The University of Manitoba

An Investigation into the Mechanism of Extraction of
Organic Compounds by Polyurethane Foam

by

Lesley J. Schumack

A Thesis

Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements for the Degree
of Master of Science

Department of Chemistry
Winnipeg, Manitoba

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ABSTRACT

The extraction of aromatic organic compounds from 10 % ethanol solutions by open cell polyurethane foam was examined using polyether and polyester foam types and compared to extractions by diethyl ether. The effect of altering pH, ethanol concentration and inert salt concentration was also examined. It was found that the compounds studied would not extract into the foam as charged species but would extract well as neutral molecules. Further, the addition of an inert salt increased the extraction of the compounds examined and it was possible to affect the extraction by altering the dielectric constant of the aqueous phase. It was concluded that the polyurethane foam behaves as a solvent extraction system. It was also noted that there is an additional bonding between hydroxyl groups on the organic compound and the foam. The bonding was labeled Polyurethane Hydrogen Bonding (PHB) and is most obvious in the polyether type foam. It is thought that the stronger hydrogen bonding between the polyether-type foam and the organic compound was due to the ability of the polyether foam to form stronger hydrogen bonds than the polyester-type foam. PHB can occur between the polyurethane foam and any group on the organic compound capable of hydrogen bonding. The thermodynamic analysis of temperature studies also support the mechanism proposed.

INTRODUCTION

Polyurethane Foam

Polyurethane polymers originated with the work of Bayer and co-workers during the Second World War.[1] The most common way of producing these polymers is by the reaction of di- or polyfunctional hydroxyl compounds such as hydroxyl-terminated polyethers or polyesters with di- or polyfunctional isocyanates.[2] Catalysts may be added to control the rate and type of reaction. The product of such a reaction is a substituted amide ester of carbonic acid known as a polyurethane.

$$OCN-R-NCO \quad + \quad HO-R'-OH \quad \longrightarrow \quad \left[\begin{matrix} O & H & & H & O \\ \| & | & & | & \| \\ -C-N-R-N-C-O-R'-O- \end{matrix} \right]_n$$

polyfunctional   hydroxyl-   urethane
isocyanates   containing
                        polymer
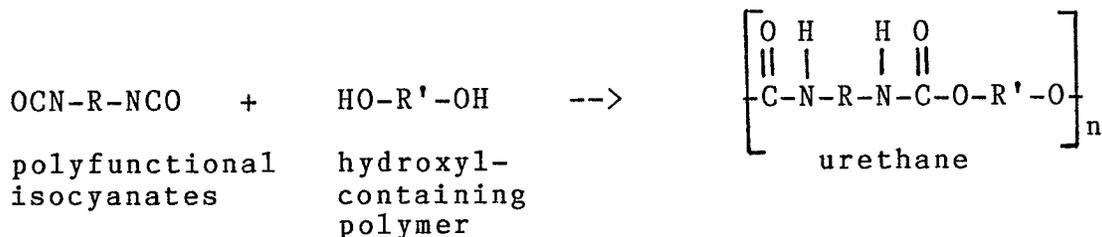
If water is included with the reactants, carbon dioxide will be produced from the reaction of the isocyanate with the water. The gas thus produced will behave as a blowing agent which will cause foamed polymers to be produced. Foams formed in this way can either be open celled or closed celled; the closed celled foams have air bubbles formed into discrete separate pockets, while the open celled foam types have the air pockets interconnected allowing air to pass through the foam.

If linear or slightly branched reactant monomers are used for the synthesis then flexible foams will be produced, but if more highly branched monomers are used, the result will be a rigid foam.

There are a number of polyfunctional isocyanates that can be used for the synthesis and these include tolylene diisocyanate and diphenylmethanediisocyanate.

The hydroxyl-containing monomer is usually a polyester or a polyether. A typical polyester is poly(ethylene adipate) produced by the reaction of adipic acid and ethylene glycol.[3]

$$n \ HOOC(CH_2)_4COOH + (n+1) \ HOCH_2CH_2OH \longrightarrow$$
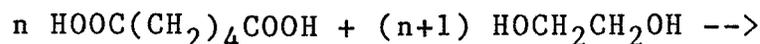
adipic acid   ethylene glycol

$$HO-[CH_2CH_2O\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}O]_n-CH_2CH_2OH + 2H_2O$$

poly(ethylene glycol adipate)
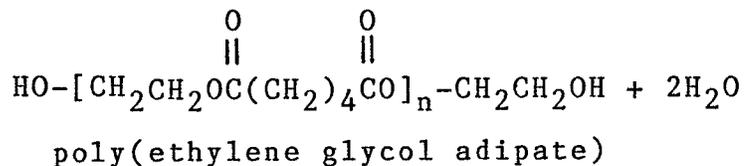
The polyethers do not have the ester groups but contain repeating ether linkages. One such polymer is polyethylene oxide polyol, which is produced by the reaction of a small amount of ethylene glycol with an excess of ethylene oxide.

$$HOCH_2CH_2OH \quad + \quad n \; CH_2 \overset{O}{-} CH_2 \quad \longrightarrow \quad HO-[CH_2CH_2O]_n-H$$

ethylene glycol   ethylene oxide   polyethylene oxide
                                             polyol
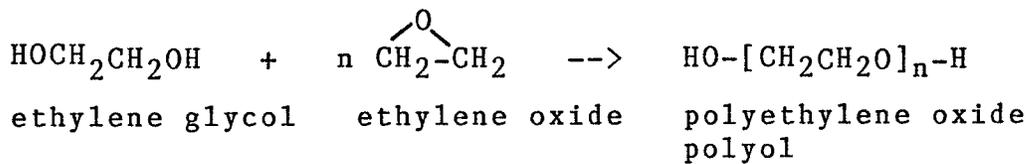
It is the type of hydroxyl containing monomer used in the polyurethane production that determines the characteristics of the polyurethane foam produced. These monomers constitute the "backbone" of the polyurethane foam and therefore greatly influence its behavior. As an example, concentrated nitric acid will completely destroy the polyester type polyurethane foam but will only partially alter the polyether type polyurethane foam.

Chemical interest in polyurethane foam was greatly increased after 1970 when Bowen[4] first used polyurethane foams to extract various substances from aqueous solutions. He extracted iodine, chloroform, benzene, and phenol from water; mercury(II) and gold(III) from 0.2 M HCl; iron(III), antimony(V), molybdenum(VI), and rhenium(III) from 6 M HCl; and uranium(VI) from saturated aluminum nitrate solution. Because of the limited surface area involved, he suggested that the extraction must occur by absorption and not by adsorption and that the extraction was similar to that obtained using diethyl ether. This work of Bowen was instrumental in opening up the field of polyurethane extraction. Later research can be divided into two categories; the extraction of chemicals by untreated foam or extraction by treated foam.

Treated Polyurethane Foams

Polyurethane foams can be treated either by altering their structure through a chemical reaction or by coating the foam with an active extractant where the foam acts as an inert solid support. Work by Gesser and co-workers[5] in 1971 showed that it was possible to increase the extraction of organochlorine pesticides from water using foam coated with chromatographic grade greases. They also measured the extraction efficiency of the coated polyurethane using suspensions of two different types of soils and found the extraction of the pesticides to occur in a fashion similar to the extraction from aqueous solutions.

Mazurski et al[6] investigated the adsorption of mercury(II) chloride and methylmercury(II) chloride by polyurethane foams treated with hydrogen sulfide. Braun and Abbas[7] in 1981 used diethylammonium diethyldithio-carbamate loaded foam to preconcentrate phenyl-, methyl-, and inorganic mercury from natural waters while they subsequently eluted with acetone.

Treated polyurethane foam has been used to extract copper and cadmium by Lypka, Gesser, and Chow[8] who used foam pretreated with benzoylacetone. Several years later Tanaka et al[9] used polyurethane foam loaded with 2-(2-thiazolylazo)-4-methyl phenol to collect ions such as copper, nickel, cobalt, zinc, and cadmium from aqueous

solutions. In 1974 Braun and Farag[10] used polyurethane foam as a solid support for various chelating agents with the loaded foam being used to separate silver from lead and copper in aqueous solutions.

Kang and Lee[11] used foam impregnated with B-diphenyl-gloxime to extract palladium(II) from platinum(IV) and nickel(II) in aqueous solution by both batch and elution methods. Further work on nickel was done by Lee and Halmann who separated nickel from other ions such as iron(II), iron(III), copper(II), cadmium(II), zinc(II), and cobalt(II)[12] using a polyurethane foam loaded with dimethygloxime. They found that temperature did not effect the adsorption of nickel(II) on the DMG treated foam. Later, Halmann and Lee[13] used a foam loaded with α-benzildioxime to recover nickel from ammoniacal media with good selectivity as well as high capacity.

Braun and Farag[14] used polyurethane foam as a solid support for chloranil in a syringe or pulsed column. A pulsed column was also used to separate and preconcentrate radioiodine on organic reagent loaded polyurethane foam[15] with a high separation efficiency of ca. 95% and good reproducibility.

In 1981, Farag and El-Wakil[16] used 1,5 diphenyl-carbazide loaded foam to extract chromium(VI) from aqueous solution. They achieved a semi-quantitative determination of 0.1 ppm and the detection of 10 ppb of chromium(IV) in

aqueous solution.

Uranium was separated from other elements by foam impregnated with trioctylphosphine oxide by Korkisch and Steffan.[17] A different approach was taken by Yu and co-workers[18] who extracted thorium with 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 loaded foam and examined the effect of equilibrium time, pH, and other factors on extraction efficiency.

Omar and Bowen[19] used polyurethane foam soaked in toluene 3,4-dithiol to extract inorganic tin in natural waters. They used a 15 cm glass column containing 0.4 g of polyurethane foam and found it was possible to get a tin extraction of $97.8 \pm 1.0\%$ from natural waters.

Work has also been done using other types of polymer supports. Silicone rubber foam treated with dimethyl-gloxime was used by Gregoire and Chow[20] for the separation of platinum and palladium from solutions containing as little as 1.0 ppm of the metal. The results showed that a pH of 4.0 provided an optimum operating pH for the complete separation of platinum and palladium. Cook and Hartz[21] looked at the adsorption of chlorinated methanes from aqueous solutions by various plastic adsorbents including polyurethane foam. Because of the inertness and relatively low cost of polyurethane foam, the potential for further work with treated foam remains large.

Untreated Polyurethane Foam Extraction

Extraction of chemicals by untreated polyurethane foam was first reported by Bowen.[4] Since that time the field has grown considerably and a large amount of research has been spent on the extraction of inorganic compounds and metals by polyurethane foam. This was started with the extraction of gold(III) chloride by Bowen[22] in 1971. Sukiman[23] compared the extraction of gold from aqueous solutions by both treated and untreated foams and found very little difference between the two in regard to extraction properties. The work with gold was extended further when polyurethane foam was used as a preconcentration matrix for gold, antimony, indium, and mercury.[24] Braun and Farag [25] used unloaded polyether-type polyurethane foam for the sorption and recovery of gold from ammoniacal cyanide media.

Gesser et al[26] used acidic chloride solutions to extract gallium into untreated foam. Later work by Gesser and Horsfall[27] compared the polyurethane foam to a "solvent extractor" for gallium and iron where it was thought that the polyurethane foam solvates the neutral metal complexes. Further evidence for solvation was gathered by Oren et al[28] with the extraction of iron(III) by untreated foam. Antimony was extracted from aqueous solutions using untreated foam by Lo and Chow[29] who speculated that the foam behaved as an organic solvent.

Mercury, zinc, and indium were extracted by untreated polyurethane foam from aqueous thiocyanate solution by Braun and Abbas[30] in 1981. Prior to that research, Maloney and co-workers[31] examined the extraction properties of cobalt(II), zinc, iron(III), cadmium, nickel(II), bismuth, lead(II), mercury(II), tin(II), and copper(II) from unloaded and loaded polyurethane foams.

Uranium was extracted from aqueous solution using polyurethane foam.[32] In this work the effect of salting out was investigated and it was found that the effectiveness of salting out was increased over the series $NH_4^+ < Ca^{++} < Al^{+++}$ when anion molarities were equal. This is same sequence that is observed for the salting out effect with the liquid-liquid extraction of uranium with ethers.

Braun et al[33] used Mossbauer spectroscopy to look at the extraction of iron complexes extracted by polyurethane foam. His results showed a similarity between diethyl ether extraction and the extraction by polyurethane foam.

Cobalt was extracted from aqueous solution by Hamon et al.[3,34] who noticed the difference in extraction between the polyester-type and polyether-type polyurethane foams. From these differences they deduced that the polymer backbone must play a part in the extraction of the cobalt complexes. The realization of the importance of the polymer backbone led to the development of the cation

chelation mechanism. According to this mechanism the negatively-charged cobalt complexes are solvated within the polymer backbone while accompanying cations are strongly solvated by "crown ether" type structures within the backbone configuration. Only the polyether-type foam could achieve these "crown ether" type structures and it was therefore a much better extractor of the complexes studied.

Work by Moody and co-workers[35] in 1983 on cobalt(II), iron(III), zinc(II) and cadmium(II) supports the cation chelation mechanism. These sorptions were carried out in potassium thiocyanate solutions and it was found that the sorption seemed to be related to the ability of the metal to form thiocyanate complexes.

Caletka et al[36] used two different extraction systems. One system was a polyether type polyurethane foam / HF-alkali-metal fluoride system while the other consisted of a cyclic polyether / HF-alkali-metal fluoride system. They found that cobalt, zinc, iron, zirconium, hafnium, tin(IV), niobium, arsenic(V), protactinium, molybdenum, and tungsten were not extracted whereas rhenium and technetium were well extracted by both systems. Later, Caletka and co-workers[37] used polyether type polyurethane to extract molybdenum, tungsten, and technetium from thiocyanate / hydrochloric acid medium and that extraction was compared to extraction using the crown

ether, dicyclohexano-18-crown-6 in dichloroethane. They found that both systems extracted these metals well, thereby supporting the cation chelation mechanism.

Lautenschlager[38] used powdered and foamed polyurethane for the extraction of inorganic and organic impurities in food and beverages, e.g., methyl anthranilate and putrescine from alcoholic beverages.

Extraction of Organics by Untreated Polyurethane Foam

The primary focus of this thesis is the extraction of organics using untreated foam as the extraction of metals from aqueous solution by polyurethane foam has been well documented. The extraction of organics from aqueous solution by foam was first reported by Bowen[4], but research in this area has increased rather sporadically since then. In 1971 Gesser and co-workers[39] applied the extraction properties of polyurethane foam to the extraction and concentration of polychlorinated biphenyls (PCBs) from water. The foam was cut into plugs and placed in a chromatographic column after which the PCBs in solution were extracted into the foam at the parts per billion level. The PCBs were then eluted from the column using acetone and hexane. At the time it was noted that organochlorine pesticides were extracted along with P.C.B.s and a detailed study of the factors affecting the extraction and recovery of various P.C.B.s and

organochlorine pesticides was carried out by Musty and
Nickless.[40] They found that uncoated foams performed the
extraction better than foams coated with chromatographic
greases.

