

**THE UNIVERSITY OF MANITOBA**

**THE EXTRACTION OF AZO DYES BY POLYURETHANE  
FOAM**

**BY**

**ROBERT J. WERBOWESKY**

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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## **ACKNOWLEDGEMENTS**

I would like to thank my supervisor, Dr. A. Chow for his many hours of editing and his unending patience throughout the last two years. I would also like to thank Dr. G. Baldwin and Dr. J. Charlton for their time and effort spent discussing my results. Finally, I would thank my wife, Joanne, for her patience and moral support.

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## ABSTRACT

Despite the advances that have been made in the past twenty years, the extraction of organic compounds using polyurethane foam has not been widely adopted. It is thought that this is at least partially due to the lack of understanding of the extraction mechanism. The extraction of twelve closely related mono-azo dyes by polyester- and polyether-type polyurethane foams were studied to gain more information regarding the mechanism(s) of the extraction of organic compounds. The effects on extraction of solution pH, dye concentration, the addition of various salts, and salt concentration were investigated. It was found that the extraction of the dyes involved a neutral zwitterionic species, and is highly dependent on the parameters studied. The dependency of the extraction on these parameters can be explained in a manner consistent with solvent extraction; however, the dual-mode sorption mechanism seems a more likely model. This mechanism involves both the absorption related to solvent extraction, and an added component for surface adsorption. While the dual-mode sorption model explains the observed extraction behaviour, the data suggests that surface adsorption plays a much larger role than previously considered.

## INTRODUCTION

For more than twenty years chemists have used polyurethane foams to extract and separate a wide variety of organic and inorganic substances from both liquid and gaseous media. The development of this field, since its beginning with Bowen's paper<sup>1</sup> in 1970, has been very well summarized by a number of reviewers<sup>2-8</sup>. This field has become so large that only those areas relevant to this thesis will be discussed in the introduction.

Flexible, open-cell polyurethane foam has drawn the most interest for the applications and the studies that this thesis addresses. There are two general varieties of polyurethanes; depending on the components used in the production of the foam, it will either be a polyester- or polyether-type polyurethane. Polyurethanes have two major components, polyfunctional isocyanates and polyols, which can be polymers themselves. These combine to form a polyurethane in a reaction which is shown here for difunctional reactants:

Whether a polyurethane is polyester- or polyether-type depends on the polyol used. If a polyol with repeating ester linkages was used, such as poly(ethylene adipate), the resulting polyurethane would be a polyester-type. Using a polyol with repeating ether linkages, such as polyethylene oxide, will give a polyether-type polyurethane. For the polyfunctional isocyanate, toluene diisocyanate is a common choice.

Polyurethane is one of the easiest polymers to use to produce a foam. One simple method involves adding water to the reactants. The water reacts with an isocyanate to produce an amine and carbon dioxide. The gas acts as a blowing agent and produces foaming of the polymer, and the amine can further react with an isocyanate to produce a urea linkage. The flexibility of the polymer is controlled by the amount of cross-linking present which in turn is determined by the proportion of polyols used and the number of hydroxyl groups they contain. Triols and other polyols can be added to increase the amount of crosslinking and therefore increase the rigidity of the resulting polymer.

The compositions of commercial foams, both major and minor components, are considered proprietary information and are

not readily available. It is currently thought that the foam derives many of its chemical properties, especially as they pertain to the extraction abilities, from the nature of the polyol used, i.e., polyester-type vs. polyether-type. As a result, much of the research to date has focused on the differences between the two types of foam rather than between various compositions within the same type. This thinking is largely based on the results of inorganic extractions and, while this thesis continues the trend, it does so skeptically. The interactions involved with the extraction of organic substances are likely different than those with inorganic substances. Organic functional groups on the foam, outside those already identified as being important, may play a significant role in the extraction of organic species.

The fact that organic chemicals are found throughout the environment comes as little surprise when one considers their widespread use in both industrial and agricultural applications. With a heightened sense of environmental responsibility comes a need for more economical methods of testing for and removal of organic pollutants. It is this area which has been a focus of research in organic applications of polyurethane foams. Because of its desirable characteristics, polyurethane foam has been

evaluated for use to remove, preconcentrate, or separate a variety of organic substances including phenols<sup>9,10</sup>, phthalates<sup>11</sup>, PCBs<sup>12</sup>, carboxylic acids<sup>13</sup>, and insecticides<sup>10,14-20</sup>. Its quasi-spherical structure and open cells offer much higher flow rates and higher concentrating ability compared with other solid sorbents<sup>9</sup>.

Aside from the work with insecticides, there has not been widespread acceptance and use of polyurethane foams for the extraction of organics from aqueous solutions, despite the number of advances made and the number of years this technology has been known. It is thought that the slow development of the area is at least partially due to the lack of understanding regarding the mechanism of extraction.

Throughout the years a number of possible mechanisms have been proposed, namely, surface adsorption, solvent extraction, ligand exchange, anion exchange and cation chelation. The cation chelation mechanism was first proposed by Hamon *et. al.* <sup>21</sup> in 1981, for the extraction of metal ions. In this mechanism, cations are effectively solvated by the oxygen atoms of the poly(ethylene oxide) portion of the foam. These sections of polymer adopt a helical structure with inwardly-directed oxygen atoms and appear



to have a cation selectivity similar to the crown ether, 18-crown-6. The polymer in polyester foam does not easily assume a helical structure which is thought to explain the lower observed extractions. For the extraction of organics, solvent extraction, also referred to as phase distribution, is the most commonly proposed mechanism. In this mechanism the foam acts simply as a solid phase organic layer.

Much of the work done on the mechanism of extraction with organics has come in a few papers. Schumack and Chow<sup>22</sup> were among the first to investigate this area. In their study they investigated the extraction of a variety of aromatic organic compounds and how the extractions were affected by extraction time, salt addition, solution pH, ethanol concentration and solution temperature. They concluded that the extraction of organic compounds occurs by an ether-like solvent extraction mechanism, and there was no evidence of a mechanism requiring an ionic species, as would be the case for ion exchange or cation chelation. In addition they found that hydrogen bonding was a significant factor in the extractions, and that compounds containing phenolic or carboxylic groups were better extracted with polyether-type polyurethane. The preference for polyether-

type foam was attributed to its ability to form stronger hydrogen bonds than those formed with polyester-type foam.

Chow *et. al.* <sup>23</sup> looked at the extraction of 59 organic dyes into polyurethane foams. Using a smaller subset of those dyes, they looked at the effects of salt addition, extraction from 50% methanol solutions, extractions using diethyl ether and ethyl acetate, and ordering the dyes in terms of polarity using thin layer chromatography. While broad in scope, this study was fairly inconclusive and reported that the extraction of the organic dyes tested showed support of both solvent extraction and cation chelation mechanisms. It is currently thought that much of the confusion with their results is related to the researchers' use of the distribution ratio,  $D$ , for comparisons among the dyes. Such comparisons are only valid if the distribution ratio is a good approximation of the distribution coefficient,  $K_d$ . For organic acids and bases, this only occurs when the predominant species is in the neutral form<sup>24,25</sup>. Because the researchers did not optimize the extractions with regards to solution pH, the distribution ratio did not approximate the distribution coefficient. Results from this current study suggest that even when the predominant species is in its neutral form, the distribution ratio is still not

suitable for making direct comparisons.

Fong and Chow<sup>26-28</sup> published three papers studying the extraction of organic compounds into polyurethane foams. They first looked at the extraction of salicylic acid, 8-hydroxyquinoline, 1-amino-2-naphthol-4-sulphonic acid, and cinnamic acid. Based on salting-out effects and pH studies they concluded that the compounds were extracted as neutral molecules via a solvent extraction mechanism. Their work also confirmed the importance of hydrogen bonding as reported previously<sup>22</sup>. The second paper involved the extraction of alkali metal tetraphenylborates. Based on the extraction sequence of the alkali metals, they concluded that these extractions could be explained using the cation chelation mechanism. However in their following paper<sup>28</sup>, which looked at the extraction of alkylammonium tetraphenylborates and dipicrylaminates, they could find no conclusive evidence to support the cation chelation mechanism. They concluded that the selectivity for the alkylammonium ions is affected by a combination of effects which are steric, inductive, and hydrophobic in nature.

While there seems to be a general consensus that the

mechanism of extraction is a solvent extraction of a neutral species, cation chelation remains a possibility. There are still many unanswered questions, especially regarding the role of functional groups attached to the analyte. Despite the shortcomings of the earlier dye study<sup>23</sup> it is thought that the wide variety of organic dyes available could be valuable probes into the sorption mechanism of organic species.

Preliminary studies done on a few of the dyes previously used confirmed the clear importance of solution pH and the functional groups present on the dye molecules. Based on these results it was concluded that a more detailed study could be designed to determine the mechanism of extraction and the role that functional groups play in that mechanism. After an extensive search of the Colour Index<sup>29</sup> and numerous supply catalogues, twelve closely related mono-azo dyes were chosen for this study. The group of dyes were chosen for their extractability, water solubility, ease of detection, and their ability to show the effect of different functional groups on the extraction.

## EXPERIMENTAL

### Apparatus and Reagents

Hewlett Packard 8452A ultraviolet - visible spectrophotometer

Orion Expandable Ion Analyzer EA 940

Mettler AE163 analytical balance

Burrell wrist-action shaker, clamps removed and replaced with  
four custom baskets, holding 24 samples each.

Waring Blender with stainless steel blending container

Soxhlet extractor

ColourpHast™ pH indicator strips

Fisher brand, 0 - 60 mL pump dispenser

Oxford, 0 - 5 mL adjustable pipette: accuracy  $\pm 50 \mu\text{L}$ ;

precision  $\pm 16 \mu\text{L}$

All chemicals were of reagent grade unless otherwise indicated,  
dye sources and stated purity as shown in Table 1.

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)**

**Polyether - Union Carbide Corporation**

**Macintosh Plus: system 6.05**

**Text written using MacWrite II (Claris)**

**Calculations done using Excel 4.0 (Microsoft)**

**Powerland 486 SX: Windows 3.1**

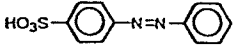
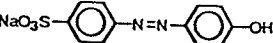
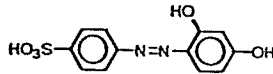
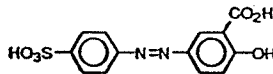
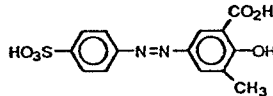
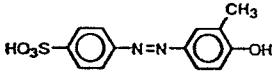
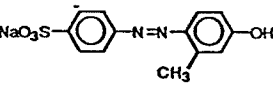
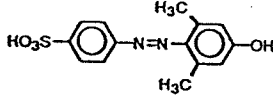
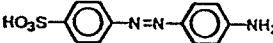
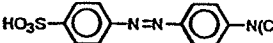
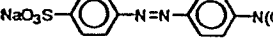
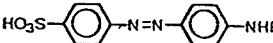
**Figures produced using Sigma Plot (Jandel Scientific)**

**Curves fitted to data using Table Curve (Jandel Scientific)**

**Tables produced using Word Perfect for windows 6.0**

**Structures drawn using Chemwindows 3.0**

**Table 1.** List of dyes used and their sources.

Dye	Source	$\lambda_{\max}$ (nm)
 4-Phenylazobenzenesulfonic acid	Pfaltz&Bauer	320
 4'-(4-hydroxyphenylazo)benzenesulfonic acid *	Pfaltz&Bauer	438, 354
 Tropaeolin O	Chem Service BS-100 Stain Kit	430, 384
 Mordant Yellow 10, 85% dye content	Aldrich Chemical Company	356
 Mordant Yellow 7, 65% dye content	Aldrich Chemical Company	362
 4'-(4-hydroxy-3-methylphenylazo) benzenesulfonic acid	Sigma-Aldrich Library of Rare Chemicals	454, 360
 4'-(4-hydroxy-2-methylphenylazo) benzenesulfonic acid *	Sigma-Aldrich Library of Rare Chemicals	428, 362
 4'-(2,6-dimethyl-4-hydroxyphenylazo) benzenesulfonic acid	Sigma-Aldrich Library of Rare Chemicals	398, 352
 4'-(4-aminophenylazo)benzenesulfonic acid	Sigma-Aldrich Library of Rare Chemicals	388, 318
 Methyl orange	Chem Service BS-100 Stain Kit	464, 504
 Ethyl Orange, 90% *	Aldrich Chemical Company	474, 480, 508
 Orange IV	Chem Service BS-100 Stain Kit	444

\* indicates dye obtained as the sodium salt.

## **Foam Preparation**

The foam was put through a number of cleaning procedures before being used in an attempt to remove or reduce the possibility of contaminants interfering with extraction. The polyether foam, obtained in large 4 cm thick sheets, was first cut into smaller pieces. In order to remove inorganic contaminants, the foam was soaked in a 1 molar hydrochloric acid bath for six hours and periodically squeezed by hand. The container was then drained and the foam squeezed by hand to remove most of the acid solution. The foam was then repeatedly soaked, squeezed and rinsed in water until the pH of the rinse water was unchanged after an hour of soaking. After the excess water was removed, the foam was Soxhlet extracted with acetone for six hours to remove any soluble organic contaminants. The majority of the acetone was then squeezed out of the foam by using a clean watch glass and inverting the Soxhlet apparatus. Finally, the foam was dried in a vacuum desiccator overnight.

The sheets of polyether foam used were mostly light yellow in colour, with deepening shades of brown near the edge of a sheet. After cleaning, the foam was separated into two main groups



according to the colour of the foam: group 1, coming from center region of a sheet and light in colour, and group 2, from the edges of a sheet and darker in colour. Group 1 consisted of approximately 75% of the bulk foam. Two smaller sub-groups, groups 3 and 4, were made by taking some of the lightest foam of group 1 and some of the darkest foam of group 2. Except for the foam degradation experiments, only those results obtained using the foam from group 1 are reported. No such discolouration of the polyester plugs was noted and therefore no special separation was needed.

The final preparation procedure was to grind the foam. This involved freezing the foam pieces with liquid nitrogen and grinding them in a metal container with a Waring blender. The procedure generally reduced the foam to one or two foam cells in size, with most particles less than 2 mm in diameter.

