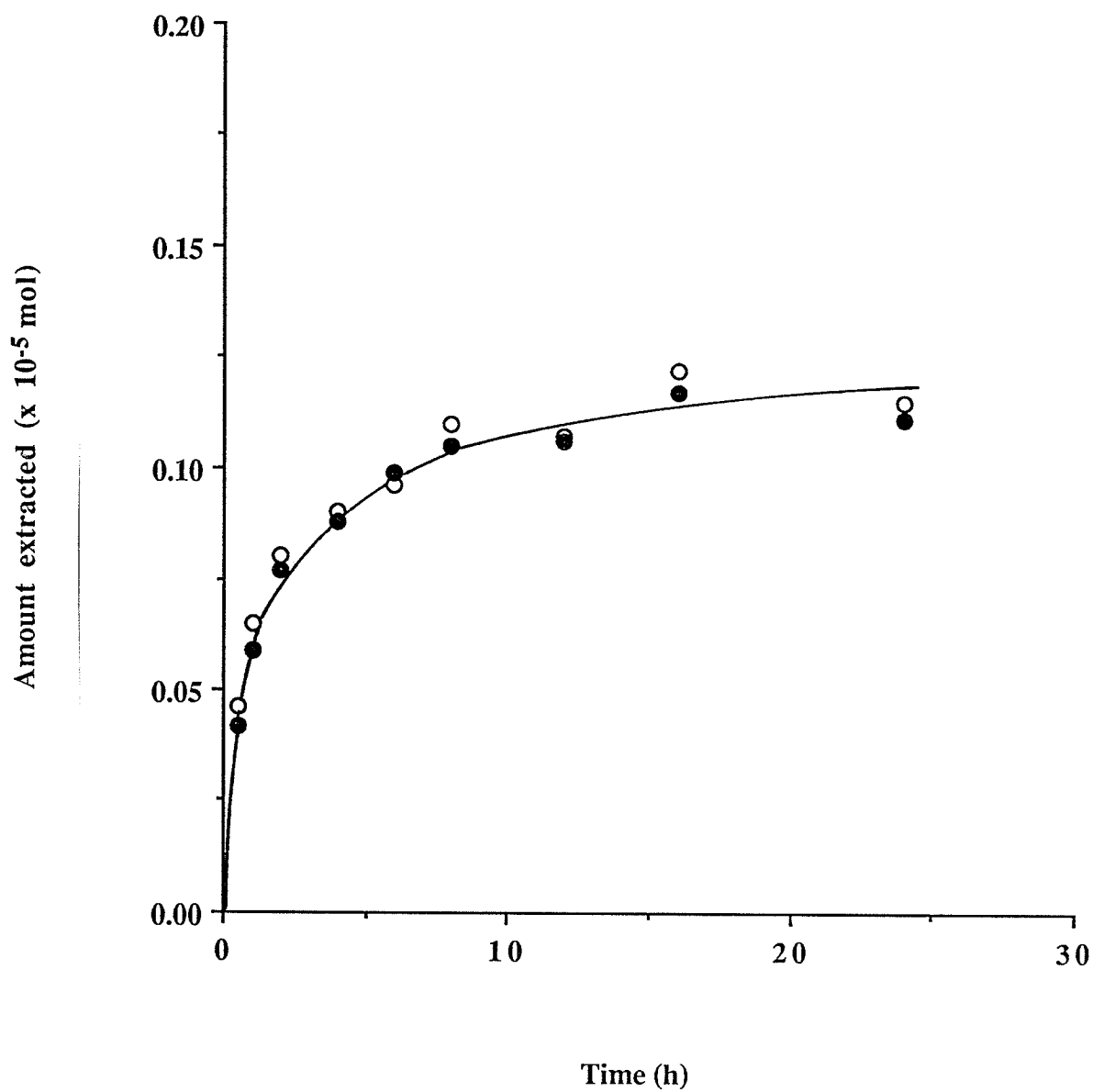
Conditions: 0.5×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH, 0.050 g powdered tin-coated
Hypol foam, 100 mL solution, pH = 9.0, (●) DPA⁻, (o) Li⁺.