The extraction and recovery of phthalate esters from
water was investigated by Gough and Gesser.[41] The
polyurethane foam was used to remove these compounds at
the ug/L level using a column packed with foam plugs and
it was found that foams coated with silicone oils did not
have increased extraction properties. It was then
concluded that the extraction occurred by absorption into
the body of the foam as the oils on the surface did not
alter the extraction. The phthalates were removed from
the foam by extractions with acetone and hexane. These
workers found that the phthalates of different structures
had different extraction values although no attempt was
made to define the type of mechanism involved. Other work
by Ahmad et al[42] looked at the extraction of carboxylic
acids by polyurethane foam. They looked at this method as
a means to separate different carboxylic acids in aqueous
solution. It was found that retention capacity decreases
as concentration decreases, and that the extraction could
be performed in the presence of foreign substances.

Lewis et al[43] investigated the sampling of
pesticides, P.C.B.s and polychlorinated napthalenes from
ambient air using unloaded polyurethane foam. The

extracted organics were removed from the foam using 5% diethyl ether in n-hexane. Phthalate esters were also extracted from air and recovered in a similar fashion by Yamaski et al.[44] Several reviews and two books describing polyurethane foam extraction have been published.[45,46,47,48]

Although there has been some speculation as to the mechanism of extraction for the inorganics, to date there has been very little work done on the mechanism of the extraction of organics by untreated open cell polyurethane foam. As was mentioned earlier, a solvent extraction mechanism was invoked for the inorganic extraction.[27,28,29,33] Bowen was the first to remark on the similarity between polyurethane extraction and the extraction by diethyl ether. In a solvent extraction mechanism the extraction occurs from a solution (raffinate phase) with high dielectric constant to a solution of low dielectric constant (solvent phase) for a compound with a low dielectric constant. Later, the cation chelation mechanism was devised to explain the extraction by polyurethane foam of several metals[34,35,36,37] but no one had investigated the possibility of this mechanism working for organic compounds. It was thus decided to look at the mechanism of extraction of organics by untreated polyurethane foam and to determine if the extraction occurs by solvent extraction, cation chelation, or some

other mechanism. It was thought that the best way to examine the mechanism initially would be by doing a survey of the extraction properties of a wide range of organic compounds. This study is a survey of the extraction characteristics of several simple aromatic compounds and an investigation into the extraction mechanisms involved. The simple aromatic compounds had many advantages for this type of research. They were strongly UV light absorbing making detection easier, they dissolved into 10% ethanol at the desired concentrations due to their polarity, and they extracted into the polyurethane foam. The investigation consisted of a study of various factors affecting the extraction of organic compounds by polyurethane foam.

EXPERIMENTAL

Apparatus and Reagents

Unicam SP500 Series 2 ultraviolet and visible
spectrophotometer.

Varian Series 634 ultraviolet and visible
spectrophotometer.

1 cm path length quartz cuvettes.

Waters Millipore ILC-1 Ion/Liquid Chromatograph with
Wisp 710B, Model 430 conductivity detector, and
740 data module.

Waters Millipore IC Pak cation column and guard column,
(using 2 mmol nitric acid as mobile phase).

Hewlett Packard 5710A gas chromatograph with flame
ionization detector.

1.8m x 2mm (i.d.) glass column packed with Waters
Porapack P.

Soxhlet extractor.

Pyrex squeezing cell (Figures 1 and 2).

Multiple automatic squeezer (Figure 3).

Temperature controlled squeezing cell (Figures 4 and 5).

All chemicals were of reagent grade unless otherwise
indicated.

Pure water was obtained from a Barnstead Nanopure II water
purification system using reverse osmosis purified
water as the feed.

Polyurethane foams:

Polyester - Dispo plugs (Canlab, Winnipeg). Size: 2.2
cm diameter x 3.8 cm length.

Polyether - Polyurethane foam mattress, 50.5 cm x
114.5 cm x 4.8 cm (Zellers department store,
Winnipeg). Foam cut into plugs. Size: 2.2 cm
diameter x 4.8 cm length.

Figure 1. Pyrex squeezing cell (assembled).

12 mm

Teflon cap.

Cotter pin.

Steel spring.

Screw cap with rubber washer.
20mm diameter thread size.

Teflon cylinder.

Cell plunger.

Cell top.

Rubber band.

Ground glass stopper.

Ground glass joint.
14/23

Cell bottom.

Foam piece.
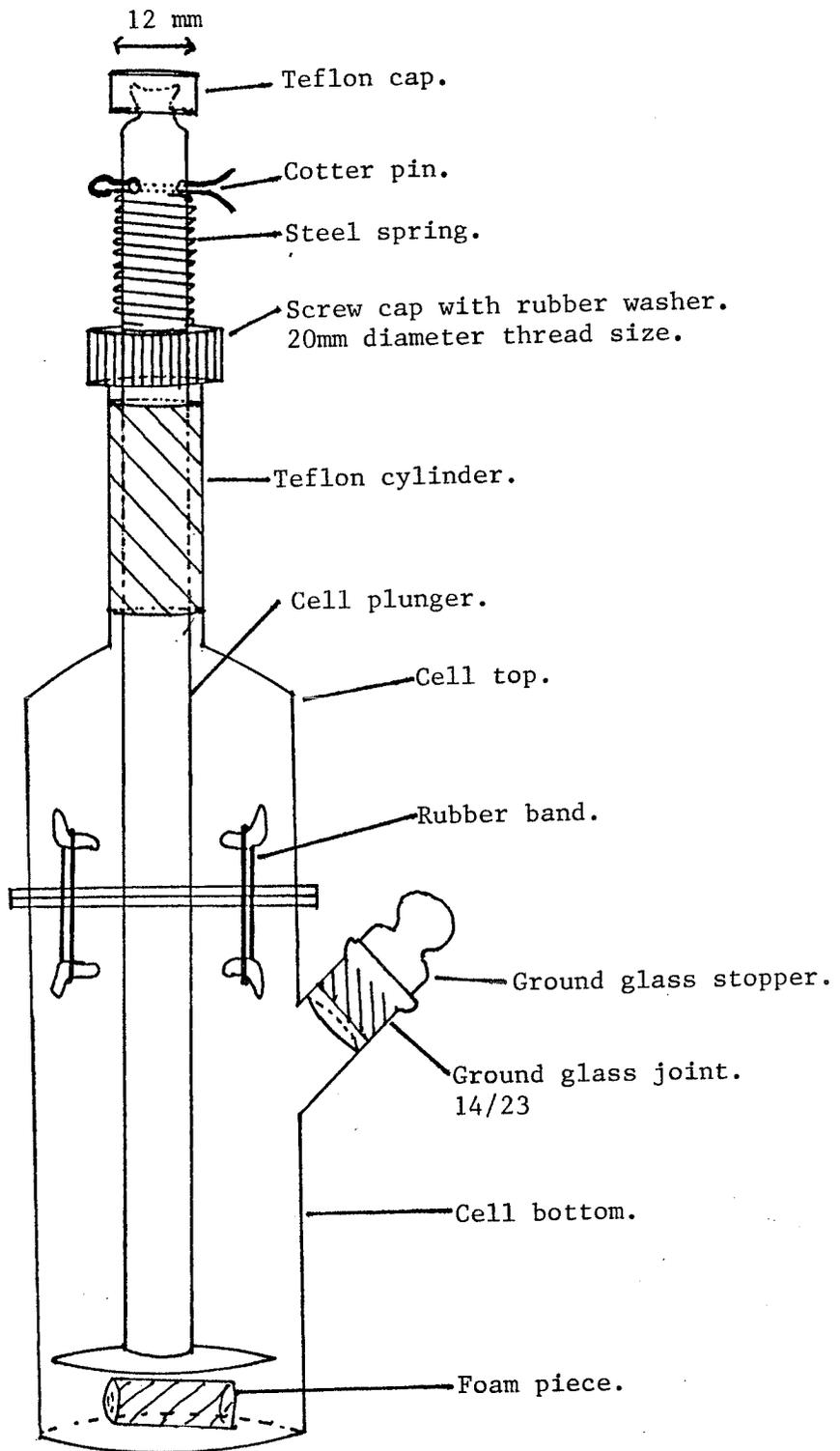
Figure 2. Pyrex squeezing cell (disassembled).

      A - Cell plunger.

      B - Teflon cap.

      C - Screw cap with rubber washer.

      D - Steel spring.

      E - Teflon cylinder.

      F - Cotter pin.

      G - Rubber bands.

      H - Cell top.

      I - Cell bottom.

      J - Ground glass stopper.

285 mm
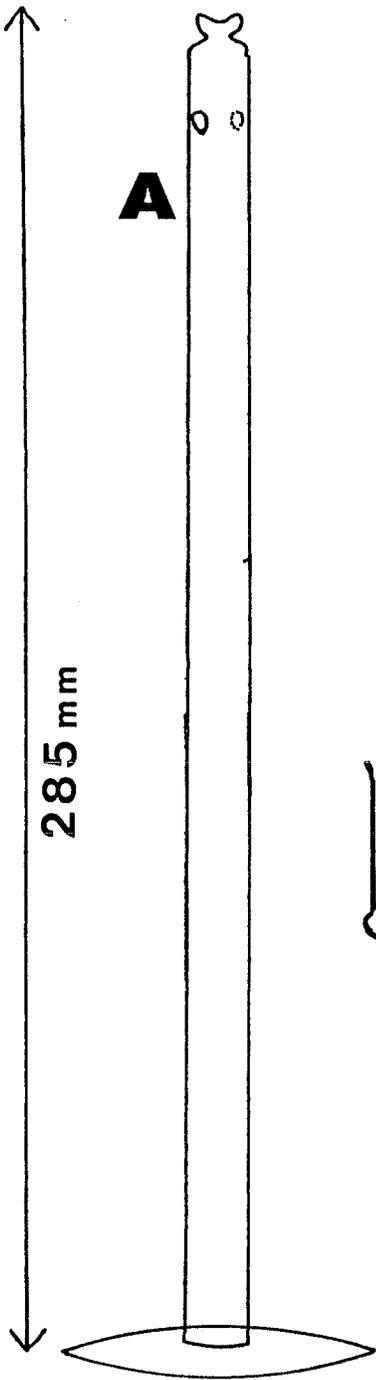
B

C
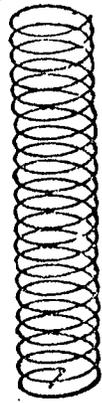
D
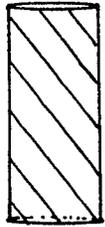
E
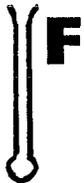
F

G
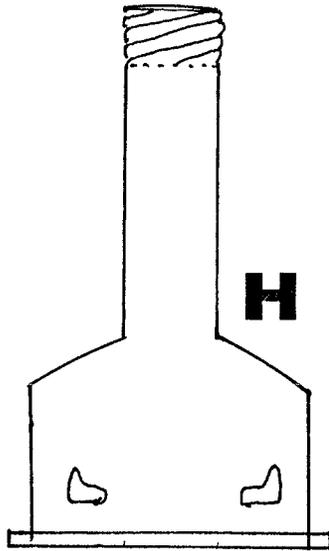
H

120 mm

55 mm

I

J

100 mm

A
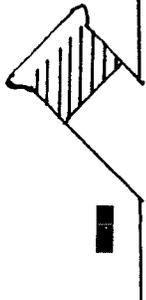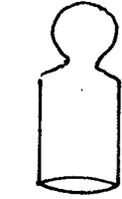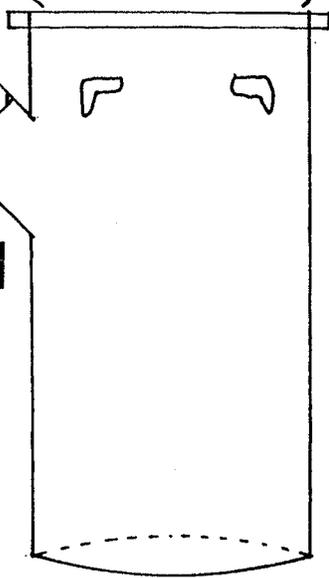
Figure 3.   Multiple automatic squeezer.

A – Restraining clamps.

B – Rotating cam.

C – Drive rod.

D – Pyrex squeezing cell.

A

B

C

D
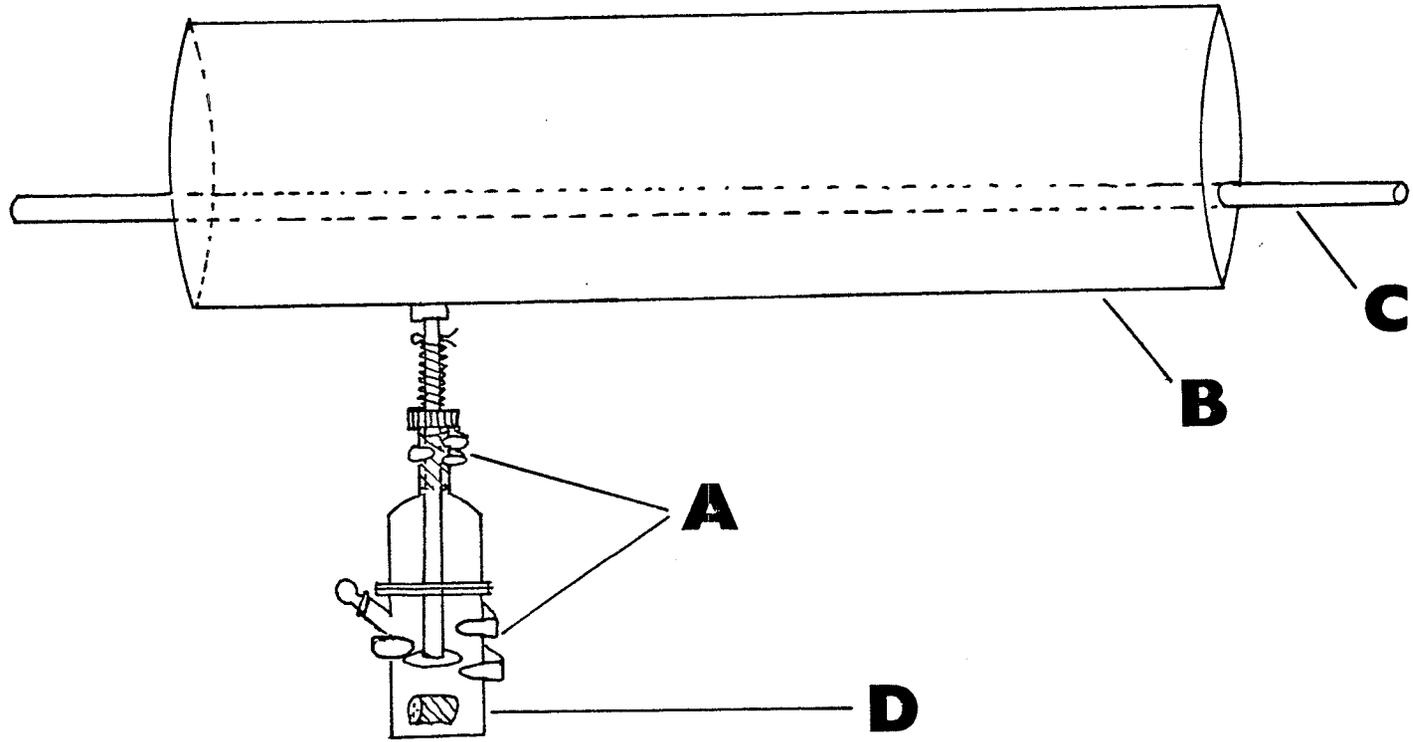
Figure 4. Temperature controlled

squeezing cell (assembled).