The foam was then stored in brown glass containers, as a precaution against photodegradation. For storage longer than a month, the foam container was generally purged with nitrogen gas before closing, as an additional precaution to help prevent oxidation.

## Preliminary Studies

The extraction procedure for the preliminary studies was based on Chow *et. al.*<sup>23</sup>. This procedure involved shaking powdered foam in an aqueous dye solution for 6 h, filtering, and measuring the UV-visible spectrum of the aqueous solution.

A 250 mL dye stock solution was prepared by accurately weighing 5 - 10 mg of powdered dyestuff into a 20 mL sample vial, which was then quantitatively transferred, using water, into a 250 mL or 500 mL volumetric flask. An aliquot of stock solution was used to prepare sample solutions in a 100 mL volumetric flask. If the pH of the sample solution was to be adjusted, an appropriate amount of dilute HCl or NaOH was added to the sample flasks before diluting to the mark with water.

Extraction samples were prepared by adding 10 mL aliquots of sample solution to 20 mL sample vials containing approximately 0.1 g of foam which had been accurately weighed. The tops of the vials were covered with a piece of plastic wrap and sealed with a screwcap. Sample solutions were used to

prepare six extraction samples, three polyether and three polyester, and one sample standard. A sample standard was prepared identically to an extraction sample except that no foam was added to the sample vial. The vials were shaken for 6 h on an automatic shaker. The extraction samples and sample standard were then filtered through Whatman #541 filter paper to remove the foam. The spectra (190 nm - 820 nm) of the aqueous layers were taken using a Hewlett Packard spectrophotometer and the absorbance at the absorbance maxima ( $\lambda_{max}$ ) recorded.

Extractions for the preliminary studies were run with three different solution conditions: acidic, where dilute hydrochloric acid was added to the sample solution to adjust the solution pH to approximately 3; "neutral", with no pH adjustment made; and basic, where the pH was adjusted to approximately 11 using dilute sodium hydroxide.

## **Experimental Design**

Several evolutions took place between the experimental method used in the preliminary studies and that used for the bulk of the thesis work. The first change was made to improve the

reproducibility of the results. It was found that during the extraction with a 10 mL sample solution in a 20 mL vial, foam particles would collect at the top of the vial and therefore were not exposed to the solution. The amount of foam not in the solution and the length of time that it was out of solution were uncontrollable and these factors were thought to explain some of the variability in the results. To correct this problem the sample volume was increased to 15 mL, which raised the liquid level allowing the foam particles collecting at the top to be replaced more often. The concentration of dye in the solution was decreased by a proportional amount so that the amount of dye available per gram of foam remained the same.

The second change made was largely economically motivated but also concerned the accuracy of the results. It was noted that when some of the dye solutions passed through a filter paper, the solution would change colour. This colour change was attributed to the filter paper changing the solution pH. Four Whatman filter papers #1, #4, #42 and #541 were then evaluated for their effects on the absorption spectrum of a solution.

To evaluate the filters, 5 mL of Tropaeolin O. solution (~13

mg/L) were run through each of the filters. The absorption spectrum (190 nm - 800 nm) of each solution was then taken and compared to the spectrum of the solution that had not been passed through a filter. All of the filters were found to reduce the absorption maxima and produce some peak broadening. However two of the filter paper grades, #541, and #4, were found to have a minimal effect on the spectrum. Since the foam particles are macroscopic, the porosity of the filter was not an issue and the decision to use Whatman #4 was based on economics (#4 is approximately one quarter the price of #541).

The previous study<sup>23</sup> used approximately the same weight of dye for each extraction. Given the unknown purity and differing absorption coefficients of the various dyes, it was decided to abandon this method and use an amount of dye that would give the sample standard a maximum absorbance (at  $\lambda_{\max}$ ) between 0.8 and 1.2. Changing the dye concentration of the sample was thought to be irrelevant since it mathematically cancels when calculating the distribution coefficient. However, it was later determined that the solution concentration is not an irrelevant factor.

Finally, the extraction was increased from 6 to 24 h. Chow

*et. al.* <sup>23</sup> had reported that while most dyes attained equilibrium before 6 h, some required up to 24 h. Therefore, although it appeared that the dyes used in these experiments came to equilibrium early, to ensure that equilibrium conditions were obtained, the shaking time was increased.

### **General Extraction**

Each experiment generally consisted of 12 separate 100 mL sample solutions, 6 for polyether and 6 for polyester. Sample solutions were prepared by adding 60 mL of stock solution to a 100 mL volumetric flask using a 0 - 60 mL pump dispenser. Other parameters such as pH and salt concentration were then adjusted, followed by dilution with water to the mark. Each 100 mL sample solution was used to provide three 15 mL extraction samples and one 15 mL sample standard. One full experiment would therefore involve 48 samples (12 sample standards, 36 extraction samples).

For each extraction approximately 0.1g (0.08-0.12) of foam was accurately weighed into a 20 mL sample vial. Sample solution (15 mL) was then transferred into the sample vial in 5 mL aliquots using a 1-5 mL adjustable pipette. Delivering three 5 mL aliquots

is inherently less precise than one 15 mL transfer; however, given the qualitative nature of the study and the number of samples being done, it was decided that the speed gained by using the adjustable pipette was worth the expected loss in precision. The vials were then covered with plastic wrap and finally sealed with a screw cap. The sample standards, excluding the foam, were prepared in an identical manner as their corresponding samples.

The 48 samples were then shaken on a Burrell wrist action shaker for 24 hours, and then filtered using a #4 Whatman filter. Once filtered, the spectrum (190 nm - 820 nm) of each sample was obtained using a Hewlett-Packard spectrophotometer and the absorbance at  $\lambda_{\max}$  recorded. The spectrophotometer was generally blanked with Nanopure water as it was determined that additives, other than the analyte, did not significantly absorb or interfere. The only cases where additives interfered sufficiently to warrant a different blank were those involving a nitrate anion. The absorption spectra of the dye samples often changed as the pH of the solutions changed. When this occurred the absorbance was recorded at the new  $\lambda_{\max}$ . A list of wavelengths used is shown in Table 1. These shifts in  $\lambda_{\max}$  did not compromise the accuracy of the results since the shifts were due to the pH of the solution and

therefore occurred in both the sample standards and sample extractions. Finally the pH of the solution was measured using an Orion expandable pH meter.

### **Organic Stock Solutions**

Sample solutions in the experiments were prepared using a concentrated stock solution, unless otherwise specified. Since the volume of stock solution added was kept constant, the concentration of the stock solution was used to vary the amount of analyte in a sample solution. The stock solution was prepared by accurately weighing the chosen amount of dye powder into a sample vial (15 - 45 mg), and quantitatively transferring it with water into either a 500 mL, or 1 L volumetric flask, and then diluting to the mark. Chow *et. al.* <sup>23</sup> have reported that some dyes are unstable over time as indicated by a change in solution colour or the formation of a precipitate. Although there was no evidence of instability with the dyes examined in these experiments, only freshly prepared solutions were used.



## **pH Adjustment**

The pH of the sample solutions was adjusted using hydrochloric acid or sodium hydroxide solutions of varying concentrations (0.0002 M to 1 M). Generally 0 - 15 mL of acid or base solution would be added to the 100 mL volumetric flask used for sample solution preparation. This gave sample solutions with a pH range of 0.5 to 12.

## **Salt Addition**

In addition to the type of salt being used, one of the solution parameters varied in some experiments was the concentration of the salt. Depending on the amount required, the salt was either weighed into a small sample vial and then quantitatively transferred to the 100 mL volumetric flask, or directly weighed in the 100 mL volumetric flask to be used for sample preparation. Solutions containing relatively large amounts of salt often required mechanical stirring and/or heating for full dissolution.

## **pK<sub>a</sub> Determination**

The acid dissociation constants (pK<sub>a</sub>s) of some of the dyes were estimated using a procedure based on a titration method for a weak acid or weak base<sup>30</sup>. A 50 mL 0.02 M dye solution was prepared by accurately weighing the appropriate amount of dyestuff and quantitatively transferring into a Erlenmeyer flask. The initial pH of solution was recorded and the solution was then titrated with a 0.02 M sodium hydroxide solution while continuously monitoring the pH. At intervals the volume of titrant and the pH of solution was recorded. After titration with a known amount of standard acid or base, the pK<sub>a</sub> was estimated to be equal to the pH of the solution after the addition of half the titrant required to reach the end point.

## Calculation of the Distribution Ratio

The degree of dye sorption was reported as the distribution ratio, D:

$$D = (VE)/W(100-E) \quad (1)$$

$$E = 100(C_o - C_{eq})/C_o; \quad (2)$$

where E is the % extraction,  $C_o$  = initial molar concentration of solution (M),  $C_{eq}$  = concentration of solution after sorption (M), V = volume of solution (L), W = mass of foam (kg).

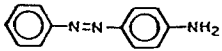
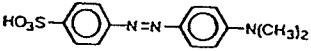
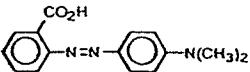
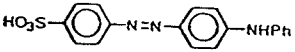
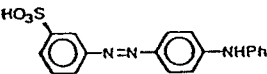
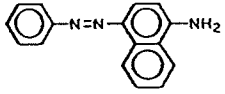
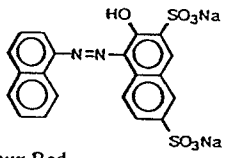
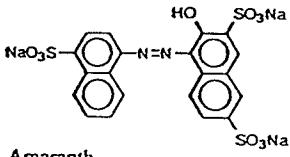
## RESULTS AND DISCUSSION

### Preliminary Studies

This research follows from an initial study done by Chow, Branagh, and Chance<sup>23</sup>, which looked at the sorption of fifty-nine organic dyes into polyether- and polyester-type polyurethanes. Their research, while broad with respect to dyes, did not involve an investigation into the effect of solution pH or salt concentration, and thus, the present investigation began by examining the effect of pH on the extraction of a few of the dyes. The dyes were initially chosen based on their extractability, and their anticipated ability to show the effect on extraction of different functional groups attached to the dye. Eight of the original fifty-nine dyes were chosen for the initial study.

The results shown in Table 2 confirm the importance of different functional groups in the dye molecule and the pH of the dye solution used for the extraction investigation. From these preliminary experiments it was concluded that a more detailed study needed to be designed which would probe the dependence of the sorption on solution pH and which could expand the present

**Table 2.** Extraction summary of the preliminary studies.

Dye	Polyether, D (L/kg)			Polyester, D (L/kg)		
	Acidic	Neutral	Basic	Acidic	Neutral	Basic
 Aniline Yellow (Chem Service)	111 ± 3	21.9 ± 0.1	-1.2 ± 0.8	62 ± 2	8.3 ± 0.8	-4 ± 2
 Methyl Orange	3100 ± 400	4600 ± 700	32 ± 1	220 ± 20	11.8 ± 0.7	-1.0 ± 0.1
 Methyl Red	1390 ± 20	230 ± 10	2.1 ± 0.3	1770 ± 48	230 ± 21	-2.1 ± 0.7
 Orange IV	∞	∞	430 ± 10	∞	78 ± 5	3.2 ± 0.4
 Mentanil Yellow Orange	11000 ± 3000	114 ± 3	3.2 ± 0.4	∞	∞	790 ± 70
 Solvent Yellow IV	---	----	∞	---	----	∞
 Bordeaux Red	120 ± 16	-1.2 ± 0.7	-13.4 ± 0.4	600 ± 200	20 ± 3	-2 ± 1
 Amaranth	8.1 ± 0.3	-2 ± 2	-13.8 ± 0.4	12.0 ± 0.9	0 ± 1	-4 ± 1

Conditions: 0.1 g foam, 10 ml dye solution ( $10^{-5}$  M), 6 h shaking time.

Values above 12,000 L/kg are listed as ∞.

understanding of the role that functional groups play in the extraction and its mechanisms.

### **Effect of Solution pH on Extraction**

The effect of solution pH on extraction was studied using the general extraction procedure described, varying the pH of the sample solutions generally from 0.5 to 12. A minimum of two full experiments (72 extraction samples, 36 polyether, 36 polyester) were done with each of the twelve dyes. The results were analysed by plotting the distribution ratio of the extraction against the equilibrium pH of the solution, producing what will be called an *extraction profile*. These profiles are shown in figures 1 - 12, and summarized in Table 3.