Figure 63   Extraction of LiDPA with tin-incorporated Hypol foam as a function of time
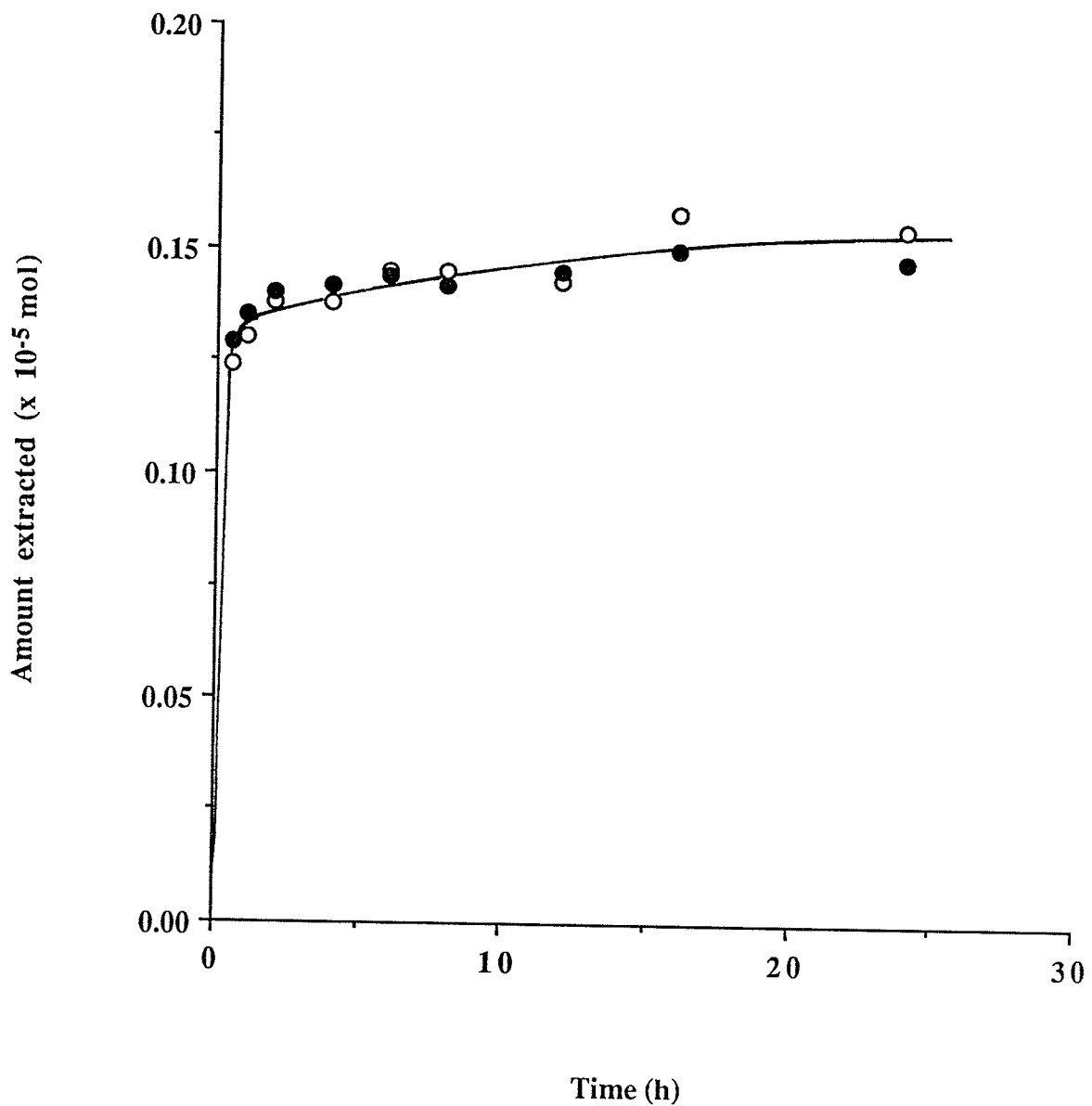
Conditions: $0.5 \times 10^{-4}\ M$ LiDPA + $0.5 \times 10^{-4}\ M$ LiOH, 0.050 g powdered tin-incorporated Hypol foam, 100 mL solution, pH = 9.0, (●) DPA^-, (o) Li^+.

The corresponding amounts of tin in 0.050 g foam are 1.2×10^{-6} mol for tin-incoporated foam and 0.03×10^{-6} mol for tin-coated foam. These results suggest that the tin compound is not likely to cause the Li^+ displacement since the tin-incorporated foam containing such a high tin content was not able to effect any Li^+ displacement.

5.3.3 Effect of CO_2 Absorption

The absorption of CO_2 from air can be time-dependent and it may result in a time-dependent displacement of Li^+. Therefore, the extraction of a solution (100 mL) containing 0.5×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH with 0.050 g polyether foam in N_2 was studied. The plastic vials were enclosed in a large plastic bag filled and purged with N_2. The bag was evacuated before filling with N_2 to eliminate air. The results for the extraction in N_2 and in air are shown in Figure 64. Although there is a small decrease in Li^+ displacement and in DPA^- extraction in N_2, an appreciable amount of Li^+ displacement is still occurring. It appears that CO_2 absorption may have a small effect but it cannot account for all the Li^+ displacement observed.

5.3.4 Effect of Decomposition

The decline of Li^+ extraction was considered to be due to the displacement by other cations because DPA^- is not known to decompose in aqueous solution. Nevertheless, if there is a gradual decomposition of DPA^- on the foam to form some neutral species, it might cause Li^+ to come off the foam and back into the aqueous solution. It was thought that if there were any decomposition on the foam, it might occur more rapidly at higher temperature. Thus, the extraction of a solution (100 mL) containing 0.5×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH with 0.050 g polyether foam at 65°C as a function of time was studied.