12 mm

Rubber seal.

Cell plunger.

Water outlet.

Cell top.

Ground glass stopper.
14/23

Cell bottom.
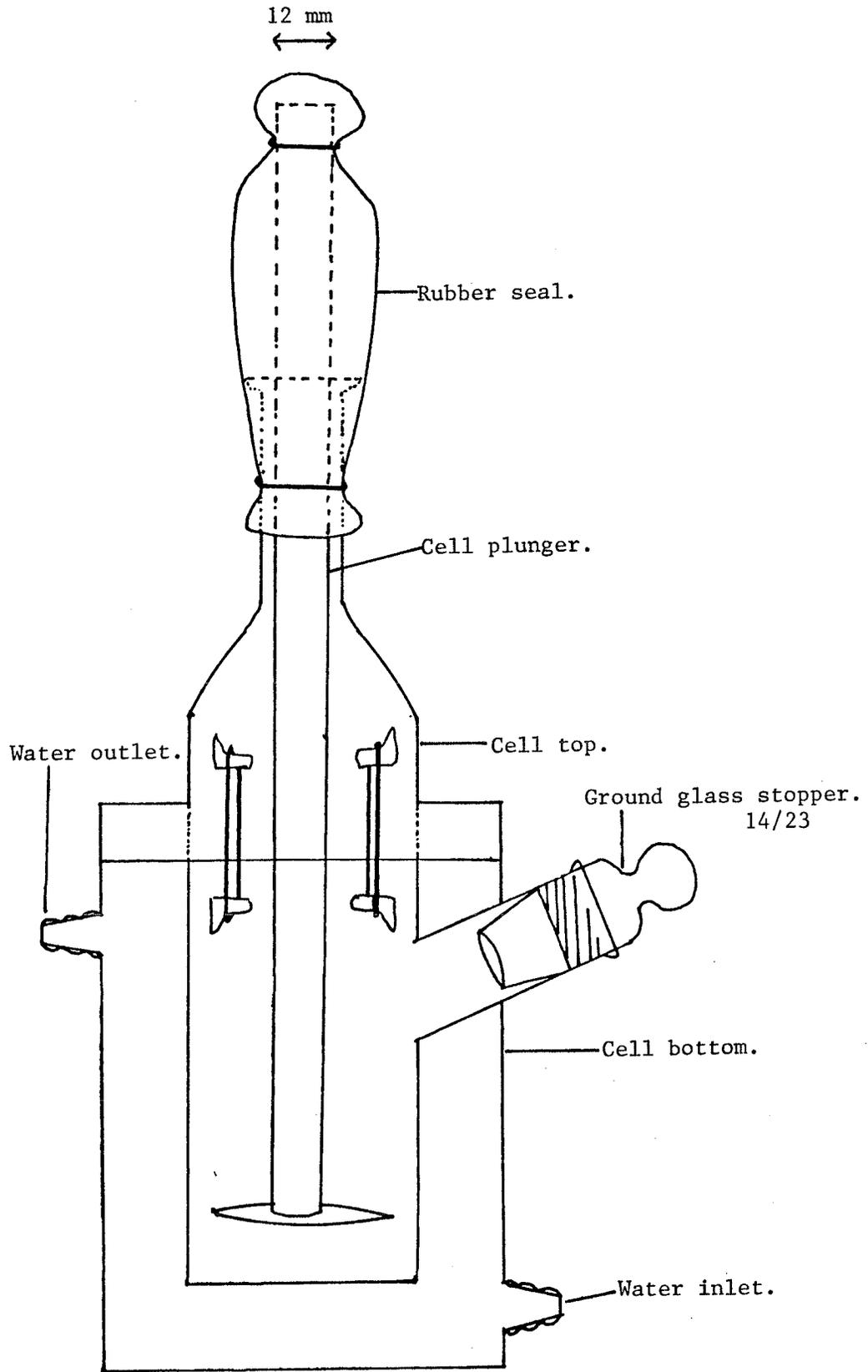
Water inlet.

Figure 5.   Temperature controlled squeezing

cell (disassembled).

     A - Cell plunger.

     B - Rubber seal (condom).

     C - Cell top.

     D - Cell bottom.

     E - Ground glass stopper.

     F - Water inlet.

     G - Water outlet.

A

B

C

D

E

F

G

105 mm

120 mm

90 mm
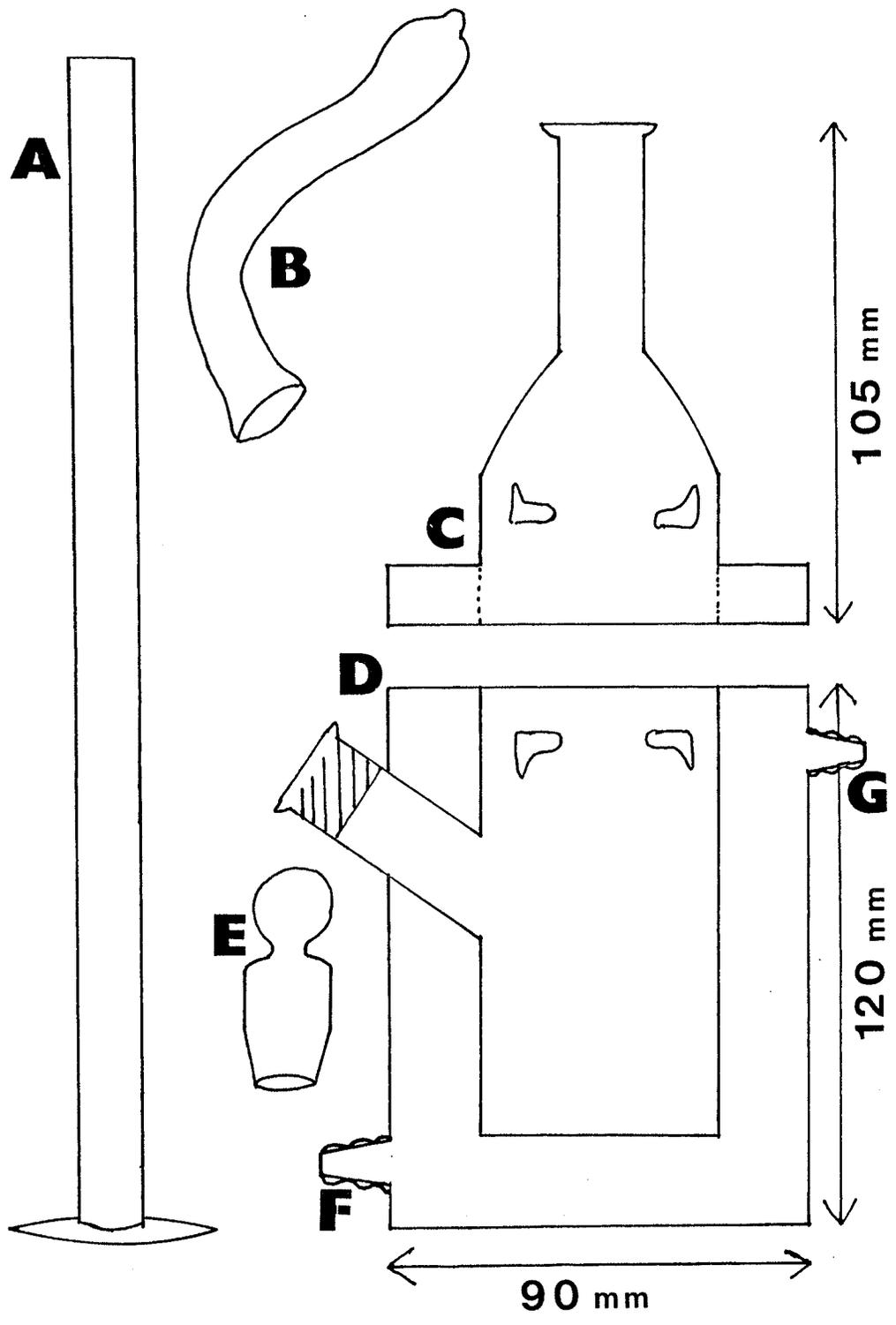
General Procedure

Standard Solutions

Ten per cent ethanol: A 10 % ethanol solution was made by adding 100 mL of reagent grade 95 % ethanol to a one litre volumetric flask and filling to the mark with pure water.

Salt solutions: The salt solutions were prepared by adding the correct amount of whichever salt was being examined to a one liter volumetric flask and diluting to the mark with pure water.

Organic standard solutions: Standard solutions for each organic compound examined were prepared by adding the chosen amount of organic compound to a 100 mL volumetric flask and diluting to the mark with reagent grade ethanol.

Foam Preparation

The polyester and polyether polyurethane foam plugs were both treated as follows. Initially the foams were washed for one hour in 1 M HCl with occasional squeezing followed by three rinses with pure water. The foams were then placed in reagent grade ethanol and manually squeezed for one hour followed by three rinses with pure water. After this, the foams were left in pure water for about 12 hours. The excess water was then squeezed out and the

foams soxhleted for three hours with acetone at about two cycles an hour. After the soxhlet step the foams were squeezed dry and placed into a vacuum desiccator overnight.

Extraction of Organics

The foam plugs were placed in a solution containing the organic compound. They were then squeezed by the automatic squeezer using the Pyrex squeezing cell or manually using the temperature controlled squeezing cell (temperature extraction only). The automatic squeezer consists of an eccentric cam of about 90 cm length x 14 cm diameter turned by a motor attached to the drive rod. This produced an up and down motion which depressed and released the glass plungers in the pyrex squeezing cells. A maximum of ten cells could be used at one time. The apparatus was located in a thermostatically controlled cabinet at $25 \pm 0.1^{\circ}C$. Foams were squeezed at the rate of 30 ± 0.5 cycles per minute.

General Survey

For each compound examined, sample solutions were prepared. Samples were prepared by pipeting 1.00 mL of an organic stock solution into a 100 mL volumetric flask and diluting to the mark with 10 % ethanol to maintain a concentration of 10 % ethanol. In the cases where an

acidic solution was required to prevent dissociation, one mL of 1 M HCl was transferred by pipet into the flask prior to dilution with 10 % ethanol.

For each compound examined, the wavelength at which a compound has the largest absorbance in the UV-visible region, (λ_{max}) was required. Wherever possible these were taken from either the Sadtler Handbook[49] or the DMS UV Atlas.[50] When the values were not available in these sources, they were determined by scanning a sample in 10 % ethanol with the Varian spectrophotometer from 400 to 200 nm. This range was chosen since all compounds tested absorb within it and there is no interfering absorbance by ethanol above 215 nm. The absorbance measurements were taken at the λ_{max} to minimize error since any small change in wavelength during measurement will have a minimal effect on the absorbance at this wavelength.

Samples were run with 10 cells at a time. A normal experiment consisted of four identical samples with one sample blank for polyether and four identical samples with one sample blank for polyester. A sample blank consisted of a clean piece of foam in the 10 % ethanol solution. Samples and blanks were placed in the Pyrex squeezing cells along with a weighed piece of foam and these were clamped into the multiple automatic squeezer and the foams were squeezed for one hour. The UV absorbance was measured before foam addition and after one hour

squeezing. Preliminary experiments showed that one hour was enough time for the extraction equilibrium to be reached. For each sample the sample blank absorabance values were subtracted from the sample UV absorbance values to give the corrected absorbance values, and these corrected values were used to calculate the distribution coefficients, D.

UV spectophotometric measurements were taken using the Unicam SP500 in the null balance mode.[51] The reference blank consisted of the 10 % ethanol solution. All absorbances were determined to three decimal places.

Diethyl Ether Extraction

The sample solutions were prepared in the manner described previously for the general survey extraction using foam. To a 50 mL Erlemeyer flask were added 20 mL of the sample solution and 10 mL of diethyl ether. The stoppered flask was shaken and placed in a temperature bath at $25 \pm 0.5^{\circ}C$. An initial UV absorbance measurement was taken prior to the addition of the ether. The ether was then added and the flask was shaken and left in the water bath for 15 minutes, after which time the final absorbance measurement was taken. Preliminary experiments showed that 15 minutes were enough to allow the solution temperature to reach 25° and for the extraction to reach the equilibrium. It was important that the flask be well

sealed during the equilibrium period as the diethyl ether has a low boiling point and evaporates readily. Care had to be taken to choose inert plastic stoppers as clear plastic wraps and Parafilm were both partially destroyed by the ether solution.

Effect of Temperature on the Extraction of Organics

The extractions at different temperatures were performed using the temperature controlled squeezing cell. Samples were prepared similar to those used in the general survey with UV absorbances taken after changes in $5^{o}C$ increments. A sample blank consisting of a piece of foam in 10 % ethanol was run in a fashion similar to the samples and the sample blank values were subtracted from the sample values at each corresponding temperature. The cell was connected to a thermostated hot water bath and the correct temperature recorded from a thermometer placed in the bath ($\pm$ $0.1^{o}C$). To compensate for heat loss at high temperatures, a correction factor was applied to the temperature recorded. A run was conducted using water, and the temperature measured in the temperature controlled cell as well as the water bath for each temperature. The difference between the two values was the correction factor that was applied to the other trials. Distribution coefficients were calculated for each temperature after each incremental change.

Distribution Coefficient Calculation

For each sample UV absorbance measurements were made before foam addition, and after foam addition and squeezing (Abs_o and Abs_f). Prior to placement in the squeezing cells, the foams were weighed to the nearest mg. The UV absorbance was proportional to the organic compound concentration over the ranges used. Therefore the corrected absorbances (Abs_{co} and Abs_{cf}) and the percent extraction (% ext) could be calculated.

$$Abs_{co} = Abs_o - Blank_o$$

$$Abs_{cf} = Abs_f - Blank_f$$

$$\% \; Ext = [(Abs_{co} - Abs_{cf}) \, / \, Abs_{co}] \; x \; 100$$

$Blank_o$ and $Blank_f$ = UV absorbances of the Blank solution before addition of foam, and after addition of foam and the required squeezing.

From the % Ext and the foam weight, the distribution coefficient, D was calculated.

D is defined as:

$$D = \frac{\text{Concentration of organic in foam} \quad \text{g/kg}}{\text{Concentration of organic in solution} \quad \text{g/L}}$$

This is calculated by:

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

The amount of organic in the foam was not measured directly but was assumed to be the difference between the initial amount of organic in solution and the final amount of organic in solution. Errors for D values were calculated as one standard deviation. The equation used was:[52]

$$S = \sqrt{\frac{\sum_{i=1}^{N}(X_i - \bar{X})^2}{N - 1}}$$

S = standard deviation.

N = number of measurements.

X_i = measured value.

$\bar{X}$ = arithmetic mean

The error values were given to two significant figures when the first two digits lay between 10 and 35 and given to one significant figure when greater than 35. This convention of reporting the data was chosen since it is simple and yet provides a more accurate method than using just one significant figure.