An obvious trend can be seen in figures 1 - 12. The results of the extractions for all twelve dyes seem to follow a  $pK_a$ -type curve. There was little or no extraction from solutions more basic than a pH of 6. As the solutions became more acidic there was an increase in extraction. This increase was always followed by a decrease in extraction as solutions became increasingly more acidic. This decrease in extraction, generally

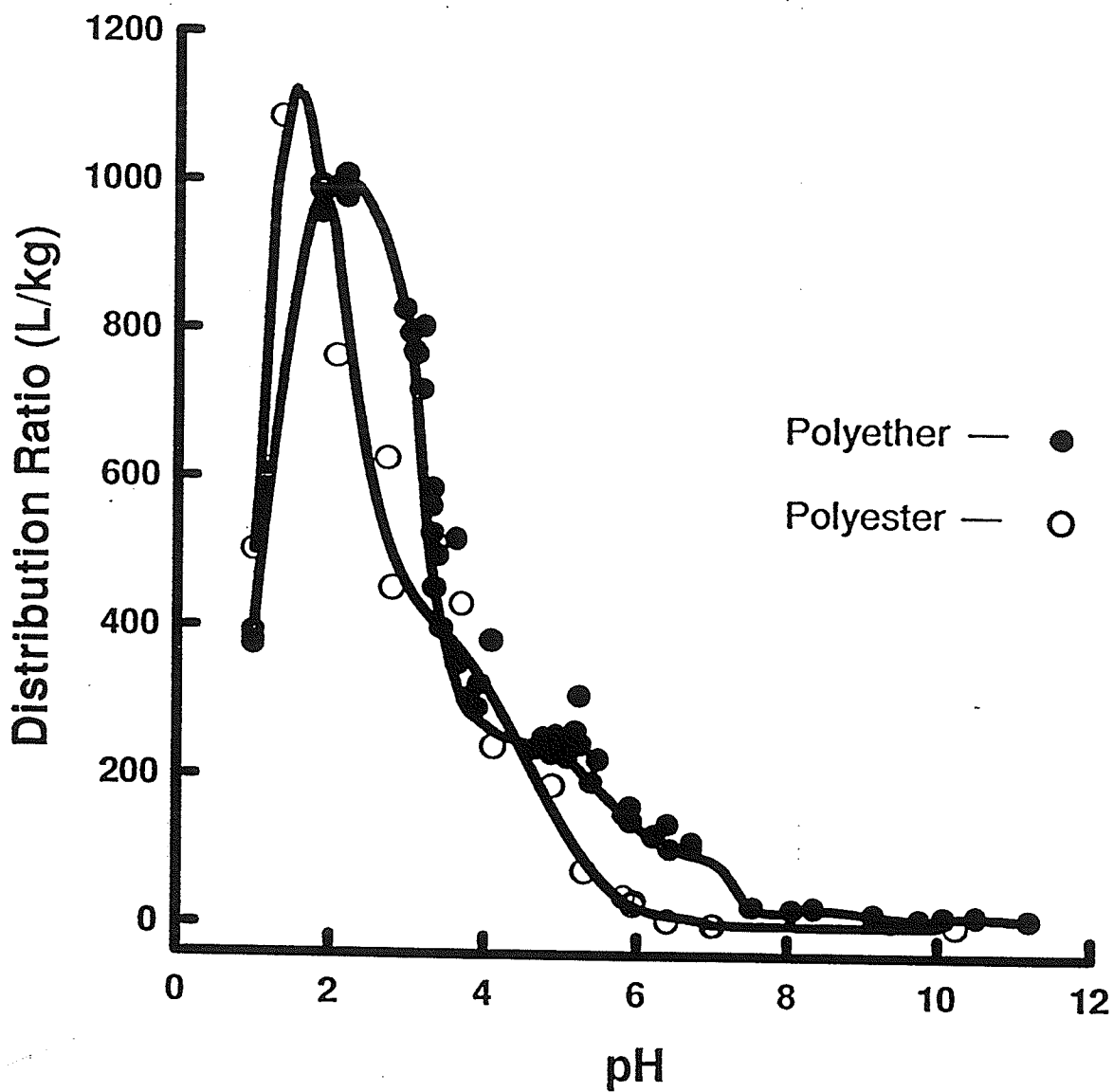
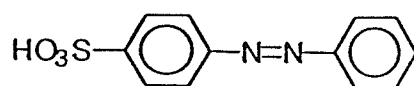
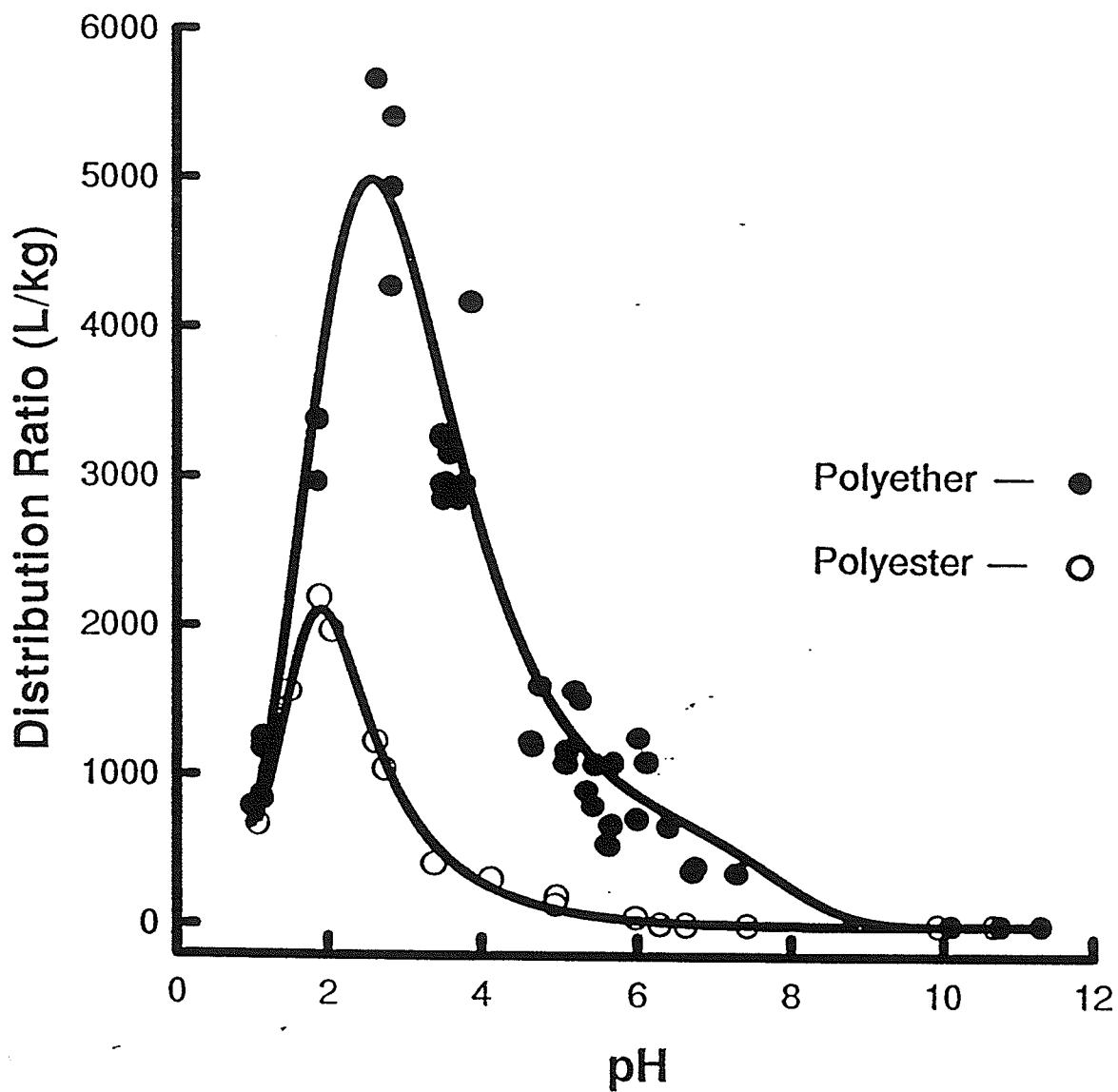
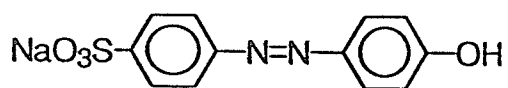
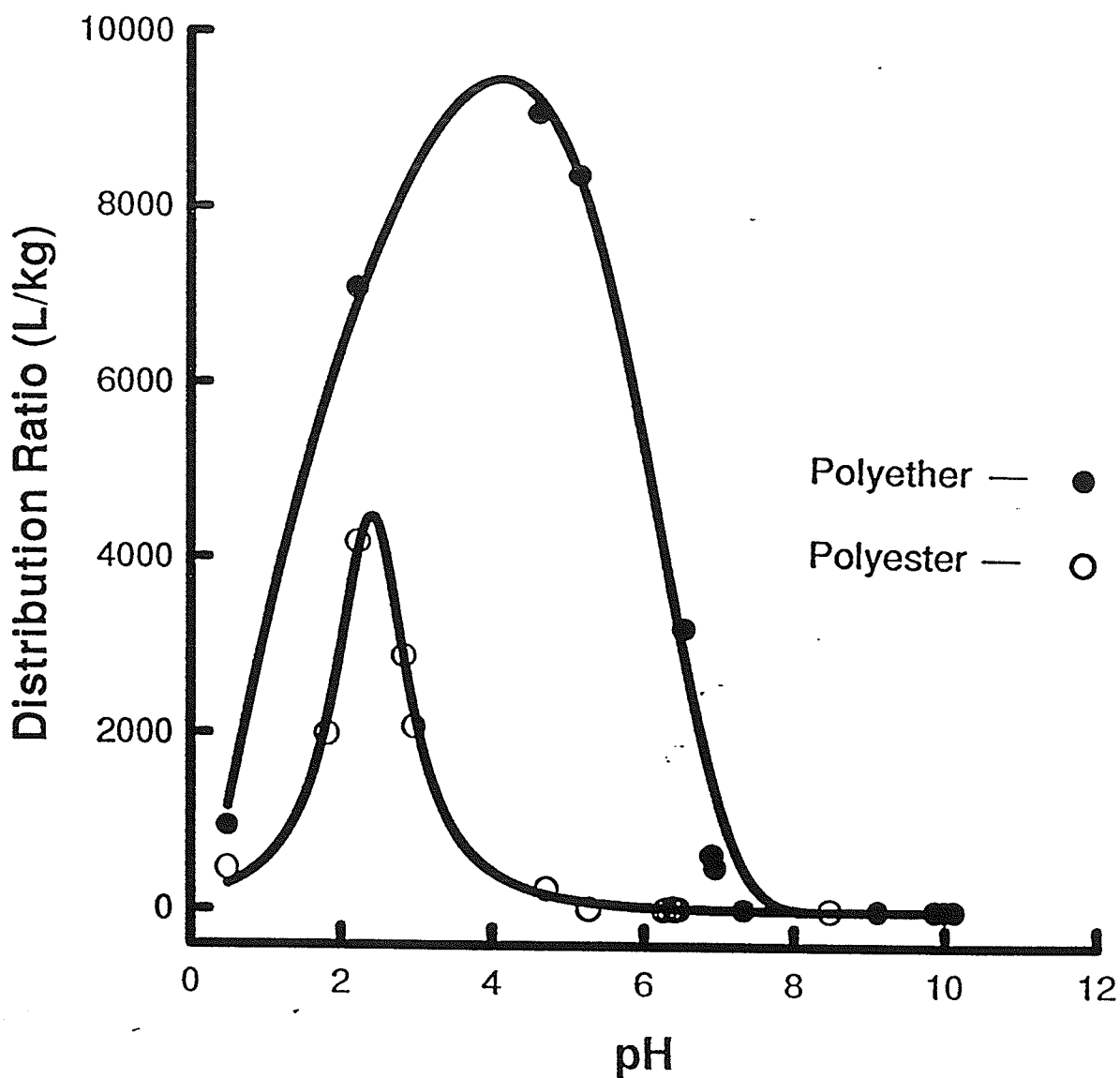
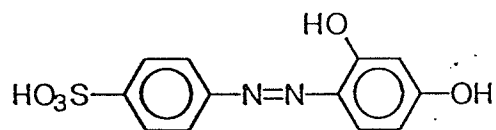


Figure 1. Extraction profile of 4-PABSA. Conditions: 0.1 g foam, 15 mL dye solution ( $\sim 10^{-5}$  M), 24 h shaking time.

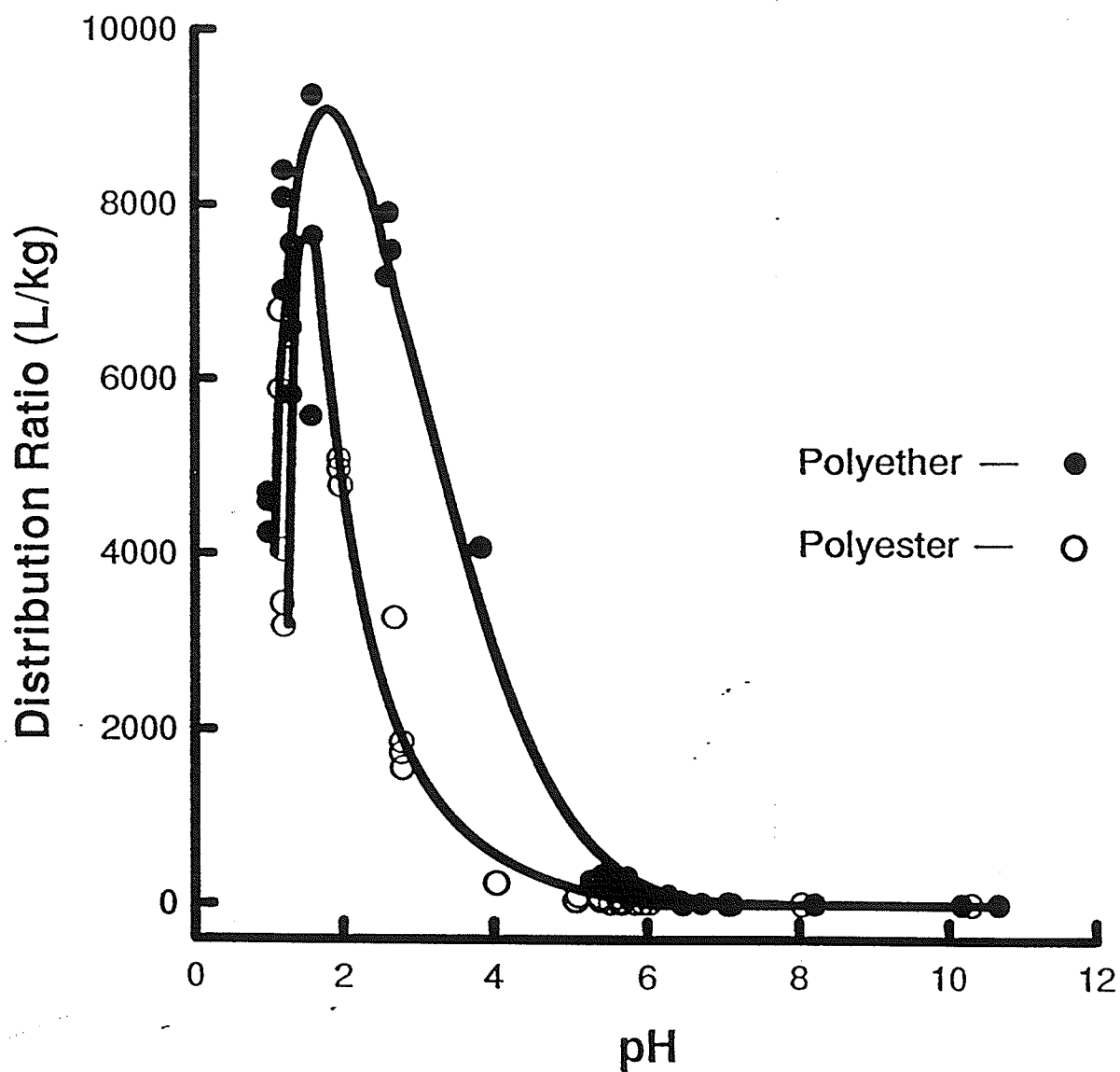
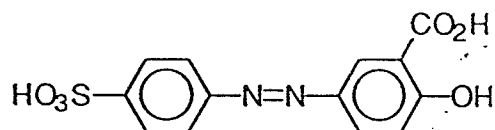


**Figure 2.** Extraction profile of 4'-(4-hydroxyphenyl-azo)benzenesulfonic acid. Conditions: 0.1 g foam, 15 mL dye solution ( $\sim 10^{-5}$  M), 24 h shaking time.