Figure 64 Effect of CO_2 absorption from air on the extraction of LiDPA with polyether foam as a function of time
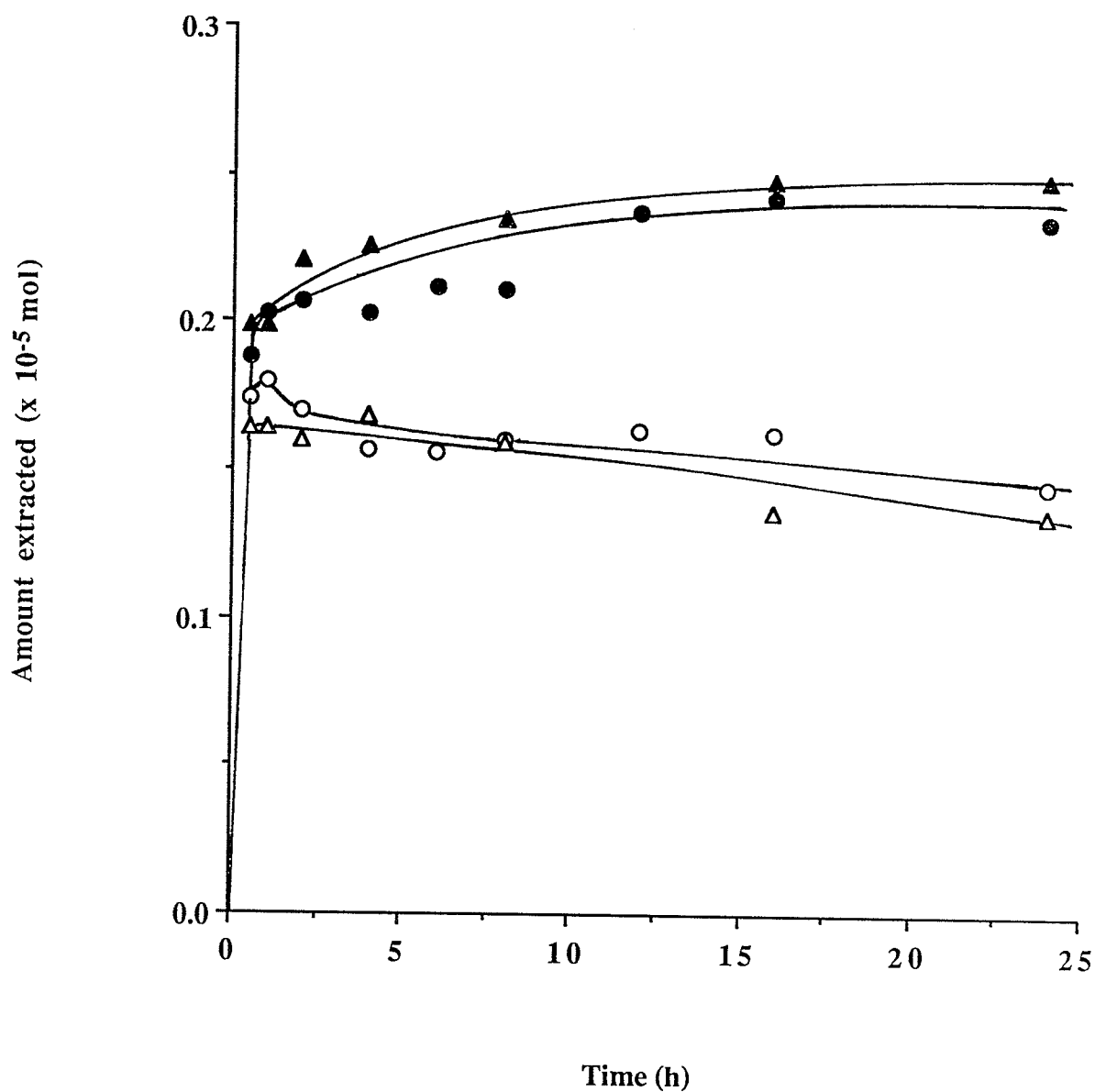
Conditions: 0.5×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH, 0.050 g powdered polyether foam, 100 mL solution, pH = 9.0; (●) DPA^-, in N_2; (o) Li^+, in N_2; (▲) DPA^-, in air ; (Δ) Li^+, in air.

The sample vials were immersed in a water bath kept at 65°C and were manually shaken periodically. Figure 65 shows that the extraction of DPA⁻ and Li⁺ decreases compared with the extraction at 20°C. Li⁺ extraction maximizes after 0.25 h and decreases rapidly with increasing extraction time, whereas DPA⁻ extraction increases steadily. These results might be interpreted as arising from DPA⁻ decomposition on the foam. It was decided to strip DPA⁻ from the foam by back-extracting into acetone. The foam after extracting with the aqueous solution for 24 h was filtered and back-extracted four times into 25.0 mL acetone. Table 51 lists the result of DPA⁻ recovery. An almost complete recovery of DPA⁻ was obtained after four extractions. Moreover, no difference in the UV-spectrum was observed for the back-extracted DPA⁻ and LiDPA in acetone, with λ_{max} at 416 nm. It is likely that DPA⁻ does not decompose on the foam. Futhermore, decomposition of DPA⁻ on the foam cannot explain why Li⁺ has the highest imbalance of the cation and the anion extractions among the alkali metal cations because it would be expected that the imbalance be the same for all the cations.