RESULTS AND DISCUSSION

Timed Extraction

Preliminary studies of the extraction of phenol and other organics followed the extractions for up to 48 hours and found no increase in extraction after the first measurement at one hour of squeezing time. A more accurate experiment was performed to determine the equilibrium time for the m-nitrophenol extraction. It consisted of squeezing one sample and checking the UV absorbance every 60 seconds for 15 minutes. For 5.0 ppm m-nitrophenol in 10 % ethanol, equilibrium was achieved in about four minutes for both the polyether and the polyester foam with foam pieces of 0.25g. No difference between the two foam types was observed when the foam pieces were of similar weight. It was also found that larger foam pieces had longer equilibrium times; six minutes for the 0.40g pieces. Greater time appeared to be required to diffuse the dissolved organics into the centres of the larger foam pieces.

General Survey

Preliminary experiments were conducted using the gas chromatograph to monitor concentration to determine if ethanol could be extracted from aqueous solution by the polyurethane foam. Using a concentration of 100 ppm

ethanol, it was not possible to detect any extraction of ethanol on duplicate extractions.

A general survey of aromatic compounds was conducted. For many of these a diethyl ether liquid-liquid extraction was conducted as well. The data is listed in Table 1. The relatively large amount of ether needed for solvent extraction resulted in some extractions of greater than 99 %. In these cases the distribution coefficient is given as greater than the highest measurable value but could be significantly higher. It was noted that for many compounds the polyether and polyester foam extraction coefficients were similar, whereas for other compounds they differed considerably. The difference between polyether and polyester distribution coefficients appeared to be related to the presence of an hydroxyl group on the compound. Organic compounds that contained the -OH group (either phenolic or carboxylic acid) displayed a large difference between the polyether and polyester foam distribution coefficients. The extraction efficiency using polyester foam was always much less than that for the polyether foam. In compounds without -OH groups, the polyether and polyester extraction efficiencies were similar.

It was also noticed that for those compounds lacking an -OH group, liquid-liquid extraction with diethyl ether system yielded similar results to extraction by the

TABLE 1 – GENERAL SURVEY EXTRACTION DATA

Conditions:
1 hour squeezing time
10 % ethanol
Temperature = 25.0°C
Method of measurement; UV absorbance
Foam size: polyether – 0.25g
           polyester – 0.40g

Compound	Number of Trials	λ_{max} (nm)	Concentration (ppm)	Distribution Coefficient (L/kg ± S)		
				Polyether	Polyester	Solvent Extraction
o-t-butylphenol	4	271	30	4840±150	1320±60	> 500
2,6-di-t-butyl phenol	4	270	50	2630±90	1900±250	> 700
2,4-di-t-butyl phenol	4	258	10	21500±1400	9800±1400	
salicylaldehyde	4	255	5	104.4±3.3	82±5	70
o-methoxyphenol	4	274.5	20	41.5±3.3	32.9±3.0	24

S = one standard deviation.
* – This compound was extracted from 20 % ethanol.

TABLE 1 - CONTINUED

Compound	Number of Trials	λ_{max} (nm)	Concentration (ppm)	Distribution Coefficient ($L/kg \pm$ S)		
				Polyether	Polyester	Solvent Extraction
triphenylphosphine	4	223	5	580±19	540±80	
benzoic acid	8	228	10	112±7	30.2±2.3	18
phenol	8	270	40	78.7±1.2	33.5±1.1	37
salicylic acid	4	235	10	206±15	20.6±2.9	7
pyrogallol	4	267	10	54±30	-3±5	5
hydroquinone	4	293.5	40	21±10	8±8	
catechol	4	277.5	10	60±9	26±5	10
resorcinol	4	275	10	53±4	27.6±1.9	6
p-nitrophenol	4	311	8	407±7	165.1±3.2	100
m-nitrophenol	4	229	10	470±10	183±6	170
o-nitrophenol	4	272	10	128±4	122.3±2.0	120
2,6-dinitrophenol	4	253	10	179±12	213±16	57
2,4-dinitrophenol	4	258	10	382±23	276±13	93
2,4-dihydroxy-benzoic acid	4	256	10	292±12	36±6	6
3,5-dihydroxy-benzoic acid	4	241	10	142±8	12.4±2.6	2

TABLE 1 - CONTINUED

Compound	Number of Trials	λ_{max} (nm)	Concentration (ppm)	Distribution Coefficient (L/kg ± S)		
				Polyether	Polyester	Solvent Extraction
azobenzene	4	314	5	3800±600	3310±240	> 500
aniline	8	230	6	20.2±2.9	26±6	14
benzaldehyde	4	244	4	40.7±1.1	44.9±1.2	30
benzonitrile	4	230	6	56.2±1.4	52.6±2.2	74
toluene	4	261	100	800±500	800±500	450
acetophenone	4	240	50	38.0±1.6	40.2±1.0	58
m-dinitrobenzene	4	233	5	120.9±2.7	167±12	67
nitrobenzene	4	251	10	123.9±2.3	116.1±2.5	120
benzene	4	254	500	470±180	440±320	> 340
biphenyl	4	247	8	6540±380	5900±900	> 340
benzophenone	4	252	9	1198±40	1087±29	
ethyl benzoate	4	230.5	5	259±7	187.6±2.3	200
phenyl ether*	4	258	50	2970±90	2210±200	> 330
chlorobenzene	4	264	100	680±160	560±110	
pyridine	4	256	10	-9.1±2.8	-3.8±2.8	2
p-nitroaniline	4	382	5	275±6	193.4±3.0	36
o-nitroaniline	4	281	10	264±6	208±11	

polyether and polyester foams. For the compounds
containing the -OH group, liquid-liquid extraction with
diethyl ether yeilded similar results to extraction using
the polyester system but the polyether foam gave higher
extraction efficiencies for these compounds.

It appeared then that the two foam types acted by a
solvent extraction type mechanism except that there was
some additional affinity between the polyether foam and
the -OH containing compounds. This affinity which will be
called polyurethane hydrogen bonding (PHB) will be
described in more detail later in the thesis. It was also
noticed that for some compounds it was possible to reduce
or eliminate this affinity by placing a strongly hydrogen
bonding and bulky group next to the -OH group. Some
examples of this are o-nitrophenol, salicylaldehyde, and
o-methoxyphenol. In these compounds strong intramolecular
hydrogen bonding occurs between the hydroxyl group and the
adjacent group. This intramolecular hydrogen bonding
would not be expected with the meta and para compounds.
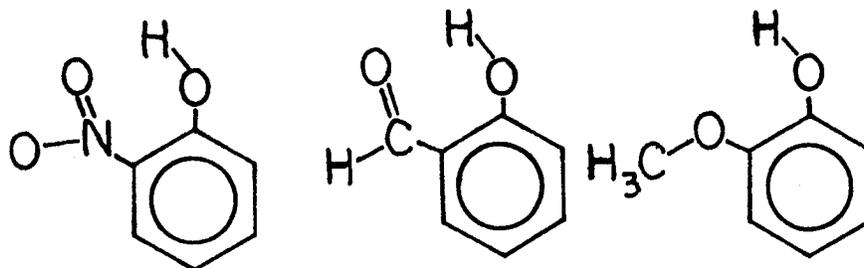
Compound	o-nitrophenol	salicylaldehyde	o-methoxyphenol
$\dfrac{D(polyether)}{D(polyester)}$	1.04	1.26	1.27

The data shows that if a strongly intramolecular hydrogen bonding group is not adjacent to the -OH group then PHB can occur.
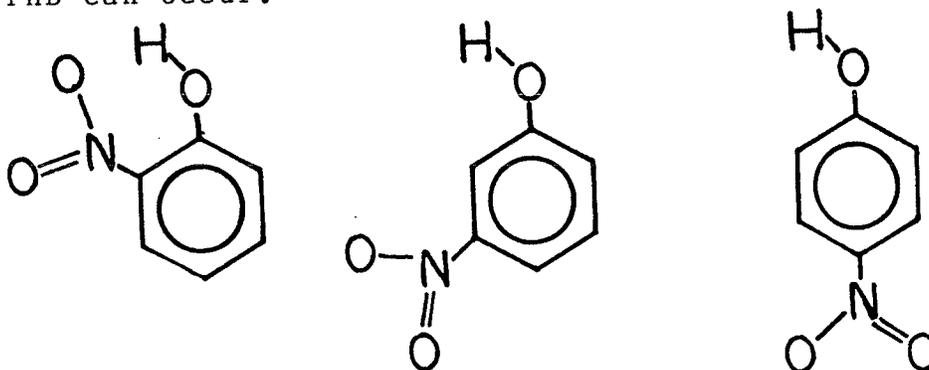
Compound	o-nitrophenol	m-nitrophenol	p-nitrophenol
$\dfrac{D(polyether)}{D(polyester)}$	1.04	2.57	2.47

This difference between these isomers may be due to a difference in dipole moment for the compounds which are given as 3.07, 4.24, and 4.60 D for the ortho-, meta-, and para-nitrophenols respectively.[53] Assuming the more nonpolar compound to be extracted to a greater extent,

then the ortho-isomer should be extracted to a greater

extent than the meta- which in turn should be extracted to

a greater extent than para-. The gradual increase in

extraction for the series para- > meta- > ortho- is not

observed in the data so that it can be concluded that some

factor other than dipole moment is responsible for the

difference in extraction values for these isomers.

In these compounds there is also an additional

induction effect. Nitro and aldehyde groups are electron

withdrawing while the methoxy group is electron donating.

This induction effect would not occur to any extent in the

meta- isomers but, because of conjugation, would be

strongest in the ortho- and para- isomers. The resonance

structures for the ortho- and para-nitrophenol compounds

are shown below:

p-nitrophenol   o-nitrophenol
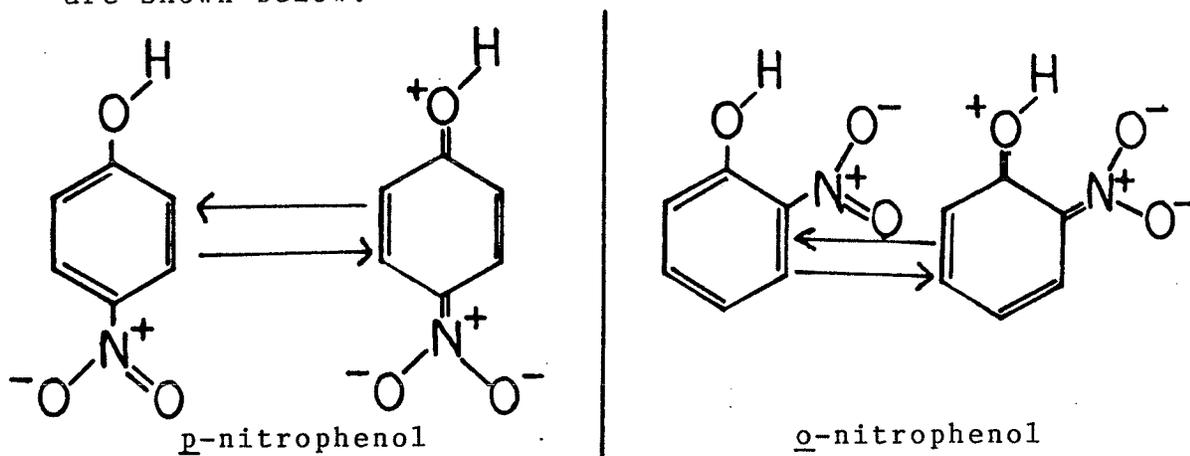
This induction effect would increase any

intermolecular hydrogen bonding or PHB in the nitro and

aldehyde compounds and decrease any intermolecular

hydrogen bonding in the methoxy compound. The effect

would be expected to be negligible in the <u>meta</u>- compound

and strongest in the <u>para</u>- or <u>ortho</u>- compounds; however,

the experimental extraction ratios show the <u>meta</u>- and

<u>para</u>- compounds to be similar. It can be concluded that

the induction effect is very small and plays a limited

role in the extraction. Thus the factor influencing PHB

is the intramolecular hydrogen bonding of groups in the

<u>ortho</u> position.

It was possible in addition to reduce the effect of

the -OH group by placing bulky groups next to it. If only

one bulky group is adjacent then PHB is largely unaltered

as is shown by the large ratio values for

<u>o</u>-(<u>t</u>-butyl)phenol and 2,4-di-(<u>t</u>-butyl)phenol.
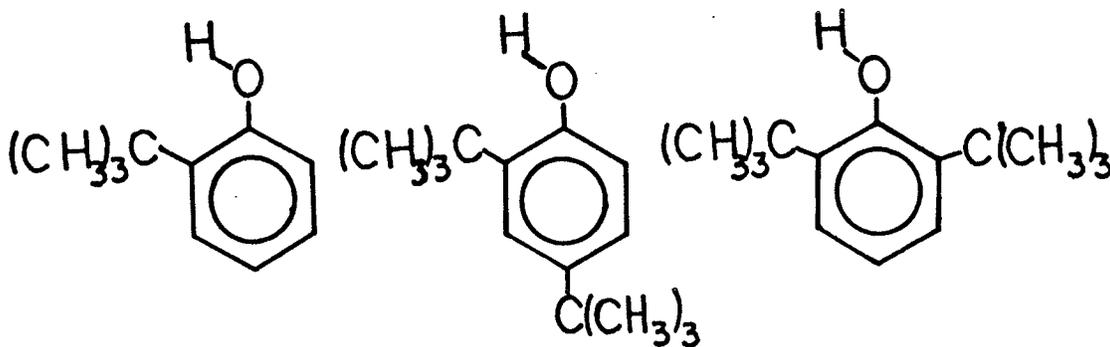
Compound	<u>o</u>-(<u>t</u>-butyl) phenol	2,4-di-(<u>t</u>-butyl) phenol	2,6-di-(<u>t</u>-butyl) phenol
$\dfrac{D(polyether)}{D(polyester)}$	3.67	2.19	1.38

Thus in the case of <u>o</u>-nitrophenol, <u>o</u>-methoxyphenol, and

salicylaldehyde, it is probably the strong intramolecular

hydrogen bonding rather than the bulkiness of the adjacent

groups that affects PHB. Only when the -OH group is

completely "boxed in" by two adjacent bulky groups is PHB prevented as in the case of 2,6-di-($\underline{t}$-butyl)phenol.

Effect of Salt Addition on Extraction of Organics

The investigation into the effect of salt addition on the extraction of organic compounds by polyurethane foam was conducted in a fashion similar to the general survey experimental method. The only differences were that a salt stock solution was used instead of the 10 % ethanol, the organic stock solutions were prepared by dissolving the organic compound in pure water instead of ethanol, and only three samples instead of four were run for each of the polyester and polyether foam types.