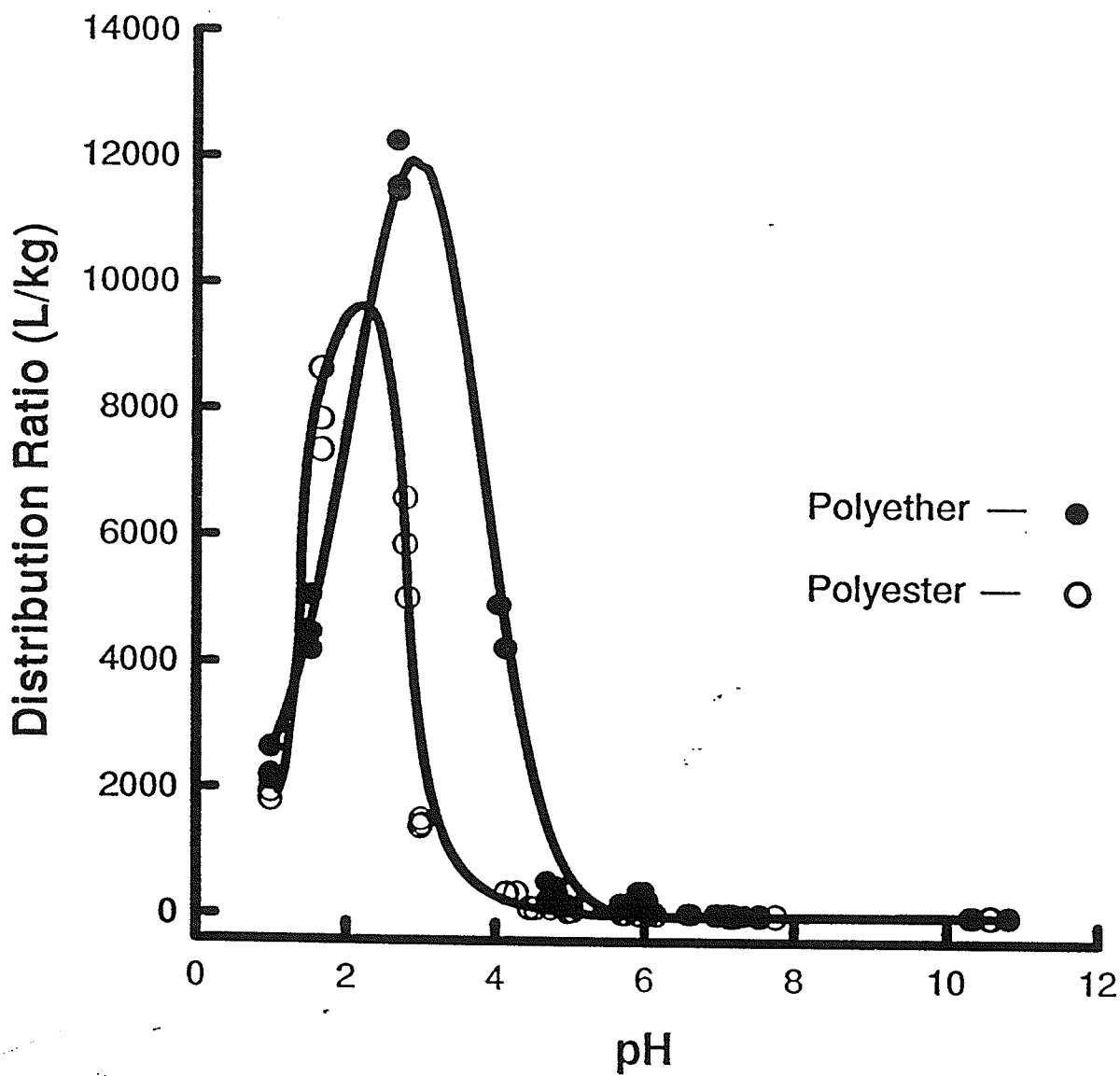
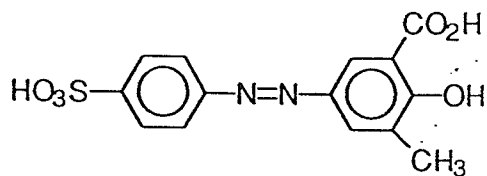


**Figure 3.** Extraction profile of Tropaeolin O. Conditions: 0.1 g foam, 15 mL dye solution ( $\sim 10^{-5}$  M), 24 h shaking time.



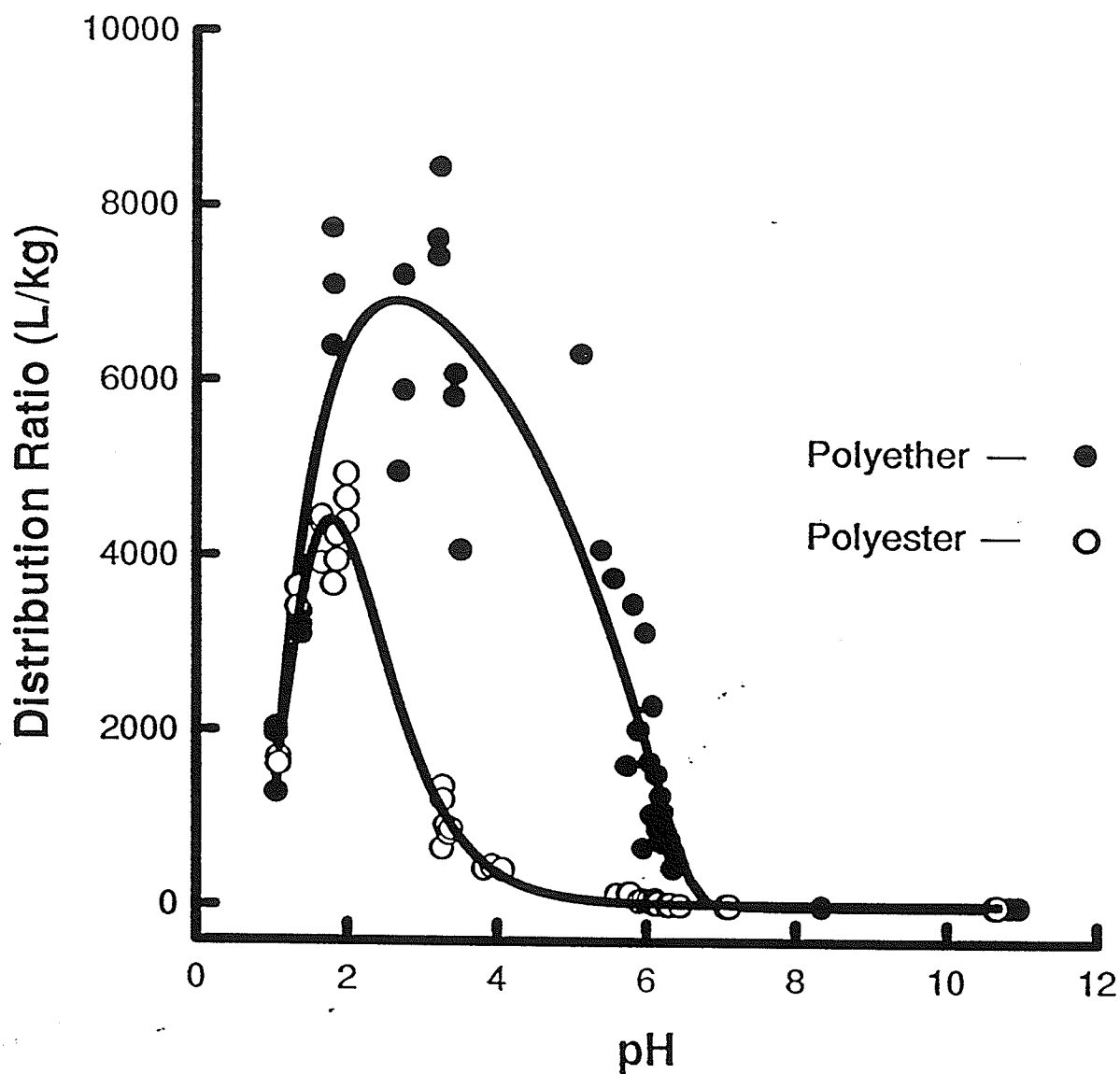
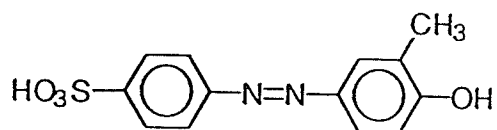
**Figure 4.** Extraction profile of Mordant Yellow 10.

Conditions: 0.1 g foam, 15 mL dye solution ( $\sim 10^{-5}$  M), 24 h shaking time.

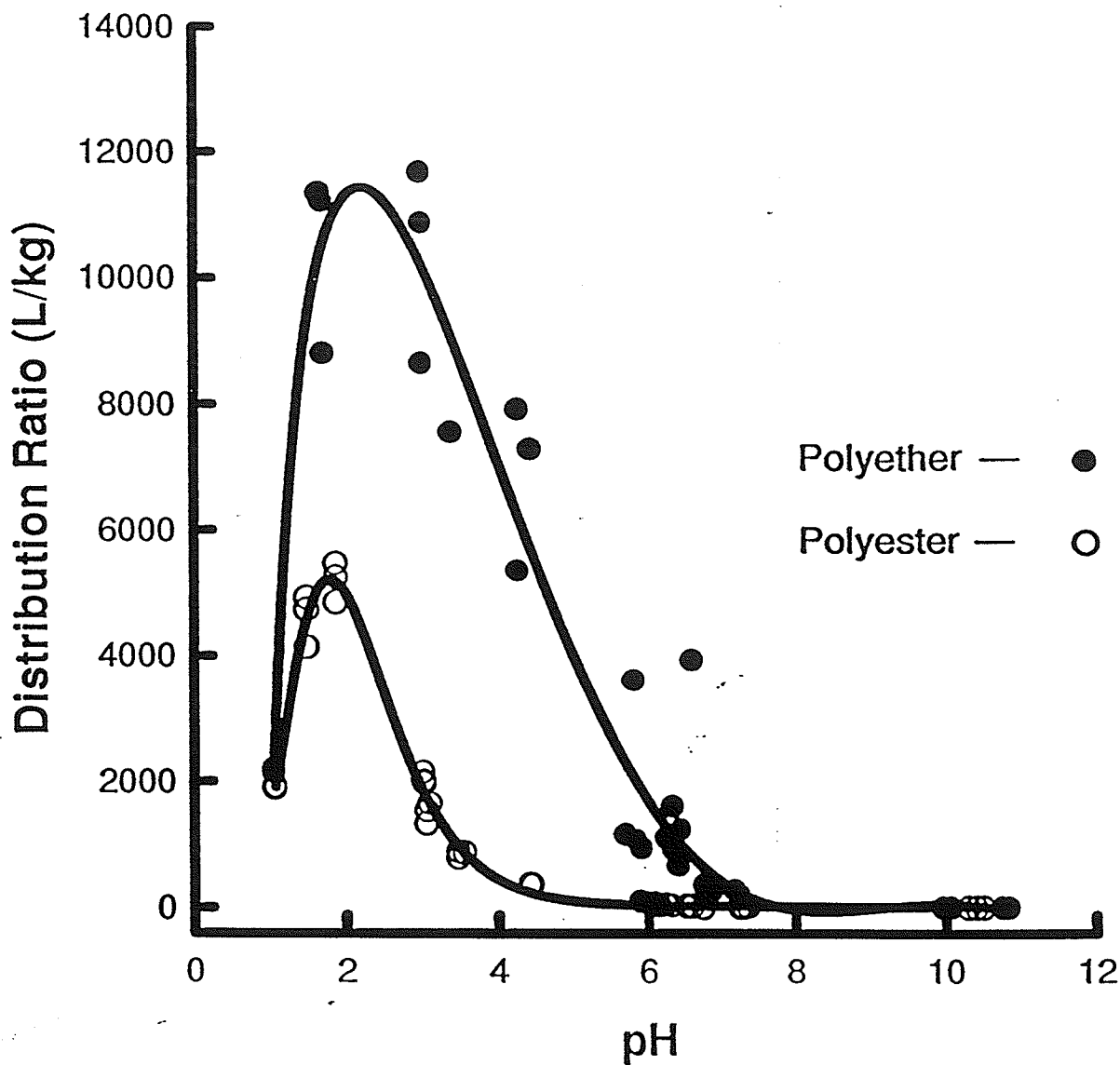
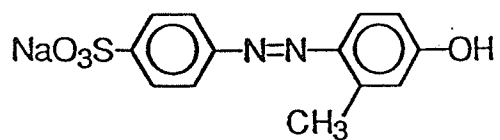