5.3.5 Effect of pH

There is not much H_3O^+ present in solution at pH 9.0. However, at this pH, much of the dissolved CO_2 is in the form of HCO_3^- in solution. If HDPA is highly extractable, a continuous shift of HCO_3^- to H_3O^+ and CO_3^{2-} in solution could result in a gradual increase of DPA⁻ extraction and a decrease of Li⁺ extraction by a displacement process with increasing extraction time. When the pH of the solution is lowered, there would be an increase of H_3O^+ in solution which may compete more effectively with Li⁺ to extract along with DPA⁻. This may have the effect of Li⁺ extraction without a maximum followed by a decline of Li⁺ extraction but with a plateau at a relatively short extraction time. Therefore, the extraction of a solution (100 mL) containing 0.5×10^{-4} M LiDPA + 0.5×10^{-4} M LiCl

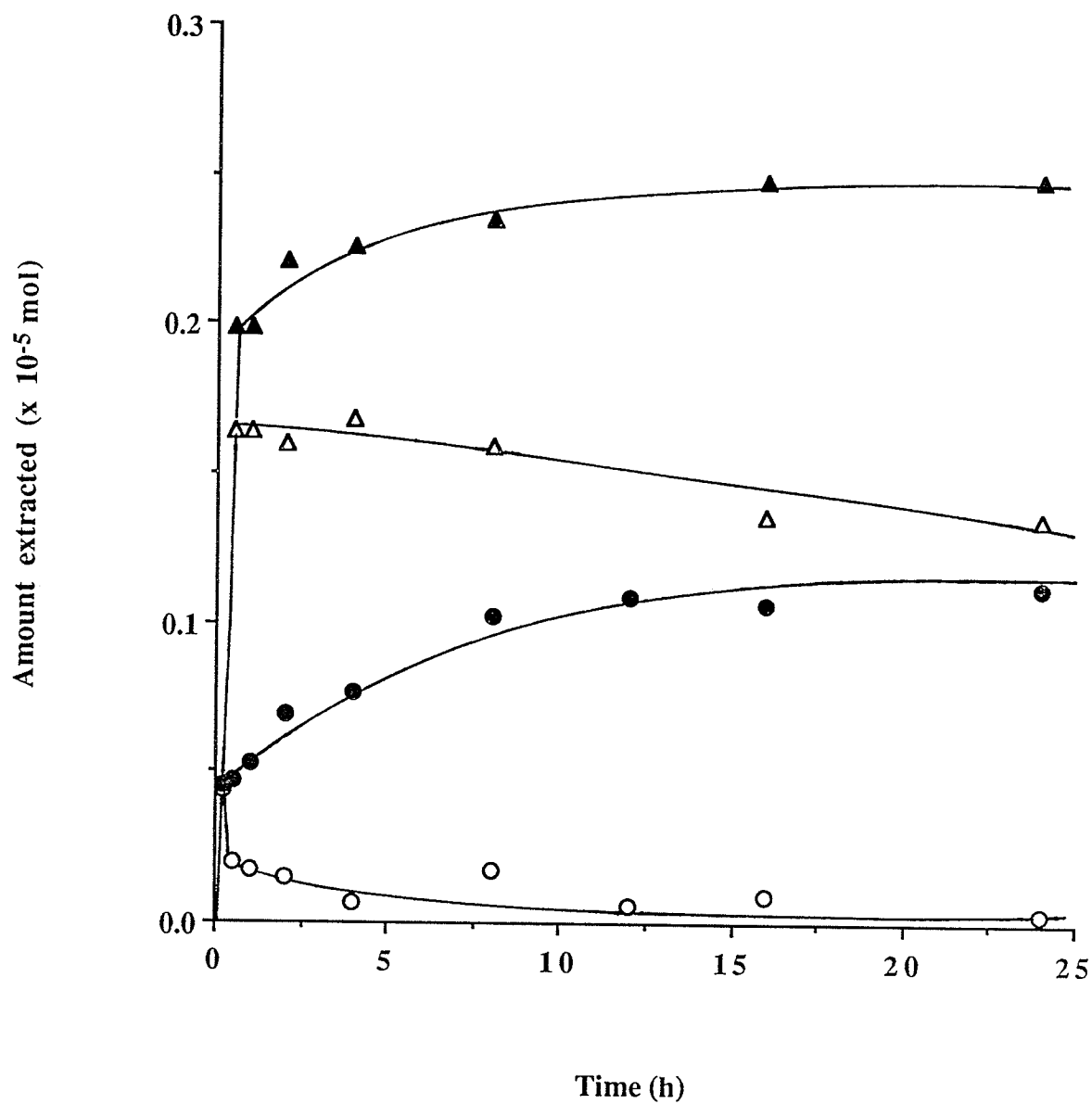**Figure 65**   Effect of temperature on the extraction of LiDPA with polyether foam as a function of time

Conditions: 0.5×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH, 0.050 g powdered polyether foam, 100 mL solution, pH = 9.0; (●) DPA^-, 65°C; (o) Li^+, 65°C; (▲) DPA^-, 20°C ; (Δ) Li^+, 20°C.