If the mechanism is a straight forward solvent extraction type mechanism then it should be possible to observe a salting out phenomenon. Extractions from various salt solutions were performed as shown in Tables 2 and 3. It can be seen that the salting out effect occurred. The effect on the distribution coefficients (D) appeared to be quantitatively proportional to the charge density on the cations in the first extraction series (monovalent ions only). Small ions such as Li^+ with the largest charge density had the greatest effect on D. The charge density for the three alkali metal cations was calculated from the radius.[54] This was then plotted against the distribution coefficients and shown in

TABLE 2 - SALT EXTRACTION DATA # 1

Conditions:
    1 hour squeezing time
    Temperature = 25.0°C
    0 % ethanol
    Method of measurement; UV absorbance
    Foam size: polyether - 0.25g
               polyester - 0.40g
    5 ppm m-nitrophenol
    λ = 229 nm

Salt	Salt (M) Concentration	Distribution Coefficient (L/kg ± S) Polyether	Polyester
LiCl	3.00	1940±26	600±50
NaCl	3.00	1550±60	544±25
KCl	3.00	871±19	339±9
$NaClO_4$	3.00	413±12	196±10
None	0.00	550±12	229±6
$CaCl_2$	1.00	1110±60	371±8
Na_2SO_4	1.00	1503±7	472±23

S = one standard deviation.

TABLE 3 - SALT EXTRACTION DATA #2

Conditions:
    1 hour squeezing time
    Temperature = 25.0°C
    0 % ethanol
    Method of measurement; UV absorbance
    Foam size: polyether - 0.25g
                polyester - 0.40g
    5 ppm m-nitrophenol
    λ = 229 nm.
    Salt = NaCl

Salt Concentration	Distribution Coefficient (L/kg ± S) Polyether	Polyester
0.00	550±12	229±6
0.50	650±110	260±22
1.00	803±11	292±4
1.50	929±28	356±16
2.00	1260±100	491±28
3.00	1550±60	544±25

S = one standard deviation

Number of trials = 4 for each value.

Figure 6. It was interesting that the $NaClO_4$ caused a reduction in the D values. At first it was suspected that this was due to a competitive extraction in which the $NaClO_4$ was being extracted by the foam. Gravimetric analysis of ClO_4 before and after extraction showed that no $NaClO_4$ had been extracted. The analysis was performed according to the method of Vogel.[55] Ion chromatographic analysis was performed before and after the extraction of $NaClO_4$ with a concentration of 100 ppm Na^+ and this also showed that no $NaClO_4$ was extracted within experimental error. The experimental error was estimated to be 5 ppm of $NaClO_4$ which is well below the extraction capacities of the foam as reported by Bowen[4]. The ion chromatographic analysis was conducted in a way similar to the general survey except that the method of monitoring the salt concentration involved injecting samples into the ion chromatograph.

The salt effect was qualitatively proportional to the relative solvation numbers of the three alkali cations; the solvation number being defined as the number of solvent molecules per ion which for sufficiently long time remain attached to a given ion so as to accompany it on its translational movements. For concentrations of 1.2 N the solvation numbers for K^+, Na^+, and Li^+ are 5.4, 8.4, and 14.0 respectively assuming the Cl^- reference ion to have a solvation number of 4.0.[56] This hierarchy is

Figure 6. The Relationship Between Cation Charge

Density and the Extraction of an Organic

Compound From a Salt Solution.

Distribution Coefficient (L/kg) vs.

Charge Density (q/nm^3).

The conditions were as follows:

1 hour squeezing time

3.00 M salt concentrations

5 ppm m-nitrophenol

0 % ethanol

λ = 229 nm.

Temperature = $25^{\circ}C$

Polyether - ☐

Polyester - △
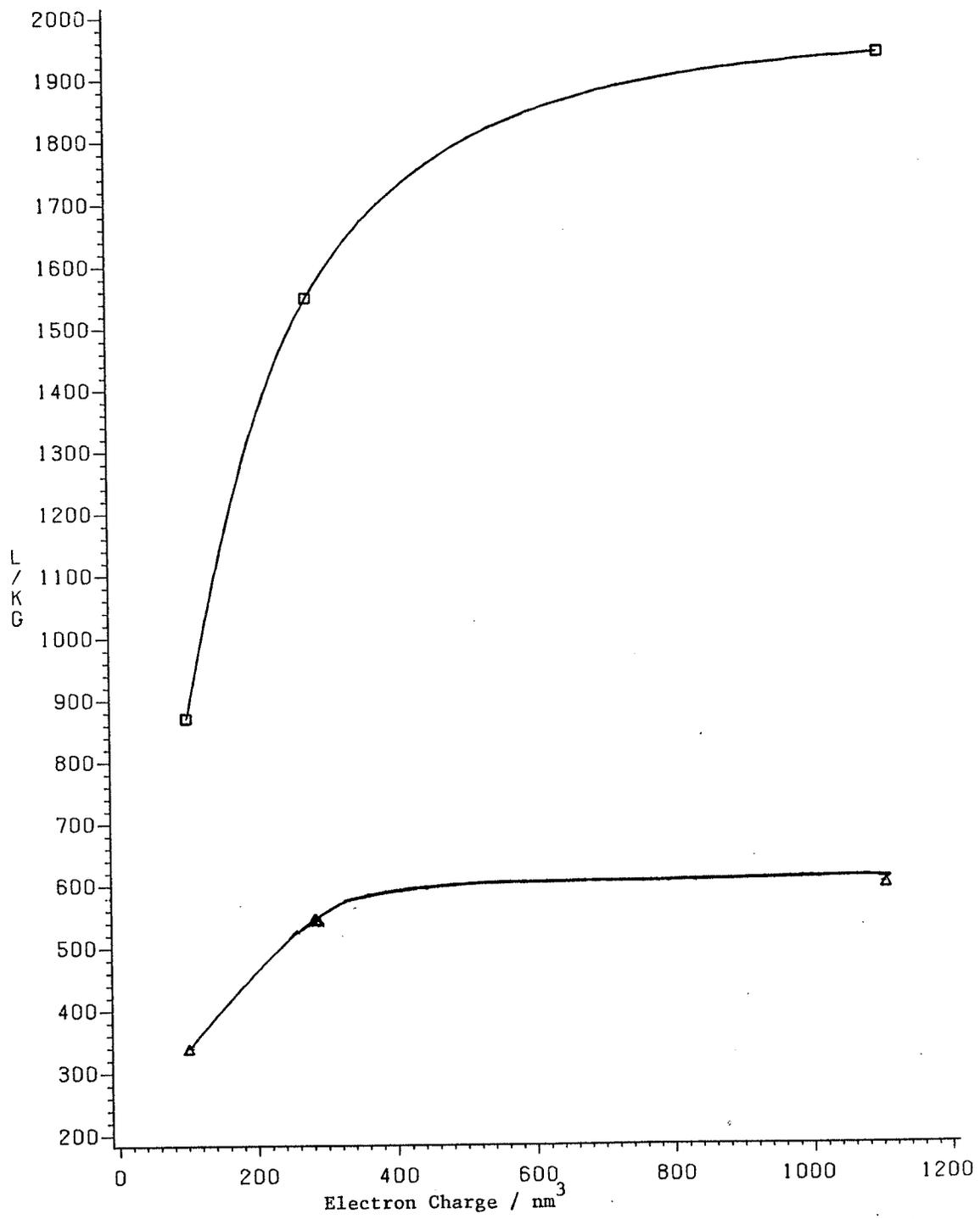
Figure 7. The Effect of Salt Concentration on the

Extraction of m-Nitrophenol From Aqueous

NaCl Solution.

Distribution Coefficient (L/kg) vs.

Salt Concentration (mol/L).

The conditions were as follows:

1 hour squeezing time

5 ppm m-nitrophenol

0 % ethanol

λ = 229 nm.

Temperature = 25.0°C

Polyether - □

Polyester - △
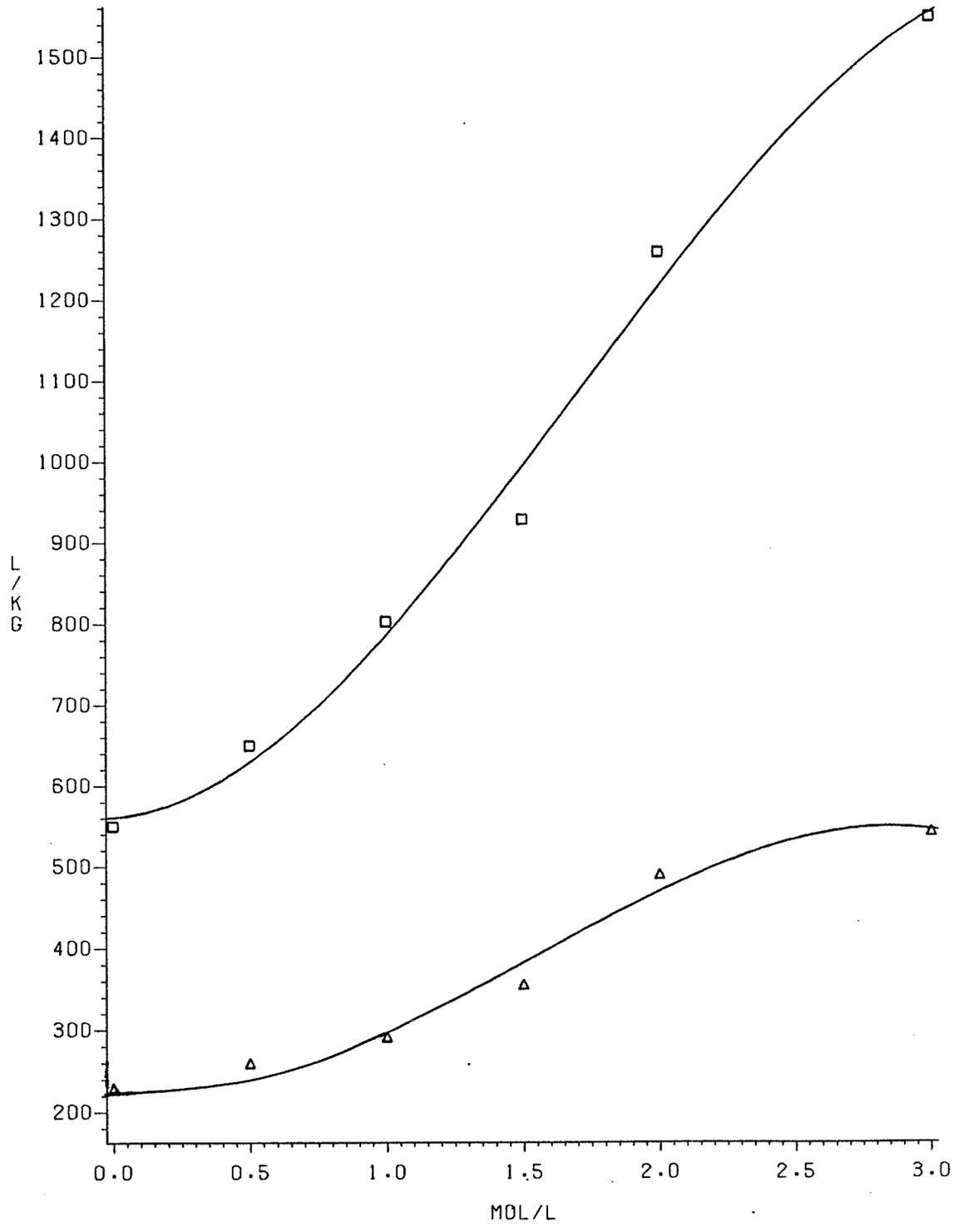
similar to that observed for the salting out effect on extraction of organics for these ions.

The salting out effect of divalent ions was also looked at briefly. There was some difficulty in finding ions that were not UV absorbing. Because it was impossible to dissolve enough of these compounds to make 3.0 M solutions the solutions were prepared with salt concentrations of 1.0 M. It was seen that the salting out effect using Ca^{++} was evident and greater than the 3.0 M KCl solution. This observation coincides with the observation by Korkisch et al[32] who noted that the hierarchy for salting out effectiveness in increasing theextraction of organics was $NH_4^+ < Ca^{++} < Al^{+++}$, (monovalent < divalent < trivalent) when anion molarities were equal.

Another salt experiment was conducted where the concentration was altered and the extraction observed. It was found for NaCl that the salting out effect was proportional to the salt concentration. The relationship is shown in figure 6. The effect of salt concentrations below 0.50 M was too small to detect within the experimental error for both the polyether and polyester foams.

The Effect of pH on the Extraction of Organics

The investigation into the effect of pH on the

extraction of organic compounds by polyurethane foam was conducted similarly to the experimental method used for the general survey. The only differences were that the extractions were run in pure water instead of 10 % ethanol, and that various amounts of HCl or NaOH were added to the samples prior to dilution to achieve the required pH.

It was found in the cases when the organic compound was ionizable that pH played an important role in extraction. Only when the organic compound was a neutral species would it extract into the polyurethane foam. If the compound become charged, it would remain in the aqueous phase. Compounds such as m-nitrophenol or benzoic acid, if found in a solution of very high pH (greater than the corresponding dissociation constant) had a distribution coefficient of zero within the experimental error.

For compounds that were not ionizable no pH effect was observable. Nitrobenzene was extracted from solutions of pH = 2 to 12 with all values identical within the experimental error and no pattern being observed.

An attempt was made to observe the cation chelation mechanism for the extraction of organic compounds. Aniline was extracted from pure water at a wide range of pH values. It was found that aniline did not extract well when protonated, even when in 0.5 M ClO_4^- solution (a good

anion for the cation chelation mechanism). For the
polyether foam it was found that for a solution of six ppm
aniline, an extraction value of 12.6±1.0 L/kg was measured
at a pH of 2.4, and that an extraction value of 25.1±2.8
L/kg was determined at pH 11.3. The distribution
coefficients were determined after one hour squeezing time
with a temperature of 25.0°C. The results for the
polyester extraction were very close to zero and due to
experimental error were not meaningful. For the anilinium
cation $C_6H_5NH_3^+$, the dissociation constant is 2.34 x 10^{-5}
(pK_a = 4.63)[57] in aqueous solution at 25°C. As can be
seen, the neutral species is extracted to an extent double
that of the protonated species. This effect can be more
clearly seen for ionizable compounds that have much larger
distribution coefficients values. If the cation chelation
mechanism is prominent here then the ionic species would
be extracted to a greater extent than the neutral species.
For aniline and other ionizable aromatic compounds it was
seen that there was no evidence of the cation chelation
mechanism occurring. The cation chelation mechanism may
not play a role in the extraction of these compounds due
to the size of the benzene ring or the poor charge
distribution on the charged species. Some mechanism other
than cation chelation must be involved for the extraction
of organic compounds by polyurethane foam.

Effect of Ethanol Concentration on the Extraction of
Organics

The effect of ethanol concentration on the extraction
of organic compounds by polyurethane foam was
investigated. This was done in a fashion similar to that
used in the general survey except that stock solutions
ranging from 0 to 30 % ethanol were prepared and used for
the extractions. Three organic compounds soluble in water
in the absence of ethanol were chosen and examined for the
effect of ethanol concentration. For phenol, the
distribution coefficients were so low that the extraction
from 30 % ethanol was thought unnecessary as it was
expected to be close to zero.