**Figure 5.** Extraction profile of Mordant Yellow 7.

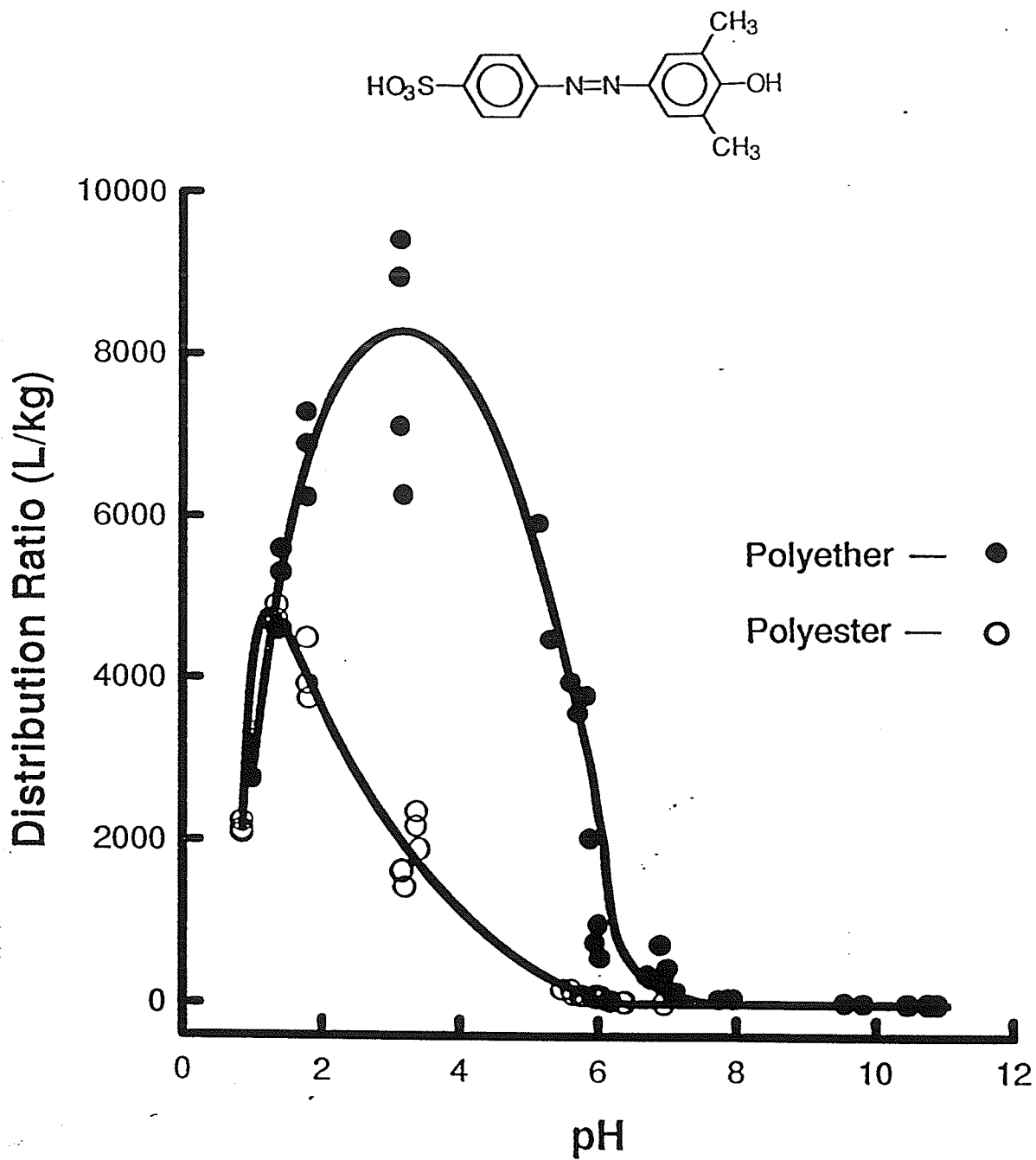
Conditions: 0.1 g foam, 15 mL dye solution ( $\sim 10^{-5}$  M), 24 h shaking time.



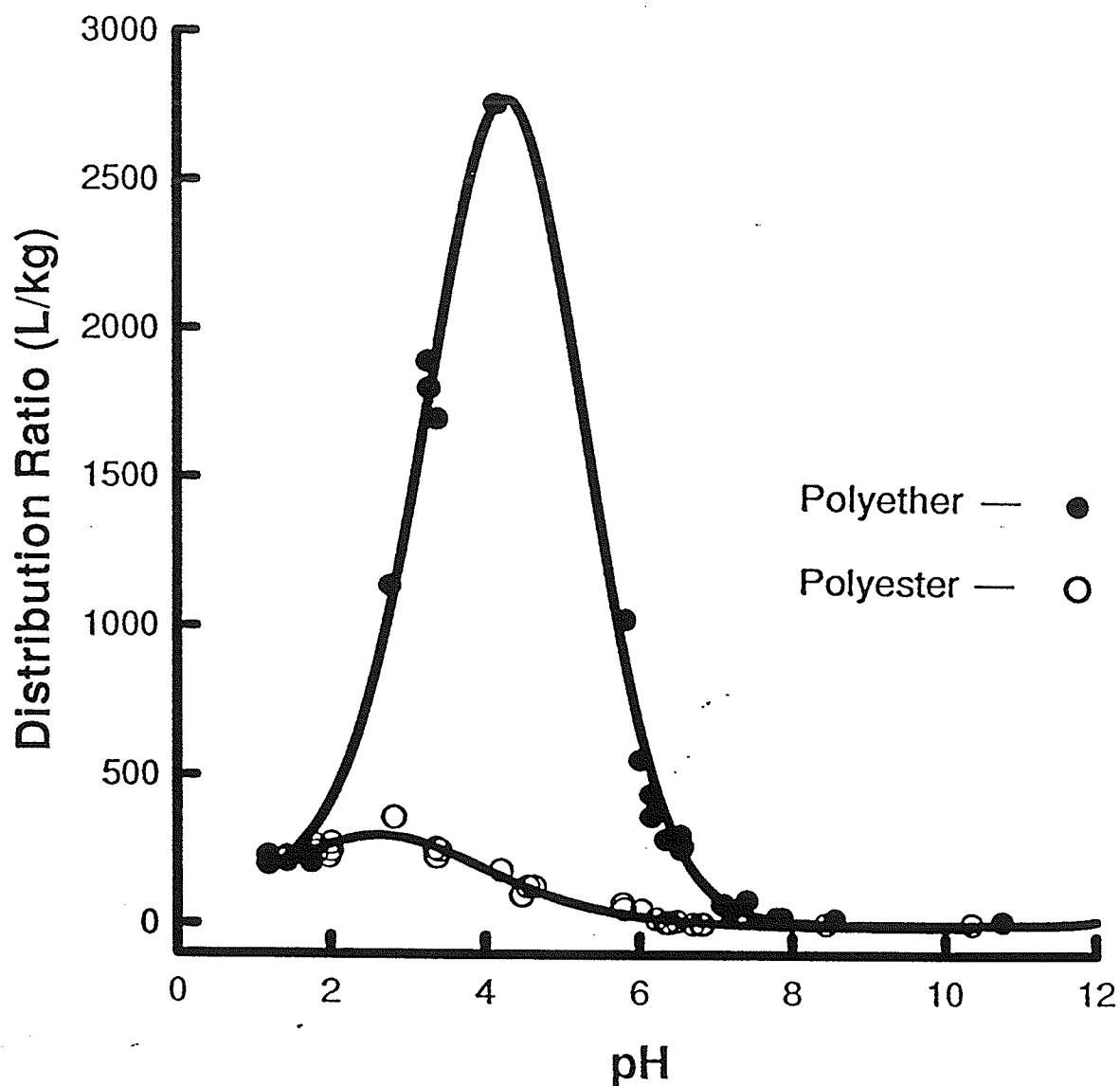
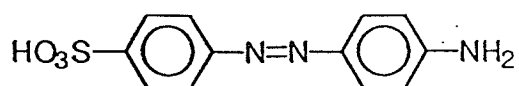
**Figure 6.** Extraction profile of 4'-(4-hydroxy-3-methylphenylazo)benzenesulfonic acid. Conditions: 0.1 g foam, 15 mL dye solution ( $\sim 10^{-5}$  M), 24 h shaking time.



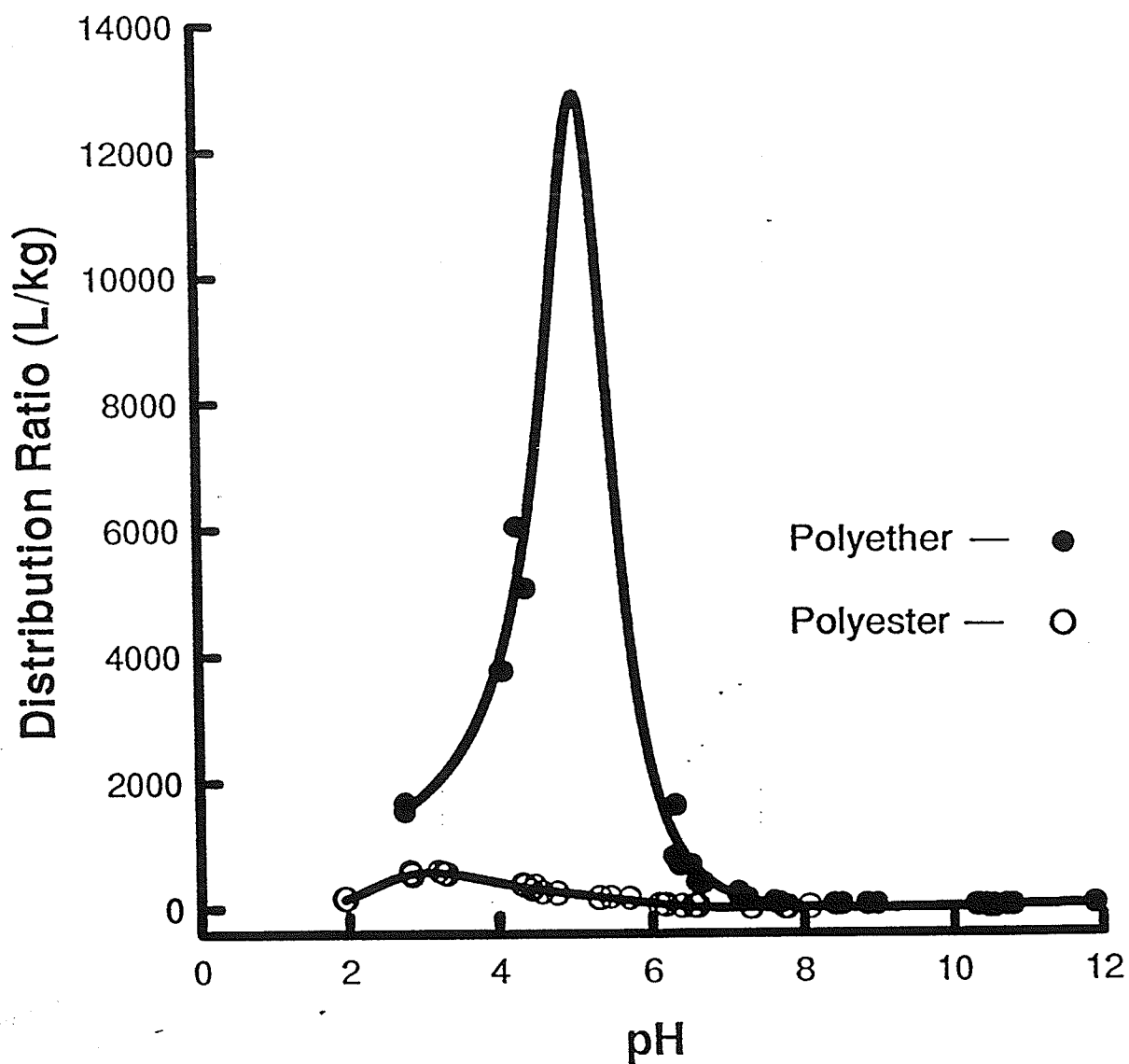
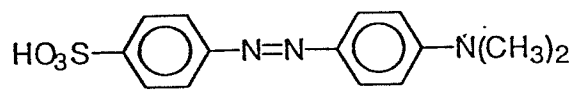
**Figure 7.** Extraction profile of 4'-(4-hydroxy-2-methylphenylazo)benzenesulfonic acid. Conditions: 0.1 g foam, 15 mL dye solution ( $\sim 10^{-5}$  M), 24 h shaking time.



**Figure 8.** Extraction profile of 4'-(2,6-dimethyl-4-hydroxyphenylazo)benzenesulfonic acid. Conditions: 0.1 g foam, 15 mL dye solution ( $\sim 10^{-5}$  M), 24 h shaking time.



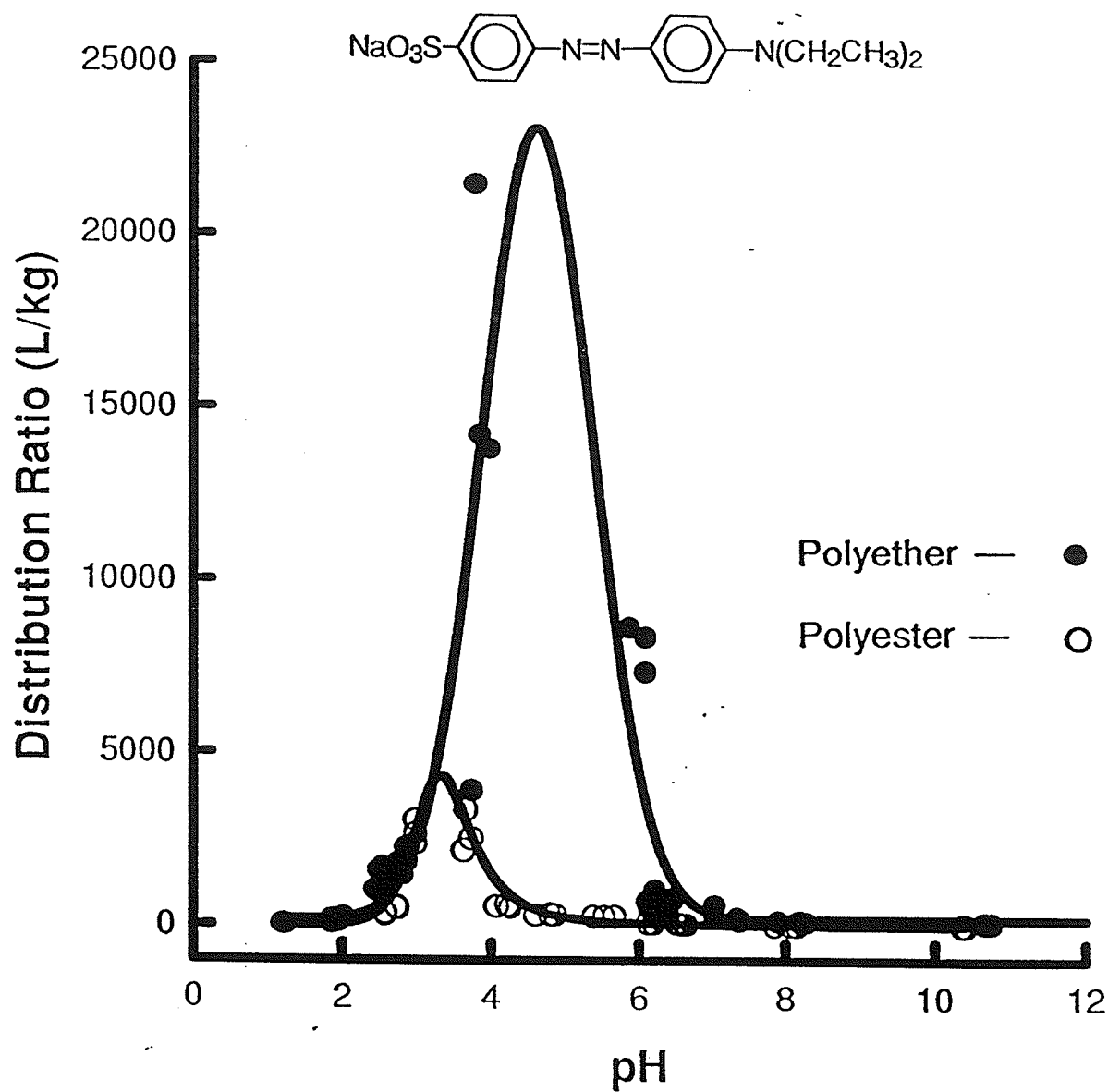
**Figure 9.** Extraction profile of 4'-(4-aminophenylazo)-benzenesulfonic acid. Conditions: 0.1 g foam, 15 mL dye solution ( $\sim 10^{-5}$  M), 24 h shaking time.