Table 51   DPA⁻ recovery by acetone from polyether foam extracted with LiDPA at 65°C for 24 h

Number of back-extractions	Extraction time with acetone (h)	% DPA⁻ recovery ± s	Cumulative % DPA⁻ recovery ± s
1	1.0	58.9 ± 4.1	58.9 ± 4.1
2	1.0	19.9 ± 1.7	78.8 ± 5.2
3	2.0	11.7 ± 2.1	90.5 ± 7.3
4	20.0	4.9 ± 3.0	95.4 ± 4.4

Conditions: Extraction of solution with foam:

0.5×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH, 0.050 g powdered polyether foam, 100 mL solution, pH = 9.0, 65°C, 24 h extraction.

Back-extraction of foam with acetone:

Foam weight = 0.025 – 0.040 g, 25 mL acetone, three trials for each value, s = standard deviation.

with 0.050 g polyether foam at initial pH 5.5 was studied. The final pH of the solution was 5.9. Figure 66 shows that DPA^- extraction increases and Li^+ extraction decreases in comparison with the extraction at pH 9.0. These phenomena can be explained by the extraction of DPA^- as HDPA and H_3O^+ competing with Li^+ for extraction. It was noted that Li^+ extraction goes to a maximum and then decreases with extraction time. A gradual increase in DPA^- extraction was also observed. These results may be explained by a conversion of the dissolved CO_2 in solution to H_3O^+ and CO_3^{2-} followed by a gradual diffusion of H_3O^+ into the foam.

Experiments were also carried out to remove the extracted DPA^- from the foam by acetone. Table 52 shows that an almost complete recovery of DPA^- was obtained for the foam extracted for 1 and 24 h after four acetone extractions. However, DPA^- recovery after one acetone extraction is higher from the foam extracted for 1 h (79.2 %) than that for 24 h (68.1 %). The respective Li^+ extracted / DPA^- extracted ratios were 0.29 and 0.08 for 1 and 24 h extraction. These results indicate that HDPA is more difficult to remove from the foam than LiDPA. Similarly, after one acetone extraction DPA^- recovery was 58.9 % from the foam extracted at pH 9 and 65°C for 24 h (Table 51), with the Li^+ extracted / DPA^- extracted ratio of 0.00 (no Li^+ extracted). It is indicative that the imbalance of Li^+ and DPA^- extractions arises from the extraction of HDPA rather than DPA^- decomposition on the foam.

To confirm that LiDPA is more easily removed from the foam, polyether foam which had been extracted with a solution of 0.5×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH for 1 h was back-extracted with acetone. The Li^+ extraction / DPA^- extraction ratio was 0.83, demonstrating that LiDPA is the major species on the foam. It was found that only one acetone extraction was required to quantitatively recover DPA^- from the foam (Table 53).

The fact that HDPA is more difficult to remove from the foam than LiDPA suggests that H_3O^+ interacts more strongly than Li^+ with the foam. However, the other alkali metal

Figure 66 Effect of pH on the extraction of LiDPA with polyether foam as a function of time