The extraction of several organics was performed with
aqueous solutions of different ethanol concentration. It
was found that by increasing the ethanol concentration,
the distribution coefficients were reduced. Thus pure
water had the best extraction value for the compounds
tested. The data is listed in Table 4. The relationship
for the 3 compounds is shown in Figures 7, 8, and 9. This
supports the idea of a solvent extraction mechanism as
addition of ethanol lowers the dielectric constant of the
aqueous solution which would be expected to decrease the
extraction. It was previously mentioned that in a solvent
extraction mechanism the extraction occurs from a solution
(raffinate phase) with high dielectric constant to a

TABLE 4 - THE EFFECT OF ETHANOL SOLVENT CONCENTRATION ON THE EXTRACTION OF ORGANICS

Conditions:
    1 hour squeezing time
    Temperature = 25.0°C
    Method of measurement; UV absorbance
    Foam size: polyether - 0.25g
               polyester - 0.40g
    λ max   m-nitrophenol = 229 nm.
              benzoic acid = 228 nm.
              phenol = 270 nm.

Compound : m-nitrophenol (5 ppm)

Solvent Concentration % Ethanol (V/V)	Distribution Coefficient (L/kg ± S) Polyether	Polyester
0.0	550±12	229±6
10	441±10	180±6
20	282±16	143±12
30	145±10	77±6

Compound : benzoic acid (10 ppm)

Solvent Concentration % Ethanol (V/V)	Distribution Coefficient (L/kg ± S) Polyether	Polyester
0.0	100±12	29.6±0.9
10	111±6	30.4±2.3
20	60±8	8±5
30	10±10	0±3.0

S = one standard deviation.

TABLE 4 - CONTINUED

Compound : phenol (40 ppm)

Solvent Concentration % Ethanol (V/V)	Distribution Coefficient (L/kg $\pm$ S)	
	Polyether	Polyester
0.0	87.6$\pm$1.7	40.3$\pm$1.9
10	78.7$\pm$1.2	33.5$\pm$1.1
20	47$\pm$4	25.8$\pm$1.4

S = one standard deviation.

Figure 8. The Relationship Between Solvent Ethanol

Concentration and the Extraction of

m̲-Nitrophenol by Polyurethane Foam.

Distribution Coefficient (L/kg) vs.

Solvent Ethanol Concentration (% Ethanol).

Conditions were as follows:

5 ppm m̲-nitrophenol

Temperature = 25.0°C

1 hour squeezing time

λ = 229 nm.

Polyether - ◻

Polyester - △
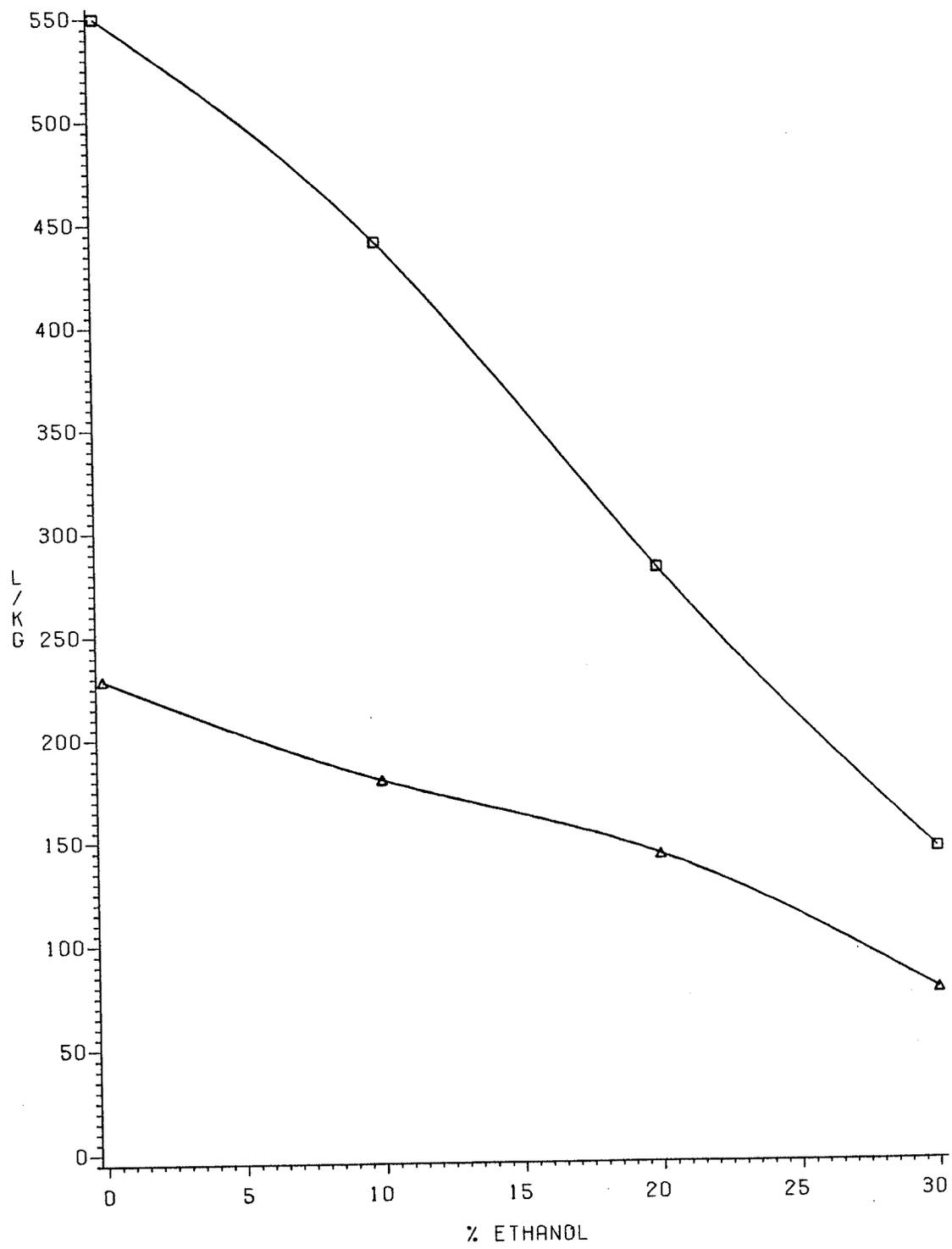
Figure 9. The Relationship Between Solvent Ethanol

Concentration and the Extraction of Benzoic

Acid by Polyurethane Foam.

Distribution Coefficient (L/kg) vs.

 Solvent Ethanol Concentration (% Ethanol).

Conditions were as follows:

10 ppm benzoic acid

Temperature = 25.0°C

1 hour squeezing time

λ = 228 nm.

Polyether - ☐

Polyester - △
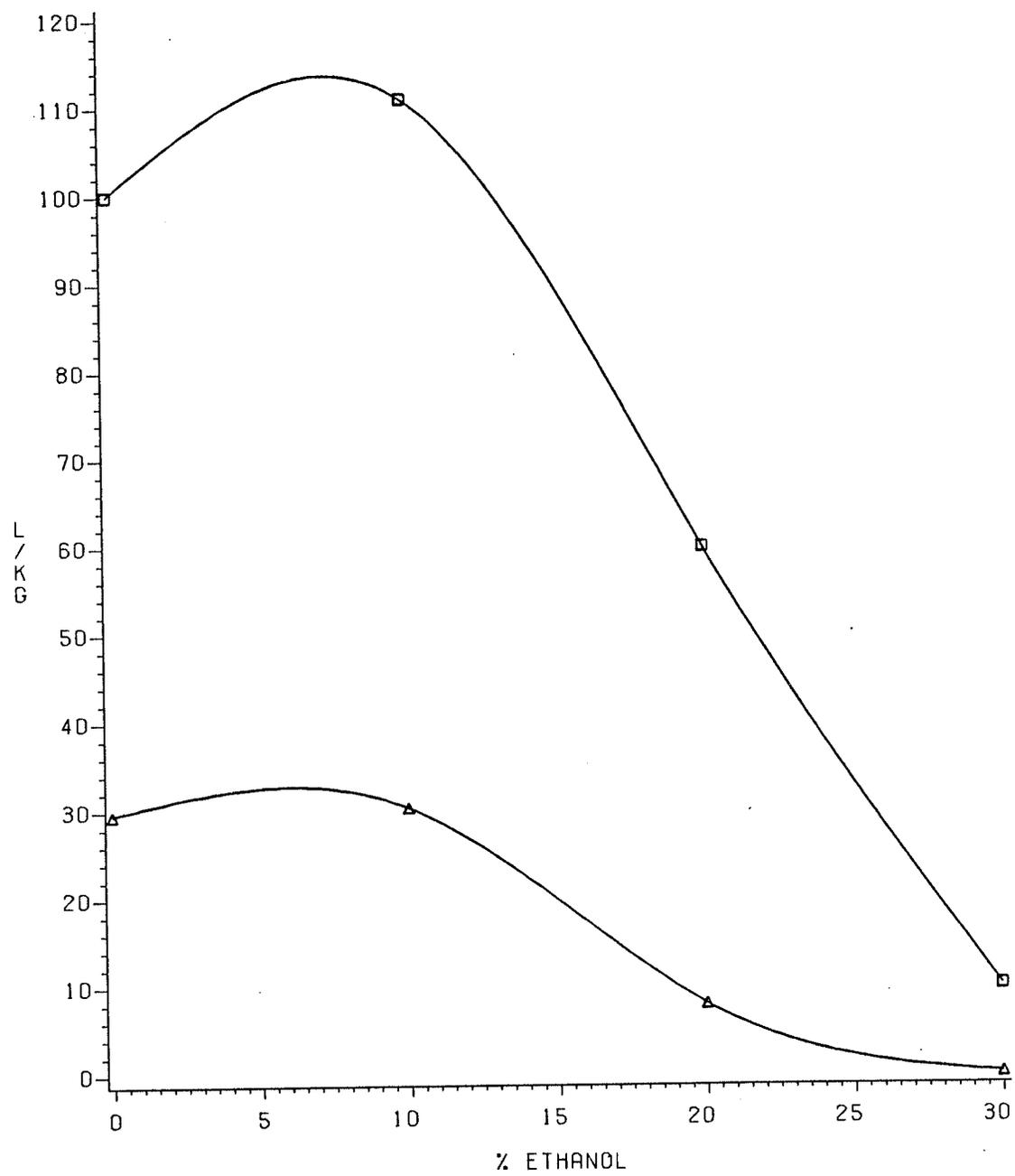
Figure 10. The Relationship Between Solvent Ethanol
Concentration and the Extraction of Phenol
by Polyurethane Foam.
Distribution Coefficient (L/kg) vs.
Solvent Ethanol Concentration (% Ethanol).
Conditions were as follows:
40 ppm phenol
Temperature = 25.0°C
1 hour squeezing time
λ = 270 nm.
Polyether - □
Polyester - △
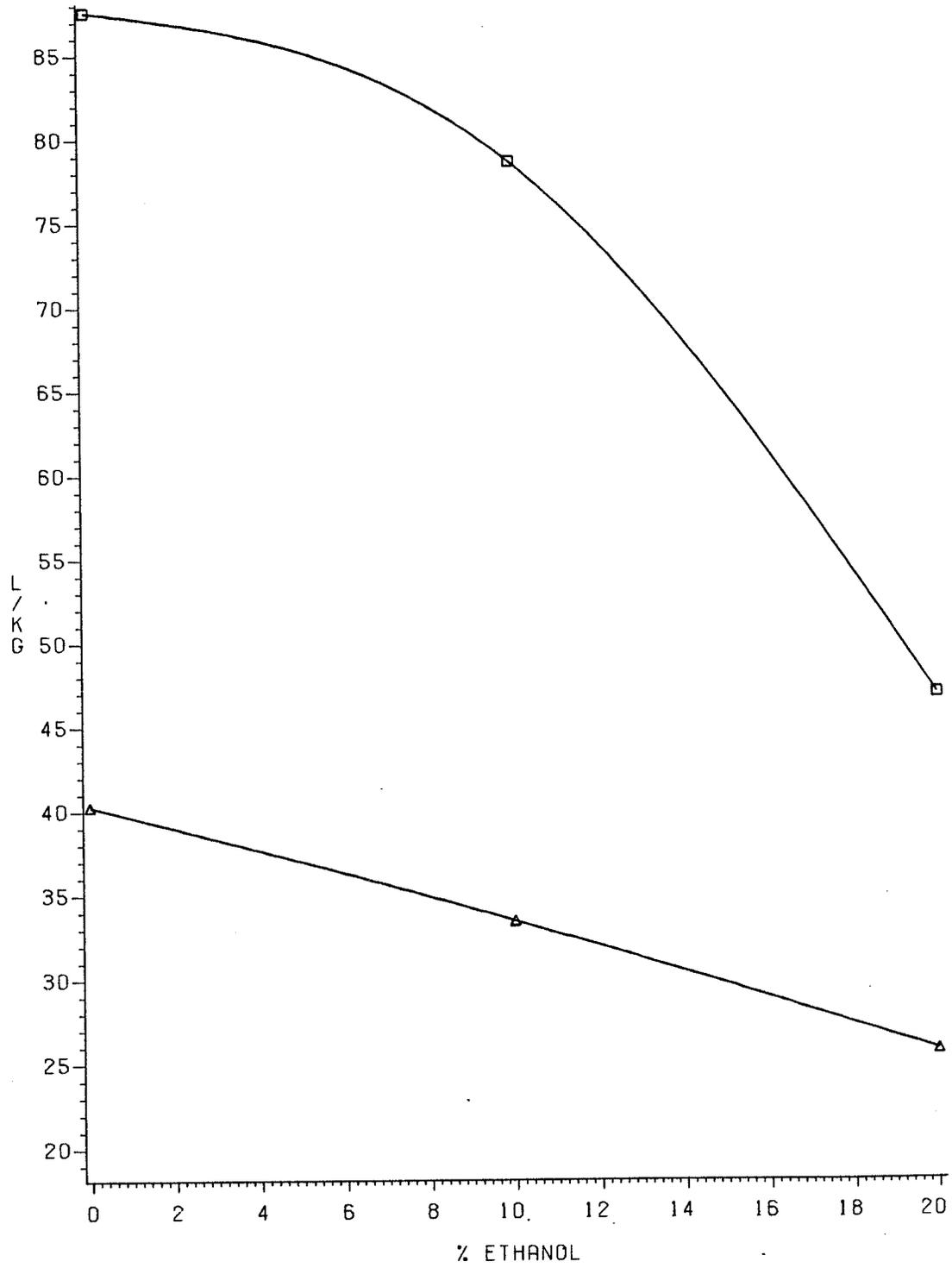
solution of low dielectric constant (solvent phase) for a compound with a low dielectric constant. This would proceed with a larger equilibrium constant than for the extraction from low dielectric constant to a low dielectric constant. If the solvent phase is kept the same, the greater the difference between the dielectric constant of the compound extracted and the raffinate phase, the greater the extraction. This is the same phenomenon that was observed, as the foam (solvent phase) was held constant but the dielectric constant of the aqueous solvent (raffinate phase) was changed as the solvent was changed by adding ethanol, resulting in changes in the extraction values.

The Effect of Temperature on the Extraction of Organics

Preliminary experiments showed that the distribution coefficient for $\underline{m}$-nitrophenol decreased as the temperature was increased. Experiments were performed using the thermostated squeezing cell whereby the distribution coefficient was calculated for every temperature after a $5^{\circ}C$ temperature increment change from $25^{\circ}C$ to $75^{\circ}C$.