**Figure 10.** Extraction profile of Methyl Orange.

Conditions: 0.1 g foam, 15 mL dye solution ( $\sim 10^{-5}$  M), 24 h shaking time.

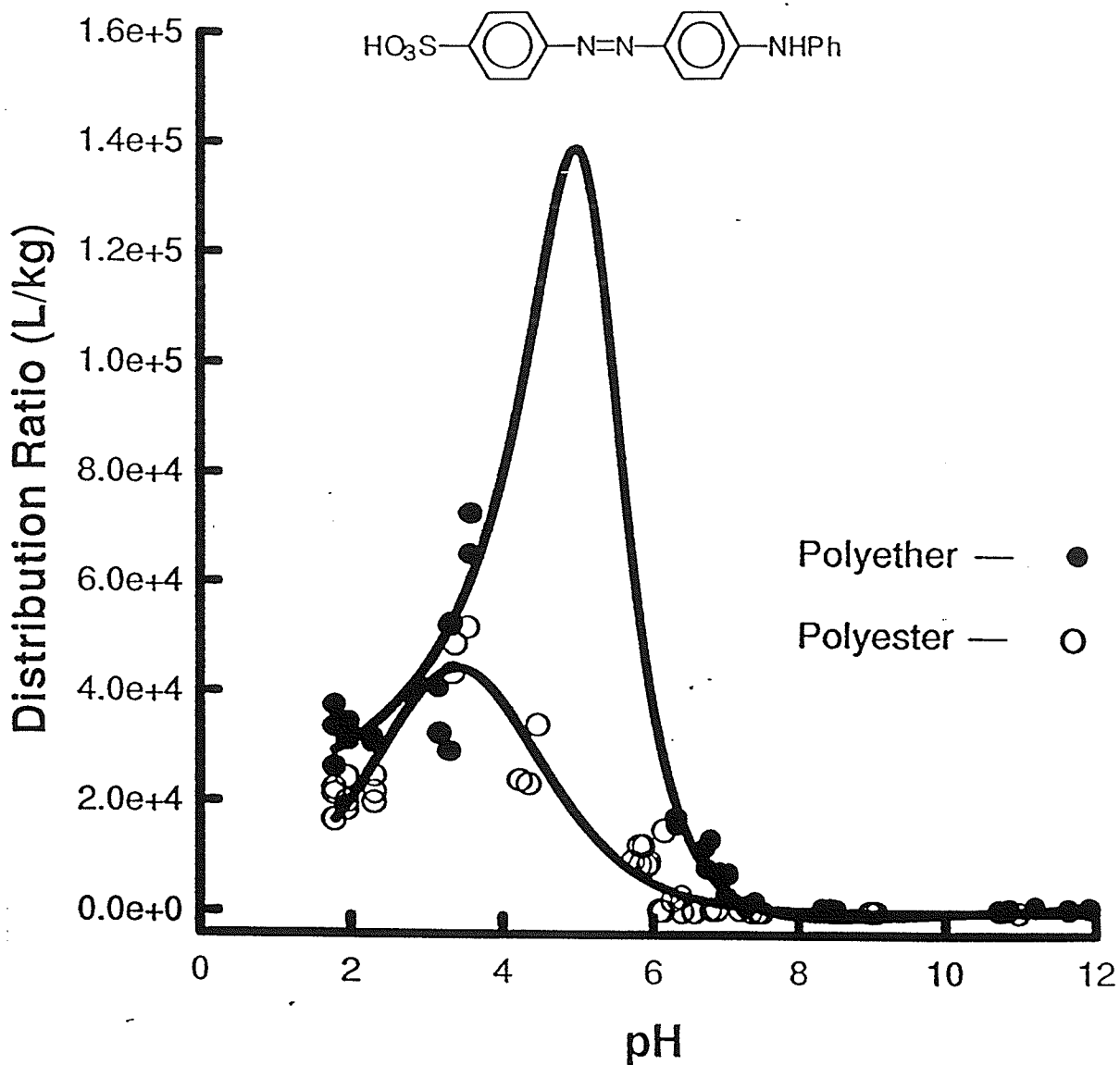




**Figure 11.** Extraction profile of Ethyl Orange.

Conditions: 0.1 g foam, 15 mL dye solution ( $\sim 10^{-5}$  M), 24 h shaking time.

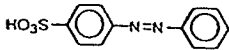
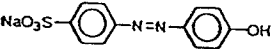
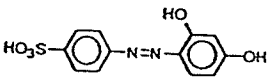
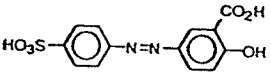
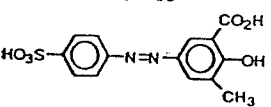
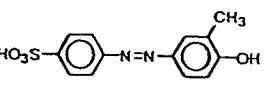
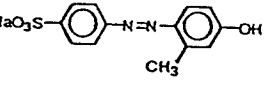
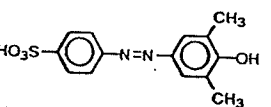
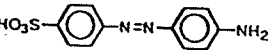
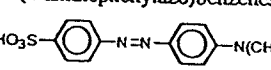
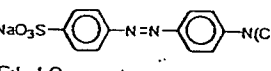
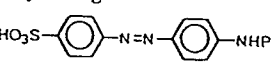
Note: Curves shown are for demonstrative purposes only; extractions above 12,000 L/kg are thought to be  $\infty$ .



**Figure 12.** Extraction profile of Orange IV. Conditions: 0.1 g foam, 15 mL dye solution ( $\sim 10^{-5}$  M), 24 h shaking time.

Note: Curves shown are for demonstrative purposes only; extractions above 12,000 L/kg are thought to be  $\infty$ .

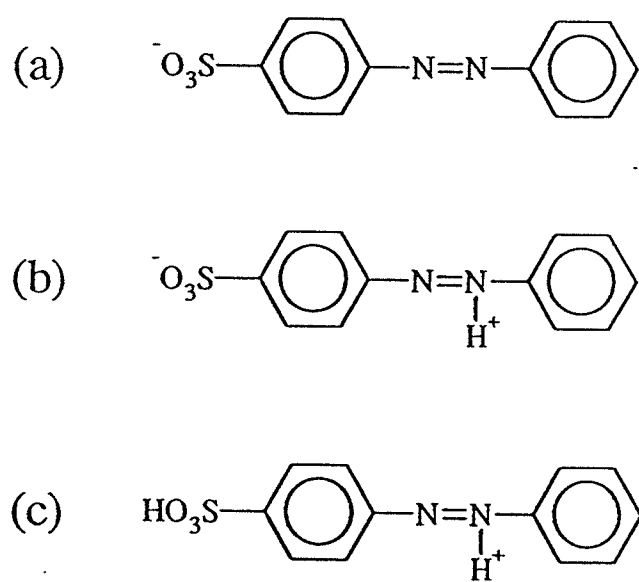
**Table 3.** Summary of the extraction profiles in Figures 1 - 12.

Dye	Maximum Distribution Ratio, (L/kg)		pH at Maximum Extraction	
	Polyester	Polyether	Polyester	Polyether
 4-Phenylazobenzenesulfonic acid	1100	1000	1.5	2.5
 4'-(4-hydroxyphenylazo)benzenesulfonic acid *	2100	5000	2.0	3.0
 Tropaeolin O	4500	9500	2.5	4.5
 Mordant Yellow 10	7500	9500	2.0	2.5
 Mordant Yellow 7	9500	12000	2.5	3.5
 4'-(4-hydroxy-3-methylphenylazo)benzenesulfonic acid	4500	7000	2.0	3.5
 4'-(4-hydroxy-2-methylphenylazo)benzenesulfonic acid *	5500	11500	2.0	2.5
 4'-(2,6-dimethyl-4-hydroxyphenylazo)benzenesulfonic acid	5000	8500	1.5	3.5
 4'-(4-aminophenylazo)benzenesulfonic acid	400	3000	3.0	4.5
 Methyl orange	500	∞	3.0	5.5
 Ethyl Orange *	4500	∞	3.5	4.5
 Orange IV	∞	∞	3.5	5.5

Values shown were interpolated from the appropriate figure.  
 Values above 12,000 L/kg are listed as ∞.

begins to occur in solutions at about a pH of 2. Notable exceptions were those dyes containing an amino-group, where the decrease in extraction occurred in solutions with a pH of 4 or less.

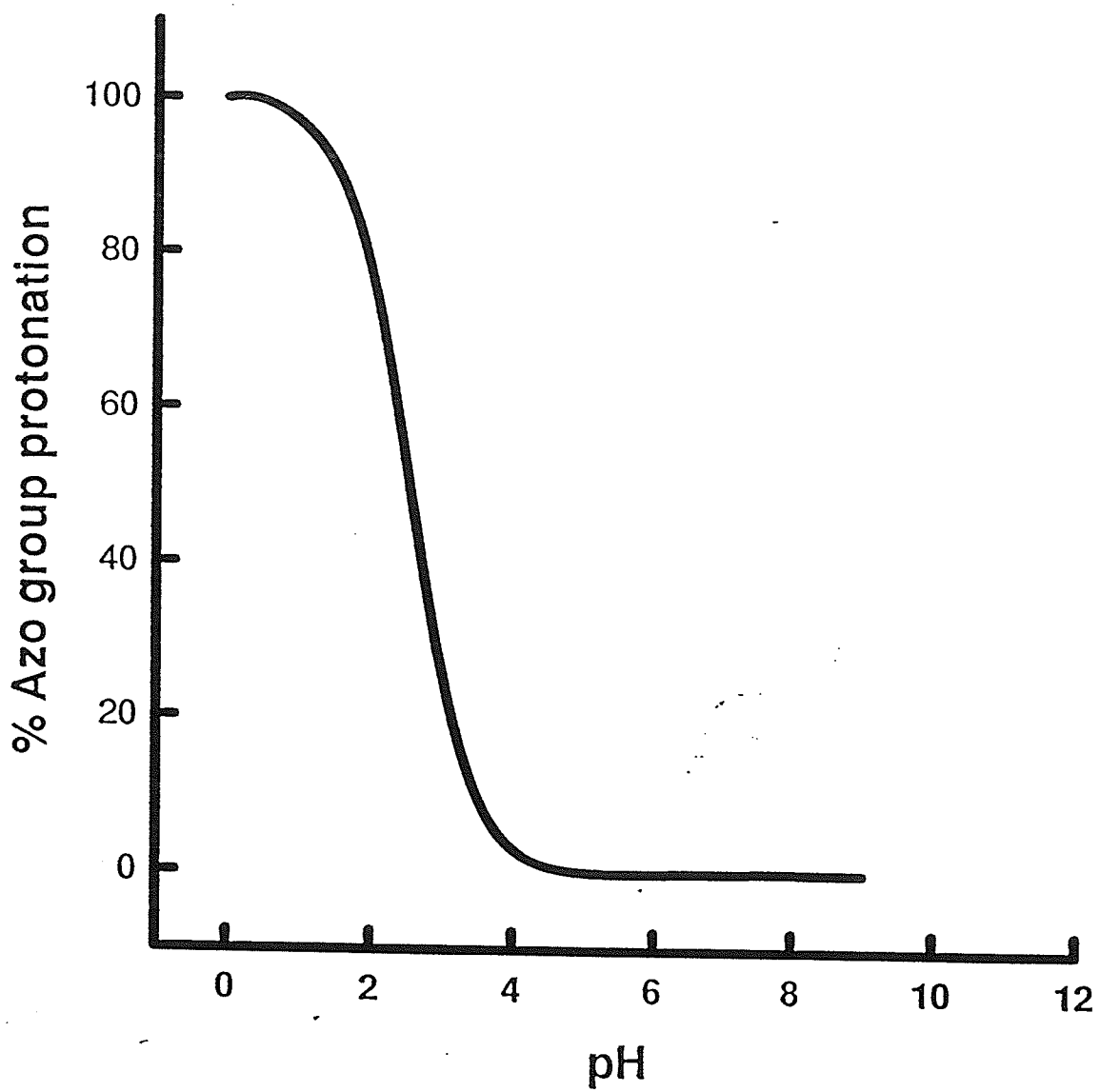
The results of this pH survey can be easily interpreted as showing only neutral species extraction. To aid in this interpretation, two of the dyes were chosen for further examination. Although the following arguments hold true for all of the dyes, only these more extensively studied dyes will be discussed. For basic solutions of 4-phenylazobenzenesulfonic acid (4-PABSA), a large percentage of the species would be expected to be negatively charged because of the unprotonated sulfo-groups (Figure 13a). As the solutions become more acidic, the azo-groups are expected to become protonated, and the molecules would become zwitterions with an overall neutral charge (Figure 13b). Such species therefore become extractable, as was observed. As solutions become very acidic ( $\text{pH} < 2$ ) some of the sulfo-groups would also become protonated (Figure 13c) producing an unextractable species (because of its overall positive charge); therefore a decrease in extraction is expected.