Time (h)
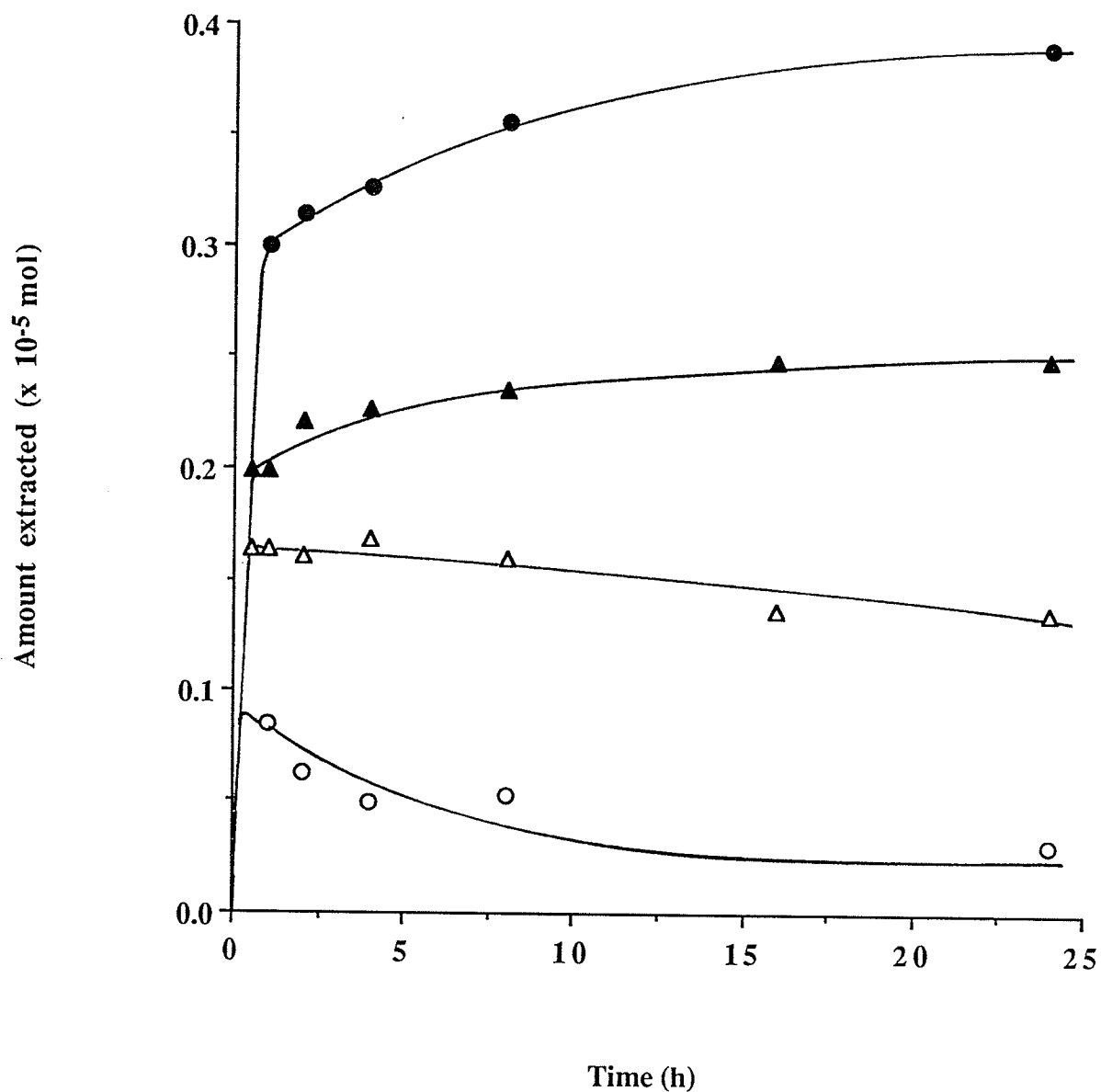
Conditions: pH = 5.9: 0.5 x 10^{-4} M LiDPA + 0.5 x 10^{-4} M LiCl, 0.050 g powdered polyether foam, 100 mL solution, (●) DPA⁻, (o) Li⁺.

pH = 9.0: 0.5 x 10^{-4} M LiDPA + 0.5 x 10^{-4} M LiOH, 0.050 g powdered polyether foam, 100 mL solution, (▲) DPA⁻, (Δ) Li⁺.

Table 52   DPA⁻ recovery by acetone from polyether foam extracted with LiDPA at pH 5.9 for 1 and 24 h

Extraction time with LiDPA (h)	Number of back-extractions	Extraction time with acetone (h)	% DPA⁻ recovery ± s	Cumulative % DPA⁻ recovery ± s
	1	1.0	79.2 ± 1.7	79.2 ± 1.7
	2	1.0	14.7 ± 1.6	93.8 ± 3.1
1.0	3	2.0	1.4 ± 0.1	95.2 ± 3.1
	4	20.0	0.2 ± 0.1	95.3 ± 2.8
	1	1.0	68.1 ± 4.8	68.1 ± 4.8
	2	1.0	14.7 ± 4.1	82.7 ± 8.9
24.0	3	2.0	5.5 ± 0.1	88.2 ± 8.7
	4	20.0	5.8 ± 1.0	94.0 ± 9.8

Conditions: Extraction of solution with foam:

0.5×10^{-4} M LiDPA + 0.5×10^{-4} M LiCl, 0.050 g powdered polyether foam, 100 mL solution, pH = 5.9, 1 and 24 h extraction.

Back-extraction of foam by acetone:

Foam weight = 0.019 – 0.036 g, 25 mL acetone, three trials for each value, s = standard deviation.

Table 53 DPA⁻ recovery by acetone from polyether foam extracted with LiDPA at pH 9.0 for 1 h

Number of back–extractions	Extraction time with acetone (h)	% DPA⁻ recovery ± s	Cumulative % DPA⁻ recovery ± s
1	1.0	100.3 ± 1.2	100.3 ± 1.2
2	1.0	2.0 ± 1.0	102.3 ± 1.6

Conditions: Extraction of solution with foam:

0.5×10^{-4} M LiDPA + 0.5×10^{-4} M LiOH, 0.050 g powdered polyether foam, 100 mL solution, pH = 9.0, 1 extraction.

Back-extraction of foam by acetone:

Foam weight = 0.022 – 0.034 g, 25 mL acetone, three trials for each value, s = standard deviation.

cations also have stronger interaction with the foam than Li^+, and hence the displacement of these cations is relatively less than Li^+. It appears that H_3O^+ interacts most strongly with the polyether foam compared with the other foams studied because the highest imbalance of the cation and the anion extractions was observed for the extraction with the polyether foam.