According to elementary thermodynamics, the equilibrium constant, K, for a chemical reaction is related to the standard enthalpy change (ΔH°) and to the standard entropy change (ΔS°) for that reaction. This relationship is given by:

$$\log_{10} K = (-\Delta H^o/2.303RT) + (\Delta S^o/2.303RT)$$

This relationship holds for the extraction;

$$ORGANIC_{(aq)} \xrightleftharpoons{K} ORGANIC_{(foam)}$$
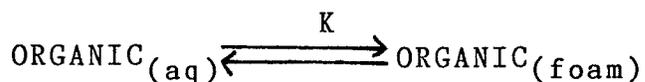
where $ORGANIC_{(aq)}$ is the amount of the organic compound in the aqueous solvent and $ORGANIC_{(foam)}$ is the amount of the organic compound in the foam.

If we assume no chelation or precipitation of the organic compound then K is equivalent to the distribution coefficient. Therefore:

$$\log D = (-\Delta H^o/2.303RT) + (\Delta S^o/2.303RT)$$

By plotting log D against 1/T we achieve a graph where the slope is $-\Delta H^o/2.303R$ and the intercept is $\Delta S^o/2.303R$. Thus, from the slope and the intercept ΔH^o and ΔS^o can be calculated. The slope, error in slope, y intercept and error in intercept were calculated using the Least Mean Squares Program by E.A. MacGregor, U. of M. (1985).

For each compound, the thermodynamic temperature extractions were done in duplicate. For azobenzene it was observed that the polyether and polyester values were the same within experimental error for both the enthalpy and

entropy change for the extraction. The entropy change was very close to zero for this compound. This indicated that the azobenzene was solvated and not tightly bound in the foam so that it had the same freedom of motion as it had when it was in the aqueous solution. The driving force behind the extraction was the enthalpy change, since the extraction results in a lower energy state. For m-nitrophenol where the -OH group was present, there was a large difference between the polyether and polyester data. With m-nitrophenol there was a decrease in free entropy by the extraction due to a loss of freedom of movement by the molecules. It was apparent that with the polyether foam there was a much greater loss of entropy. Therefore once extracted into the polyether foam, the freedom of motion of the m-nitrophenol was restricted to a much greater extent than when extracted into the polyester foam. Even with this entropy loss, the extraction proceeded due to a loss in enthalpy as the molecules moved to a lower energy state. As the temperature increased the entropy effect became more important and the extraction was reduced until eventually it was not thermodynamically possible. The difference between the ΔH^o values for the polyether and polyester foams was 9.3 kJ/mole. This energy value was comparable in magnitude to a weak form of hydrogen bonding. Hydrogen bonding in H_2O has a bond energy of about 21 kJ/mole[58].

Overall, it appeared that the main mechanism was a solvent extraction mechanism that was similar for both the polyether and polyester foam types. If no -OH groups were present, then only the solvent extraction mechanism would be observed (as in azobenzene) and the polyether and polyester foams would behave similarly. Since the polyether polyurethane foam and polyester polyurethane foam are very similar in structure it can be assumed that they have dielectric constants that are similar but slightly different due to the small structural differences. This similarity between dielectric constants would explain why the extraction values for many organic compounds are similar for the polyether and polyester foam types. Any small differences between extraction values for the two foam types can be attributed to the expected small difference between the two dielectric constants. Where there is an -OH group present then an additional factor is involved in the mechanism which distinguishes between the polyether and polyester foam types. This was previously referred to as Polyurethane Hydrogen Bonding (PHB) and can increase the distribution coefficient of an organic compound several fold.

Figure 11a. The Effect of Temperature on the

Extraction of Azobenzene by

Polyurethane Foam, - Trial 1.

Log D vs. 1/Temperature (1/K).

Conditions were as follows:

10 % Ethanol

5 ppm azobenzene

λ = 314 nm.

Temperature controlled squeezing cells

Polyether - □

Polyester - △
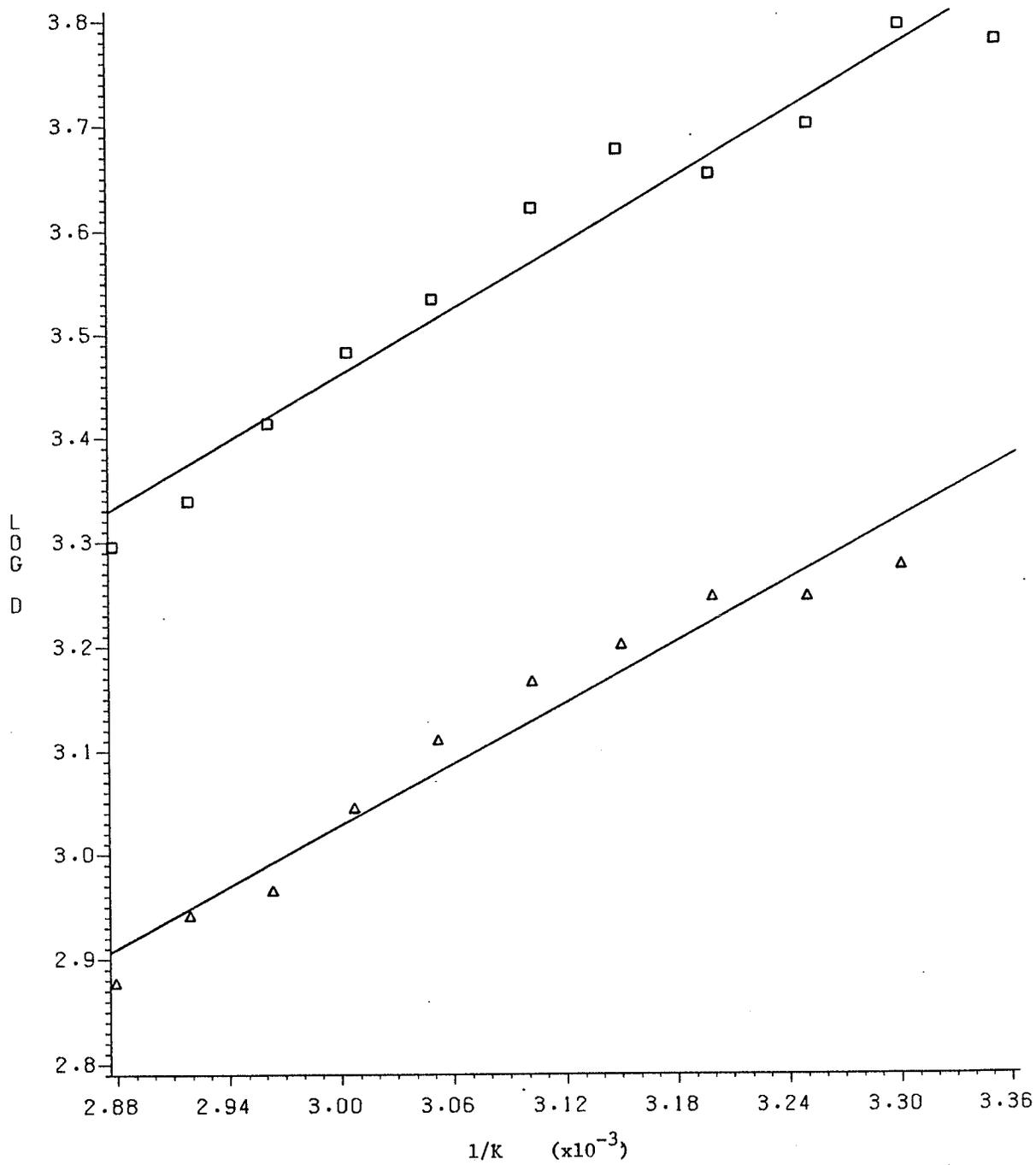
Figure 11b. The Effect of Temperature on the

Extraction of Azobenzene by

Polyurethane Foam, - Trial 2.

Log D vs. 1/Temperature (1/K).

Conditions were as follows:

10 % Ethanol

5 ppm azobenzene

λ = 314 nm.

Temperature controlled squeezing cells

Polyether - $\triangle$

Polyester - $\square$
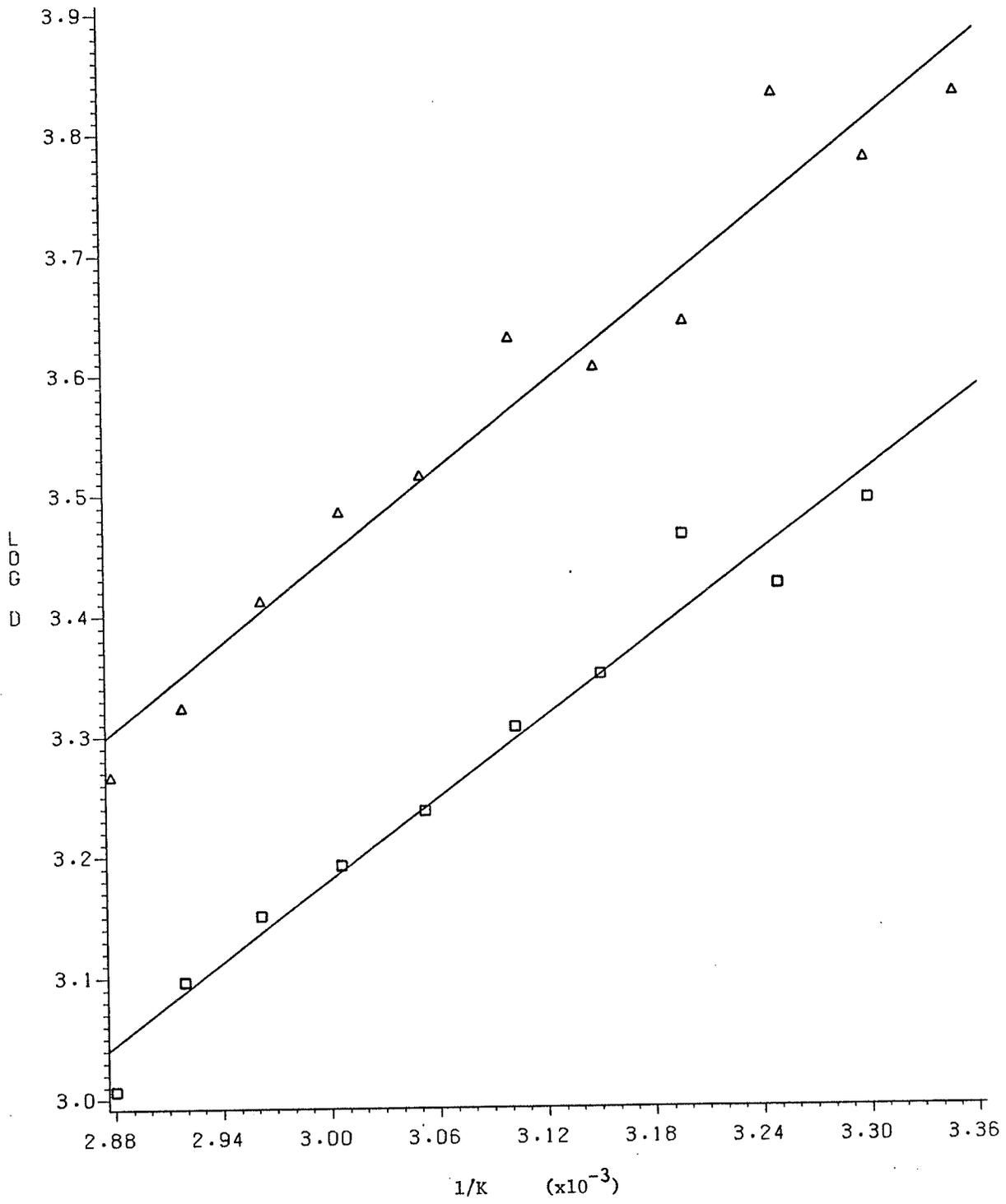
Figure 12a. The Effect of Temperature on the

Extraction of m-Nitrophenol by

Polyurethane Foam, - Trial 1.

Log D vs. 1/Temperature (1/K).

Conditions were as follows:

10 % Ethanol

10 ppm m-nitrophenol

λ = 230 nm.

Temperature controlled squeezing cells

Polyether - □

Polyester - △
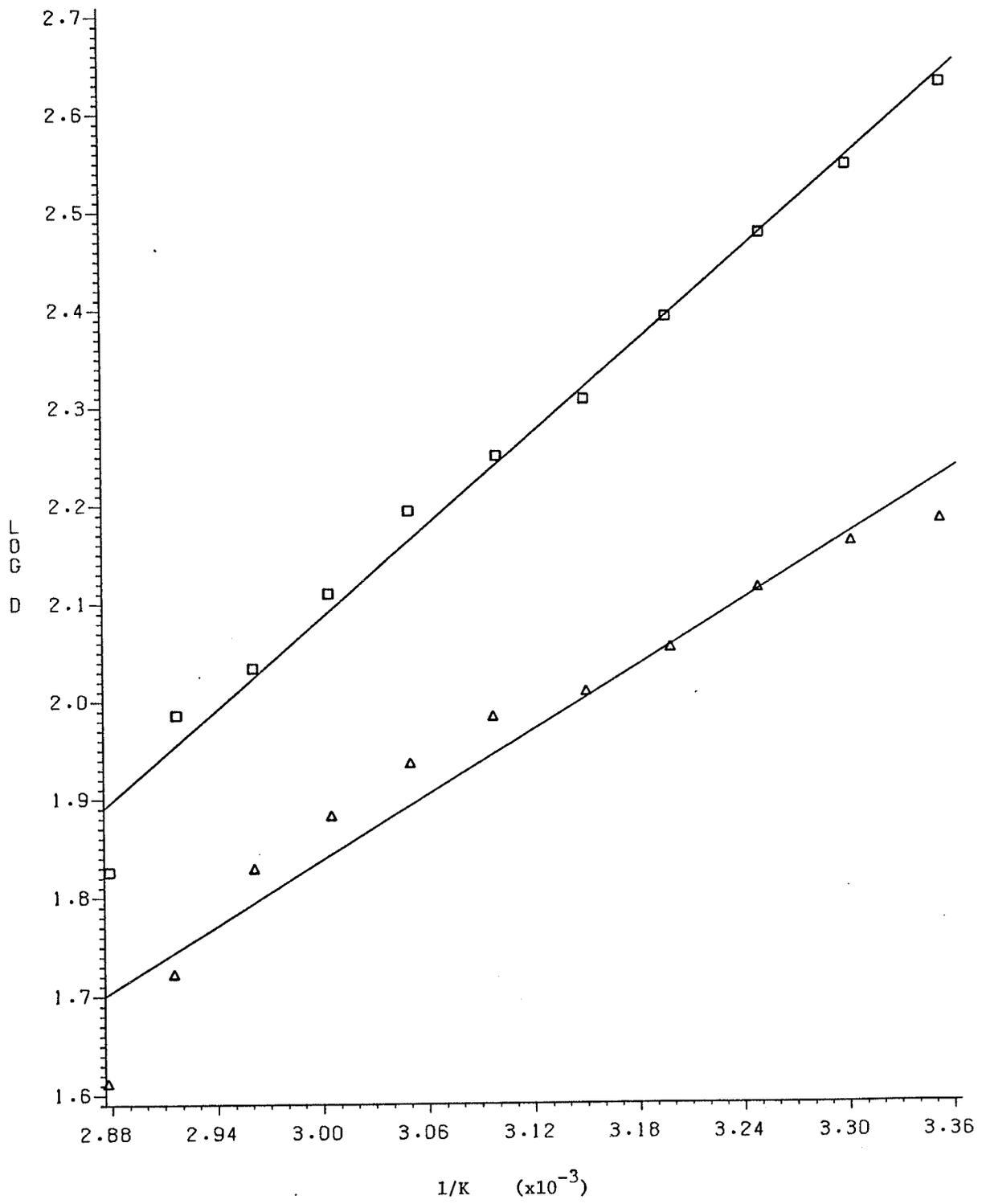
Figure 12b. The Effect of Temperature on the

Extraction of m-Nitrophenol by

Polyurethane Foam, - Trial 2.