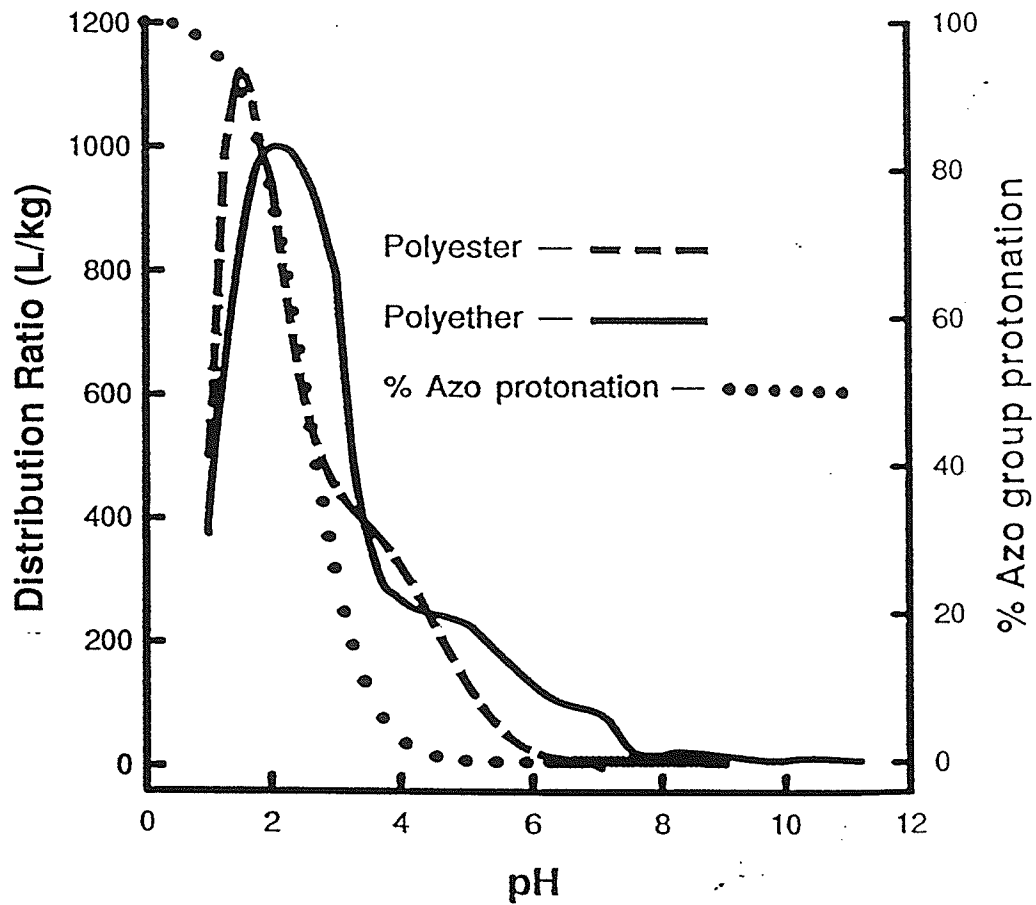
**Figure 13.** Protonation states of 4-PABSA.

In order to further test the idea of neutral species extraction, the first  $pK_a$  of 4-phenylazobenzenesulfonic acid, that of the azo-group, was experimentally determined and estimated to be 2.55. Using this  $pK_a$  the percentage of monoprotonated species was plotted vs. the corresponding pH to produce the protonation profile shown in Figure 14. When the sulfo-group is unprotonated, upon protonation of the azo-group the molecule becomes a neutral zwitterion. Since above a pH of 1 the vast majority of the sulfo-groups are in an unprotonated state, a plot of the percentage of protonated azo-groups is therefore also a plot of the neutral species available.

The relationship between the protonation profile and the extraction profile of 4-phenylazobenzenesulfonic acid is emphasised by overlaying figures 1 and 14 as shown in Figure 15. Although the extraction proceeds to some extent in solutions where there should only be a small percentage of neutral species, the sharp rise in extraction and the extraction maxima seem to correspond with the amount of neutral species available. These results suggests that the extraction mechanism involves mainly the neutral species of the dye. This mechanism can also explain



**Figure 14.** Protonation profile of 4-PABSA.



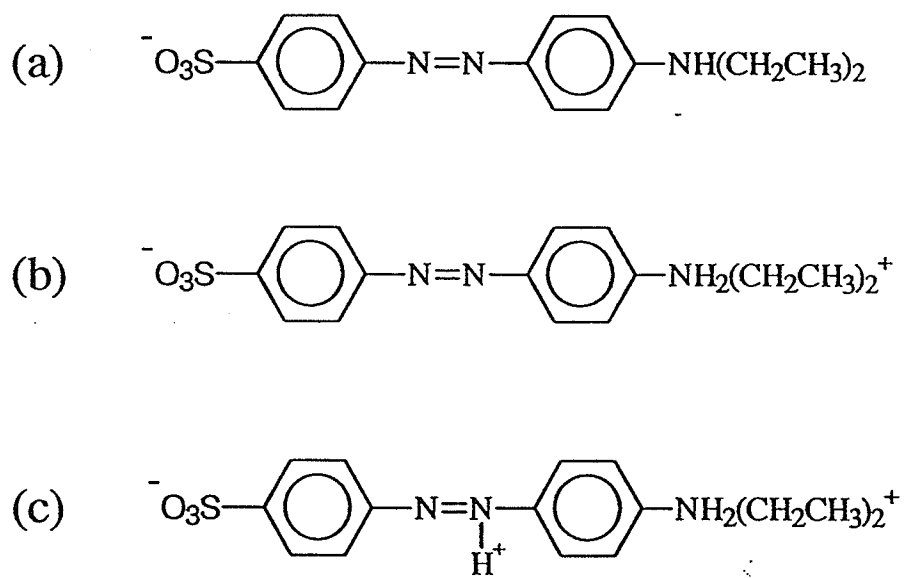
**Figure 15.** Overlay of figures 1 and 14. This emphasises the correlation between the extraction of 4-PABSA and the percentage of neutral species available.

Note: Data points have been removed for clarity.

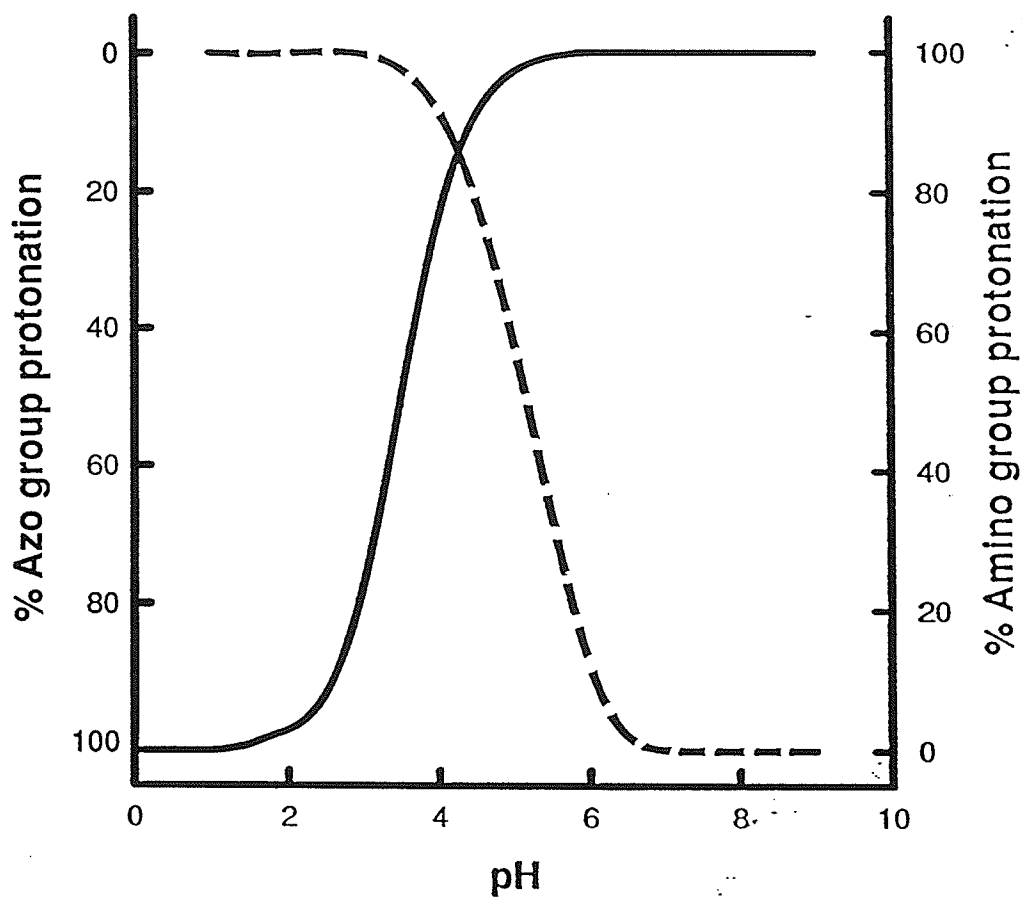


the sharp decrease in the extraction in acidic solutions. This decrease is thought to occur because as the sulfo-group becomes protonated, it gives an overall positive charge to the molecule. Unfortunately, because of the acidity of the solution and therefore the instrumental error associated with measuring such low values of pH, attempts to experimentally determine the  $pK_a$  of the sulfo-group were unsuccessful. Literature values for the acid constant in aqueous solutions of this or any similar dye were also unavailable.

The reliance of the mechanism on the presence of a neutral species is more clearly illustrated by analysing the results of the extraction of Ethyl Orange. The first  $pK_a$  of Ethyl Orange is for the amino-group and as with 4-PABSA, the monoprotection of the dye yields an overall neutral, extractable, zwitterion (Figure 16b). As with 4-PABSA, upon being doubly protonated, this time with the protonation of the azo-group, the molecule becomes positively charged (Figure 16c) and unextractable. In this case the neutral species involves a protonated amino-group and an unprotonated azo group. Therefore to graphically represent the percentage of neutral species present, both the percentage of protonated amino-groups, and the percentage of unprotonated azo-groups need to be



**Figure 16.** Protonation states of Ethyl Orange.

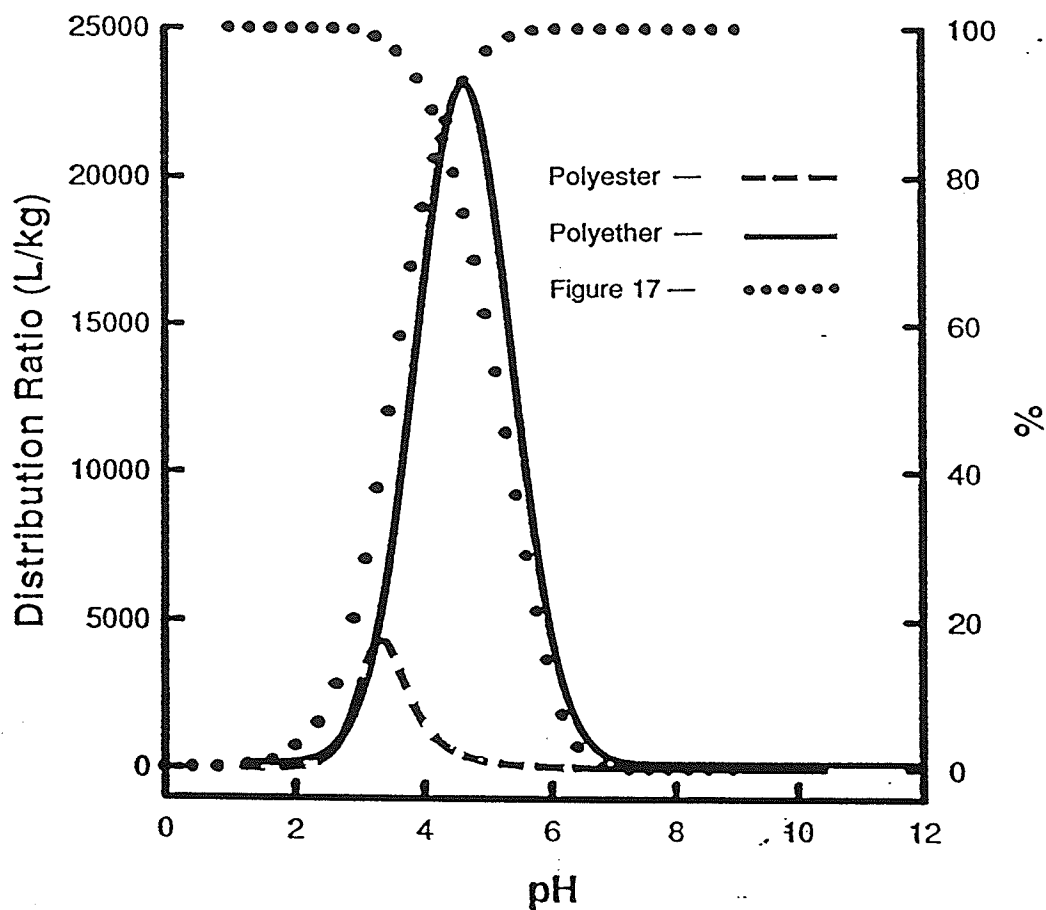


**Figure 17.** Protonation profile of Ethyl Orange. The percentage of neutral species is represented by ( — ) the percentage of protonated azo-groups left of the intersection, and ( - - - ) the percentage of protonated amino-groups to the right.

plotted. In Figure 17 the two percentage curves are shown; the neutral species is represented by the protonated azo-group curve on the acidic side of their intersection ( $\text{pH} < 4$ ), and the protonated amino-group curve on the basic side of their intersection ( $\text{pH} > 4$ ).

The overlay of the extraction profile of Ethyl Orange and the protonation profile is shown in Figure 18. Although the curves are shifted by 0.5 pH, the extraction using polyether-type polyurethane closely follows the percentage of Ethyl Orange that is predicted to be present as a neutral species. The increase and decrease of the Ethyl Orange extraction mimic those percentages, which leaves little doubt that the extraction is of a neutral species.