5.4   Conclusion

The imbalance of the cation and the anion extractions can be considered to be due to some time-independent and time-dependent effects. The extraction of LiDPA with polyether and Hypol foams under different conditions was examined to determine the possible causes of these effects.

The pH of the aqueous solution decreases when it is in contact with the foam, and the lowering of pH increases with increasing foam weight. It suggests that there is residual H_3O^+ on the foam. The result that the amount of Li^+ extraction and the Li^+ extraction / DPA^- extraction ratio increase after 1 h extraction with polyether foam washed with KOH compared with the acid-washed foam demonstrates that residual H_3O^+ is highly likely to cause the time-independent imbalance of the cation and the anion extractions.

No decline of Li^+ extraction with time was observed for the extraction of LiDPA with Hypol foam, which contains no tin catalyst for preparation. It was reasoned that tin in polyether foam might cause the time-dependent decrease of Li^+ extraction. However, the amount of tin present in polyether foam determined by graphite furnace atomic absorption analysis was found to be too small to account for the imbalance of Li^+ and DPA^- extractions. Moreover, tin which was coated on or incorporated in Hypol foam has no enhancement effect on Li^+ displacement. It is likely that tin in the foam cannot give rise to the decline of the cation extraction with extraction time.

The decomposition of DPA^- on the foam causing the decrease of Li^+ extraction is not very likely because a nearly quantitative recovery of DPA^- from polyether foam extracted with LiDPA at 65°C for 24 h by acetone was obtained and no difference in the UV-spectrum of the recovered DPA^- and LiDPA in acetone was observed.

An increase in DPA^- extraction and a decrease in Li^+ extraction were observed for the extraction of LiDPA at pH 5.9 in comparison with that at pH 9. It is evident that HDPA is highly extractable. DPA^- recovery studies show that HDPA is more difficult to be removed from the foam, suggesting that H_3O^+ interacts more strongly with the foam than Li^+. A steady increase in DPA^- extraction with increasing extraction time may arise from a time-dependent diffusion of H_3O^+ resulting from the dissolved CO_2 in solution, which extracts with DPA^- as HDA into the foam.

It can be concluded that residual H_3O^+ is possibly responsible for the time-independent imbalance of the cation and the anion extracted and the gradual displacement of the cation by H_3O^+ as a result of the dissolved CO_2 in solution probably causes the time-dependent decline of the cation extraction.

CHAPTER 6

CONCLUSIONS

The work presented in this thesis deals with the mechanism of extraction by polyurethane foam. The extraction of various organic compounds including salicylic acid, 8-hydroxyquinoline, 1-amino-2-naphthol-4-sulfonic acid and cinnamic acid was examined. It was found that these compounds are extractable only in the neutral form by a solvent extraction mechanism. The mechanism was confirmed by the salting-out effect and by varied pH studies. The anionic species are too hydrophilic to be extracted from aqueous solution in the presence of alkylammonium and alkali metal cations. These results demonstrate the importance of the hydrophobicity of the ions for the effective extraction of the ions as ion-pairs by polyurethane foam.

All the compounds studied contain –OH or –COOH groups and the extraction is higher with polyether than with polyester foam with the exception of 8-hydroxyquinoline. This result was interpreted to be a result of hydrogen bonding between polyurethane foam and –OH or –COOH groups on the organic compounds. The ability of polyether to form stronger hydrogen bonds than polyester foam can account for the higher extractability of these compounds by polyether foam. There is no difference for the extraction of 8-hydroxyquinoline with polyether and polyester foams. This can be explained by the absence of hydrogen bonding between the foams and 8-hydroxyquinoline where strong intramolecular hydrogen bonding in the compound occurs.

These results suggest that polyurethane foam can extract relatively hydrophilic organic compounds in their neutral form. This can be achieved by proper control of the pH of the solution. Thus, polyurethane foam has potential in applications for removing organic contaminants from aqueous solution.

These studies have shown that alkylammonium and alkali metal ions are extractable from aqueous solution by polyurethane foam in the presence of very bulky and hydrophobic anions such as tetraphenylborate (TPB$^-$) and dipicrylaminate (DPA$^-$). The results suggest that steric hindrance of the alkylammonium ions to fitting into the cavity formed by the polyethylene oxide portion of polyether foam may have some effect on the extraction. For example, the extraction trends: NH$_4^+$ > t-butylammonium > isopropylammonium > ethylammonium > methylammonium for polyether foam, but isopropylammonium $\approx$ t-butylammonium > NH$_4^+$ > ethylammonium > methylammonium for polyester foam are consistent with this concept. However, these results can also be explained by the weaker hydrogen bonding with polyester foam resulting in increasing extractions of isopropylammonium and t-butylammonium through hydrophobic interaction relative to NH$_4^+$. In general, hydrophobic interaction exerts a major effect on the extraction of the alkylammonium ions. The extractability of the alkylammoniums increases with increasing alkyl chain length as shown in the extractability sequence of n-butylammonium > n-propylammonium > ethylammonium > methylammonium. In addition to the length of the alkyl group, the number of alkyl groups attaching to the nitrogen of the amine group also plays a role in the extraction of the alkylammoniums. Increasing the number of the alkyl groups results in decreasing the number of N–H groups available to form hydrogen bonds with foam and in lowering the N–H polarity for hydrogen bonding. Thus, the low extraction of dimethylammonium and trimethylammonium can be attributed to the inductive effect of the alkyl groups. Although the steric effect may affect the extraction of the alkylammonium ions, there is no conclusive evidence for the cation chelation mechanism occurring for the extraction with polyether foam. The extraction of the alkylammoniums is affected by hydrophobic interaction, steric and inductive effects.