Log D vs. 1/Temperature (1/K).

Conditions were as follows:

10 % Ethanol

10 ppm m-nitrophenol

λ = 230 nm.

Temperature controlled squeezing cells

Polyether - ▢
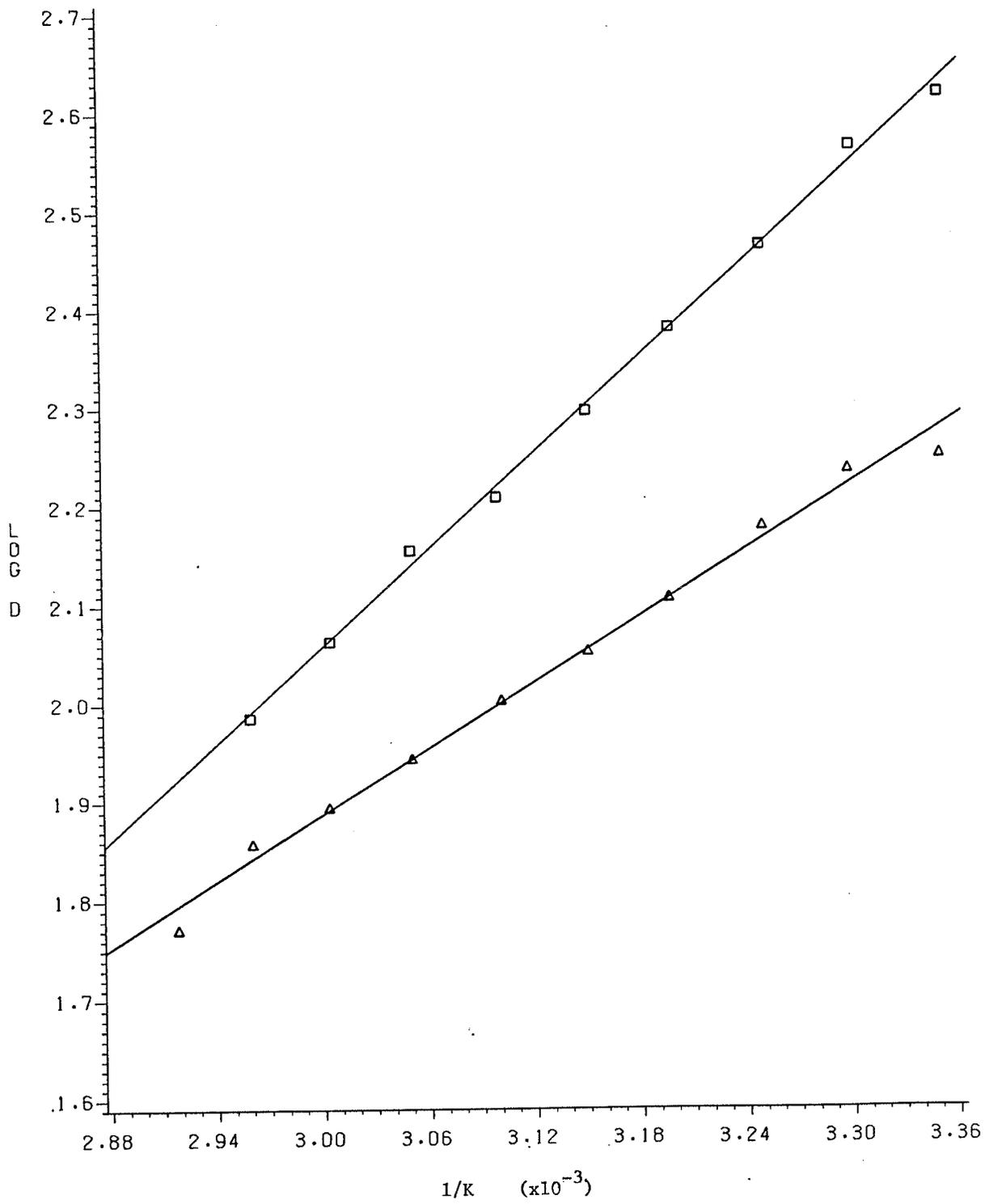
Polyester - △

TABLE 5 - THERMODYNAMIC TEMPERATURE EXTRACTION DATA

Conditions:
      10 % ethanol
      5 ppm azobenzene
        λ = 314 nm.
      10 ppm m-nitrophenol
        λ = 230 nm.

Compound : azobenzene

		Polyether	
	Trial 1	Trial 2	Average
ΔH^O kJ/mole	-20.3±1.5	-23.0±1.7	-21.6±1.9
ΔS^O J/mole·K	5±5	-3±5	1±6

		Polyester	
	Trial	Trial 2	Average
ΔH^O kJ/mole	-18.8±1.5	-21.6±1.4	-20.2±2.0
ΔS^O J/mole·K	2±4	-4±4	-1±4

Compound : m-nitrophenol

		Polyether	
	Trial 1	Trial 2	Average
ΔH^O kJ/mole	-29.9±1.1	-31.3±0.5	-30.6±1.0
ΔS^O J/mole·K	-49.9±3.4	-54.5±1.7	-52.2±3.3

		Polyester	
	Trial 1	Trial 2	Average
ΔH^O kJ/mole	-21.2±1.6	-21.4±0.7	-21.30±0.14
ΔS^O J/mole·K	-28±5	-28.1±2.1	-28.05±0.07

Note : All values ± one standard deviation (S).

INTERPRETATION

There has been a large amount of work done on the extraction of compounds from aqueous solution by polyurethane foam and several authors have made attempts to describe the mechanism involved. Several mechanisms have been mentioned in the Introduction. To date there has been no reference to a mechanism specific to the extraction of organic compounds by polyurethane foam although a solvent extraction mechanism might be expected. The mechanisms for extraction by polyurethane foam that have been mentioned are the ether-like solvent extraction mechanism[27,28,29,33] and the cation chelation mechanism.[34,35,36,37]

The evidence accumulated in this work indicates a polyurethane extraction mechanism consisting of a solvent extraction type mechanism for organic compounds. In the case of the diethyl ether extraction it was found experimentally that the extraction occurs very quickly; i.e., within 15 minutes with periodic shaking. According to Hamon[3] the cation chelation mechanism (CCM) takes up to 18 hours to reach equilibrium for pieces of foam that are only 0.05 g in weight. The experimental values for the time of extraction of organic compounds that were recorded in this thesis are of the same magnitude as the ether extraction time of equilibrium and several orders of magnitude smaller than the CCM values. This similarity in

extraction times would support the idea that the extraction occurs predominantly by an ether-like solvent extraction (SE) mechanism whereas the difference in equilibrium times does not support the CCM.

The existence of the salt addition effect on the extraction also supports the idea of a solvent extraction type mechanism. Various singly and doubly charged species can be used to produce this effect. It was found that the addition of the doubly charged ions produced a larger increase in extraction then the addition of the singly charged. This can be seen when comparing 3.0 M KCl and 1.0 M $CaCl_2$. Although the KCl concentration is three times greater, the increase in extraction is still greater for the $CaCl_2$. This comparison was chosen as Ca^{++} and K^+ are located side by side in the same row of the periodic table and are nearly identical in size. Thus the hierarchy for salting out effectiveness is determined to be $K^+ < Ca^{++}$ which is similar to the hierarchy by Korkisch[32] of $NH_4^+ < Ca^{++} < Al^{+++}$ for uranium extraction by polyurethane foam and uranium extraction by liquid-liquid ether extraction. Owing to their high UV absorbance, it was not possible to investigate the salting out effectiveness of NH_4^+ and Al^{+++}. The increase in the salting out effect with the increase of charge density on the cations could also be explained by a SE type mechanism according to solvation theories as the ions with the

larger charge density would attract more water molecules which would then be unable to solvate the organic compound. This greater attraction of water molecules is shown by the solvation numbers of the alkali cations which was listed earlier, where the hierarchy was $K^+ < Na^+ < Li^+$ [56] which is the same hierarchy observed experimentally for the salt addition effect of extraction. For a solvent extraction mechanism this inability to solvate the organic compound would drive the organic compound from the aqueous solution and increase the extraction. Also noted was the relationship between extraction and salt concentration. As the number of salt ions is increased, more water molecules will be used to solvate the salt ions resulting in a reduction in the number of water molecules available to solvate the organic compound. This will decrease the solubility of the organic compound and thereby increase the extraction.[59] Such a relationship would be expected if a SE mechanism was being used.

Changing the dielectric constant of the solvent by altering the ethanol concentration drastically changes the extraction of the organics tested. An extraction by a SE mechanism is influenced by the dielectric constant of the raffinate and solvent phase. Thus by changing the dielectric constant of the raffinate phase (10 % ethanol) the extraction should be altered. The experimental results therefore support a SE mechanism.

The distribution coefficients for the diethyl ether solvent extraction were always of the same magnitude as the polyurethane distribution coefficients and in many cases were very close in value. These values show a similarity in extraction mechanism between the diethyl ether and the polyurethane foam.

The pH experiments show that only the neutral species of these compounds will extract into the foam in any appreciable amount. These studies show no evidence of any kind of mechanism that requires ionic species such as the cation chelation mechanism. These results are consistent with a solvent extraction mechanism.

This basic mechanism is supplemented by weak hydrogen bonding between the -OH group on the organic compound and the polyether foam. This bonding may occur in the polyether backbone between the ether oxygens and the phenolic hydrogens and has been referred to as Polyurethane Hydrogen Bonding (PHB) in this thesis. In the case of the polyester foam, the ester groups are not as strongly hydrogen bonding as the ether groups in the ether type foam. This is shown by the fact that an ether group is easier to protonate than an ester group and that the ability to form hydrogen bonds is proportional to the ability for a group to be protonated.[60] The amide linkages would be better than either the ether or ester groups at forming hydrogen bonds so that the more amide

linkages that a foam has the greater the increase in distribution coefficient due to PHB. The negative entropy values for m-nitrophenol indicate that there is a loss in entropy and it is therefore held more tightly by the foam than azobenzene where there is no change in entropy, and no loss in freedom of movement. Thus the presence of the -OH group is responsible for additional bonding to the polyurethane foam. PHB is strongest for the polyether-type foam, but does occur for the polyester-type foam. The existence of PHB in the polyester-type foam is indicated by the negative ΔS^o value for m-nitrophenol and the polyester foam.

The strength of the PHB for a compound such as m-nitrophenol can be estimated to be approximately 10 kJ/mole (the difference between the polyether ΔH^o and the polyester ΔH^o for m-nitrophenol). This calculation is accurate if it is assumed that almost no PHB occurs in the polyester type foam. From such an assumption it is possible to see why a group such as an aldehyde that is adjacent to the -OH group can interfere with or prevent PHB. According to NMR calculations the strength of the intermolecular hydrogen bond in salicylaldehyde has as energy of about 30 kJ/mole[61]. This energy value is several times as strong as the estimated strength of PHB and explains why no PHB is observed for this compound. Other compounds such as o-nitrophenol and o-methoxyphenol

have calculated intramolecular hydrogen bonds of about 30 kJ/mole[62] and 10 kJ/mole[63] respectively, and the PHB effect is not observed for them. In the case of the nitrophenol compounds, the electron withdrawing nitro group would increase the hydrogen bonding properties of the hydroxyl group by removing some electron density from the hydroxyl oxygen and weakening the hydroxyl bond between the oxygen and hydrogen atoms. This effect would not be noticeable in the meta- compound due to the lack of a conjugated system. The resonance structures for the ortho- and para- compounds have been previously listed. Although the induction effect would be expected to increase any intermolecular hydrogen bonding, there is a competing intramolecular hydrogen bonding that occurs only in the ortho- position. The data for the nitrophenols show that the induction effect is very minor as the meta- and para- compounds have similar extraction ratios even though the induction effect will occur in the para- but not in the meta- compound. This leaves the major factor affecting the PHB to be the intramolecular hydrogen bonding.

If PHB does exist for the -OH group then it should occur for other functional groups such as $-NH_2$ and -SH. A few amine compounds were surveyed but they did not display a large PHB effect between the polyether and polyester foam types. This is probably due to the weaker strength

of the $-NH_2$ PHB as compared to the $-OH$ PHB. The $-NH_2$ PHB effect is present but not as easily seen with the experimental error involved although some evidence exists to show the existence of $-NH_2$ PHB. The polyether/polyester extraction ratios for p-nitroaniline and o-nitroaniline are 1.42 and 1.27 respectively with larger ratio for p-nitroaniline due to the partial interference of the $-NH_2$ PHB by the adjacent nitro group in the ortho compound. But because of the weakness of $-NH_2$ PHB, this effect is far from obvious. In the $-OH$ type PHB the effect can be clearly observed.

The evidence points to a mechanism for organic compounds consisting of a solvent extraction mechanism supplemented by the additional Polyurethane Hydrogen Bonding. The main force at work is a solvent extraction type mechanism similar to that encountered with a diethyl ether extraction system. Factors affecting a SE mechanism such as salting out and dielectric constant also effect this mechanism. Wherever the organic compound has a functional group capable of intermolecular hydrogen bonding the PHB will further increase the extraction. This PHB can be prevented by strong intramolecular hydrogen bonding with an adjacent basic group. Experiments in varying pH showed no evidence of the CCM. Future work should investigate the aliphatic organic compounds to see if this mechanism evaluation is correct

for them as well. Through the use of Raman or Infrared

spectroscopic techniques it may be possible to observe

directly the polyurethane hydrogen bond and perhaps

determine where it occurs in the foam. Other work may be

done to look at the possibility of separating ionizable

compounds by altering the pH of the solution as it was

observed that only neutral organic species were extracted.

CONCLUSION

Aromatic organic compounds can be extracted from
aqueous solution by polyurethane foam. This appears to
occur by a solvent extraction mechanism similar to that
occurring during a diethyl ether extraction. This
extraction can be assisted by the salting out phenomenon
where the addition of large concentrations of inert salts
can increase the extraction, and by altering the
dielectric constant of the raffinate phase (10 % ethanol).
Research done with varying pH showed no evidence of a
mechanism requiring the ionic species. There is an
additional factor involved known as Polyurethane Hydrogen
Bonding. This occurs mainly between the polyether type
foam and any group such as $-OH$ and $-NH_2$ with which it can
hydrogen bond. Because esters form weaker hydrogen bonds
than ethers, PHB is not as noticeable in the polyester
foam. This SE mechanism modified by PHB wherever
applicable may be responsible for the extraction of all
organic compounds by polyurethane foam. Future studies on
aliphatic organic compounds may confirm this conclusion.

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