The extraction of alkali metal ions with TPB$^-$ and DPA$^-$ follows the orders: K$^+$ $\approx$ Rb$^+$ > Cs$^+$ > Na$^+$ > Li$^+$ for polyether foam and K$^+$ $\approx$ Rb$^+$ $\approx$ Cs$^+$ > Na$^+$ > Li$^+$ for

polyester foam. The high extractability of K^+ seems to suggest that the cation chelation mechanism is operative for the extraction with polyether foam. However, the same extractability sequence of $K^+ \approx Rb^+ > Cs^+ > Na^+ > Li^+$ was obtained for the extraction with 100% polypropylene oxide polyether foam. Since 100% polypropylene oxide polyether foam contains no polyethylene oxide, and hence cannot adopt a compact helical structure like polyethylene oxide, it indicates that a hole-size / cation-diameter relationship is not required for the strong interaction of K^+ with the foam.

Studies of the extraction of alkali metal DPAs from methanol by polyurethane foam illustrate the importance of the solvent effect. The results indicate that the water-structure enforced ion-pairing (WSEIP) exerts a major influence on the extraction of the ion-pairs. The extraction of alkali metal hydroxides with polyester foam follows the order: $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$, which is the same as that for the association of the ion-pairs in methanol. However, the extractability sequence of alkali metal DPAs with polyether foam is $K^+ \approx Rb^+ > Cs^+ > Na^+ > Li^+$. The result is indicative of a strong interaction between K^+ and polyether foam which is strong enough to compensate for the lower association of KDPA in methanol relative to RbDPA and CsDPA. Therefore, the selectivity for the cation is determined by a delicate balance of the ion-pair formation in methanol and the interaction of the cation with the foam.

The strong interaction of K^+ with the foam was confirmed by the results of the displacement of the cations from the foam, which follows the order $Li^+ > Na^+ > Cs^+ > Rb^+ > K^+$. Unsolvated Li^+ should have the highest interaction with the foam based on electrostatic attraction. It appears that the extracted cations are solvated and Li^+ and Na^+ cations are more strongly solvated than K^+. The stronger interaction of K^+ as well as the other alkali metal ions with polyether foam in comparison to polyester foam can be a result of the ether oxygens being not as far apart from each other as the ester oxygens for polyester foam.

Similar to the extraction of alkali metal DPAs from methanol, the high extractability of K^+ from aqueous solution by 100% polypropylene oxide polyether foam can be explained by the strong interaction of K^+ with the foam. The polypropylene oxide units of the foam are able to provide ether oxygens to interact with K^+ strongly enough to offset the lower association of KDPA relative to RbDPA and CsDPA in water even without a helical arrangement of the ether oxygens.

This interpretation of the extraction mechanism agrees with the cation chelation mechanism in that there is a strong interaction of the cation with the foam. However, the strong interaction is not necessarily due to a hole-size / cation-diameter relationship. This interaction can be provided by polyether foam containing either a mixture of polyethylene oxide and polypropylene oxide or polypropylene oxide alone with presumably sufficient ether oxygens present and positioned not too far apart.

There is a characteristic imbalance of the cation and the anion extracted. It can be considered to be due to some time-independent and time-dependent effects. It seems that residual H_3O^+ is probably responsible for the time-independent imbalance of the cation and the anion extracted, and the gradual diffusion of H_3O^+ from dissolved CO_2 in solution into the foam resulting in the displacement of the cation may cause the time-dependent decline of the cation extraction.

On the basis of these results, it was concluded that molecular species are extracted by polyurethane through a simple solvent extraction mechanism. The extraction increases with the increasing ability of the compound to form hydrogen bonds with the foam. The extraction mechanism for ionic species involves: (1) ion-pair formation in the aqueous phase, (2) interaction of the cation and the anion with the foam. Ion-pairing is favored by increasing hydrophobicity of the ions and is facilitated by the water-structure enforced ion-pairing process. The foam can interact with the cation and the anion by hydrogen bonding, hydrophobic and ion-dipole interactions. However, it is difficult to predict the selectivity

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for the cations since it is dependent on the overall effect of the ion-pair formation in water and interaction of the ions with the foam which are affected by the nature of the foam and the solution chemistry.

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