There is additional evidence that the majority of the extraction is dependent on the charge of the dye species, and not on a foam-related phenomenon. This comes from the fact that the increase in extraction, from basic to acidic solutions, follows the  $\text{pK}_a$  curve of the dye being extracted. Specifically, this can be seen by comparing the extraction profiles of 4-PABSA and Ethyl Orange. If this were a foam-related phenomenon, the extraction



**Figure 18.** Overlay of the extraction profile of Ethyl Orange with Figure 17. This emphasizes the correlation between the extraction of Ethyl Orange and the amount of neutral species present.

Note: Data points have been removed for clarity.

increase would be expected to occur in solutions with similar pH regardless of the dye being extracted. Instead, the extraction appears to follow the  $pK_a$  curve of the dye being extracted.

It seems clear that the overriding mechanism involves the sorption of an overall neutral species. There is however some evidence of an additional extraction mechanism which has a less significant effect on the extraction. In Figure 1, the slow increase in extraction of 4-PABSA as the solution is changed from a pH of 5 to 8, could be interpreted as showing two minor increases in extraction, between pH of 7 and 8, and between pH of 5 and 6. These small increases in extraction are not easily explained using a neutral species extraction. One possible explanation for this behaviour lies in the protonation of nitrogen- and oxygen-containing groups on the foam; as the foam group becomes protonated it might act as a ion exchange site. However, given the small amount of extraction attributable to this mechanism when compared to neutral species extraction, this hypothesis was not further explored.

## **Polyester vs. Polyether**

The composition and structure of a polyester-type polyurethane is quite different from that of the polyether-type, so it is not surprising that they have different extraction characteristics. Although the extraction profiles have the same general shape, extractions with polyester foam are usually different from those using polyether. The two main differences are in the maximum amount of dye extracted and the solution conditions necessary for extraction to occur.

The extraction profiles show that the increase in extraction from basic to acidic solutions, and the maximum extraction, occur in more acidic solutions with polyester than with polyether foam. There seems to be a consistent need for solutions to be generally 1 to 3 pH units more acidic for a comparable extraction into polyester compared to polyether foam (see Table 3). This suggests that the above effect is not a dye-related phenomenon, but rather it is likely due to the differences in the dielectric constants of the two foams<sup>31</sup>. This shift of two pH units does not apply for the decrease in extraction, which occurs in the same pH range for the two foams. Since the extraction with both foams

decreases as the percentage of neutral species declines, this can be interpreted as further proof of a neutral species extraction by both types of foams.

Another difference, seen throughout the extraction profiles (figures 1 - 12), is that the extractions with polyether foam often have a higher maximum distribution ratio than those extracted using polyester. The extractions showing this behaviour involve dyes with either a hydroxyl or amino functional group. Trends similar to this have been reported by previous researchers<sup>22,26</sup>. Schumack and Chow<sup>23</sup> found that compounds containing phenolic or carboxylic groups were extracted more efficiently by polyether than polyester foam. Through a comparison of *ortho*-, *meta*- and *para*-nitrophenols they determined that the difference in extraction can be attributed to the presence of hydrogen bonding. Hydrogen bonds are likely to be much stronger with a polyether than with a polyester foam<sup>32</sup> and therefore compounds containing hydrogen bonding functional groups are likely to be better extracted by a polyether than a polyester foam.

From Table 3 it can be seen that differences between polyether to polyester extractions are higher with those dyes



containing an amino-group than those hydroxyl-containing dyes. Fong and Chow<sup>26</sup> reported similar results using 1-amino-2-naphthol-4-sulfonic acid. In their extraction, it is likely that the amino-group was protonated; they suggested that an additional ion-dipole interaction might explain the higher differences of their distribution ratios. This interaction could also explain the extraction behaviour of the amino-containing dyes found in this study.

### **Comparison of Maximum Extractions**

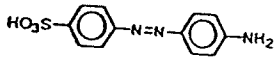
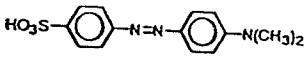
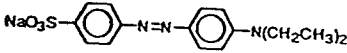
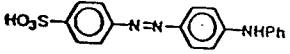
One of the aims of this study was to gain some insight into the role that functional groups play in the extraction process. This objective was a major consideration when choosing the dyes for this study. As stated earlier, the dyes were selected for their similarity in structure with the exception of additional functional groups or the position of those functional groups on the ring structure. The effect that the functional groups have on the extraction of the compounds might then be ascertained by comparing the maximum distribution ratios,  $D_{\max}$ , of the similar dyes. These comparisons should be valid since the maximum distribution ratio should be a good approximation of the

distribution coefficient<sup>24,25</sup>. The maximum distribution ratios were taken from the extraction profiles, figures 1 - 12, which show how these functional groups can change the outcome of an extraction.

The most significant trend can be seen in those dyes containing an amino functional group (figures 9 - 12). In this series, the hydrogens on the amino group are replaced with increasingly non-polar groups. As the size of this replacement group increased, the extent of extraction dramatically increased with both polyester and polyether foams. This trend is summarized in Table 4. Additional trends can be seen involving hydroxyl or hydroxyl-containing groups and methyl groups.

The effect of the addition of a hydroxyl-group is evident when the extraction of 4-PABSA (Figure 1) is compared with the extraction of 4'(4-hydroxyphenylazo)benzenesulfonic acid (4'-4-HPABSA, Figure 2). As discussed earlier the effect of the hydroxyl group is larger with polyether foam than with polyester foam. The maximum distribution ratio,  $D_{max}$ , for 4-PABSA is approximately 1000 L/kg for polyether extractions and 1100 L/kg for polyester extractions. For 4'-4-HPABSA the  $D_{max}$  with polyether foam is

**Table 4.** Summary of the extraction profiles of the dyes containing an amino group.

Dye	Maximum Distribution Ratio, (L/kg)		pH at Maximum Extraction	
	Polyester	Polyether	Polyester	Polyether
 4'-(4-aminophenylazo)benzenesulfonic acid	400	3000	3.0	4.5
 Methyl orange	500	∞	3.0	5.5
 Ethyl Orange *	4500	∞	3.5	4.5
 Orange IV	∞	∞	3.5	5.5

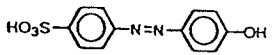
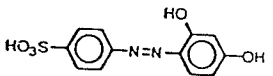
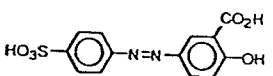
Values above 12,000 L/kg are listed as ∞.

5000 L/kg, a 500% increase, and with polyester foam  $D_{\max}$  increases only to 2100 L/kg, an approximate 100% increase. The addition of another hydroxy group to the same ring doubles the effect. This is seen with Tropaeolin O (Figure 3) whose  $D_{\max}$  for polyether extraction is close to 10,000 L/kg and is over 4000 L/kg when using polyester foam.

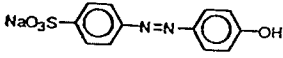
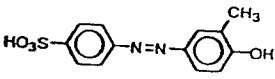
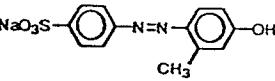
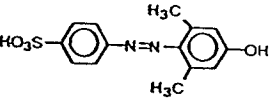
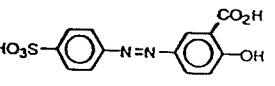
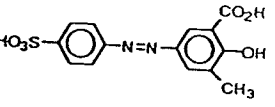
For polyether extractions, the addition of a carboxyl group to the same ring seems to have the same effect as an additional hydroxyl group. This suggests that the interaction of dyes with polyether is largely through the hydroxyl of the carboxyl group on the dye. However, this does not seem to be the case with extractions using polyester foam. The addition of a carboxyl group to the ring has a much larger effect than the addition of a hydroxyl group. This can be seen in the comparisons of the extractions of 4'-4-HPABSA (Figure 2), Mordant Yellow 10 (Figure 4) and Tropaeolin O (Figure 3) which are summarized in Table 5. This suggests that with the polyester foam the interaction is not limited to the hydroxyl, but involves the whole carboxyl group.

Table 6 shows that the addition of a methyl group to the ring structure seems to have the same effect as the addition of a

**Table 5.** Summary of the extraction profiles of the dyes containing a carboxyl group.

Dye	Maximum Distribution		pH	
	Ratio, (L/kg)		at Maximum Extraction	
	Polyester	Polyether	Polyester	Polyether
 4'-(4-hydroxyphenylazo)benzenesulfonic acid	2100	5000	2.0	3.0
 Tropacolin O	4500	9500	2.5	4.5
 Mordant Yellow 10	7500	9500	2.0	2.5

**Table 6.** Summary of the extraction profiles of the dyes containing methyl groups compared with 4'-4-HPABSA and Mordant 10.

Dye	Maximum Distribution Ratio, (L/kg)		pH at Maximum Extraction	
	Polyester	Polyether	Polyester	Polyether
 4'-(4-hydroxyphenylazo)benzenesulfonic acid *	2100	5000	2.0	3.0
 4'-(4-hydroxy-3-methylphenylazo)benzenesulfonic acid	4500	7000	2.0	3.5
 4'-(4-hydroxy-2-methylphenylazo)benzenesulfonic acid *	5500	11500	2.0	2.5
 4'-(2,6-dimethyl-4-hydroxyphenylazo)benzenesulfonic acid	5000	8500	1.5	3.5
 Mordant Yellow 10	7500	9500	2.0	2.5
 Mordant Yellow 7	9500	12000	2.5	3.5

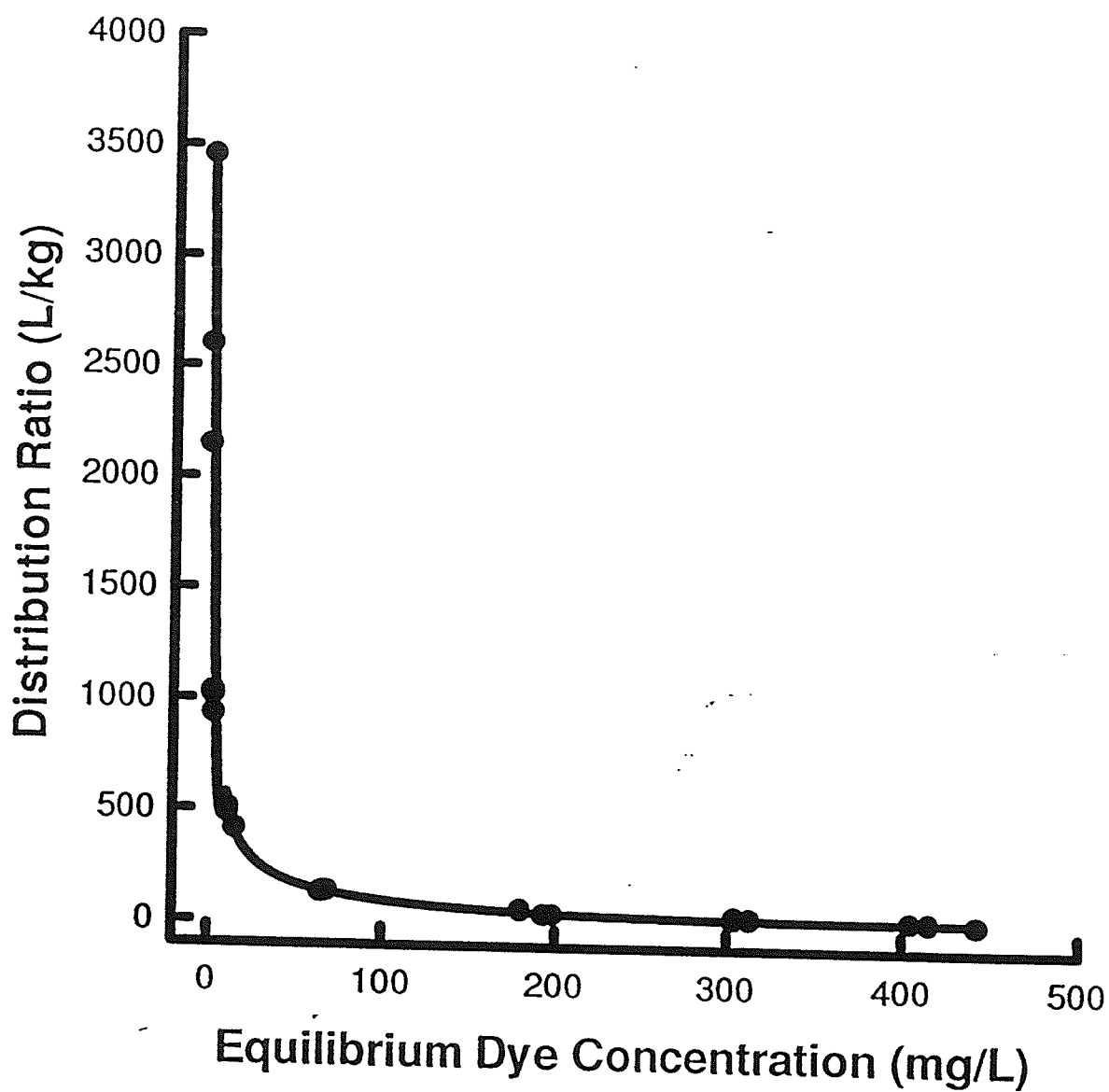
hydroxyl group. Comparing the maximum distribution ratios of Mordant Yellow 7 (Figure 5), Mordant Yellow 10 (Figure 4) and 4'(4-hydroxy-3-methylphenyl-1-azo)benzenesulfonic acid (Figure 6) with 4'-4-HPABSA (Figure 2), a trend, similar to that observed with the hydroxyl group, can be seen. In this case it is attributable to the addition of the methyl group. However the addition of two methyl groups to 4-PABSA, giving 4'-2,6-dimethyl-4-HPABSA, does not double the extraction. In addition, it seems that the position of the methyl group on the ring is a factor. It is evident when comparing 4'(4-hydroxy-3-methylphenylazo)benzenesulfonic acid with 4'(4-hydroxy-2-methylphenylazo)benzenesulfonic acid. The appearance that placement of a functional group has an effect on extraction might suggest that there are inductive or steric factors to be considered, and indeed there may well be. However the apparent changes in the amount of extraction between these and the other dyes could have another explanation as will be discussed next. The explanations in the following section confine the above arguments and comparisons, even the most obvious ones, to speculations that cannot be used with complete confidence.

## Equilibrium Dye Concentration

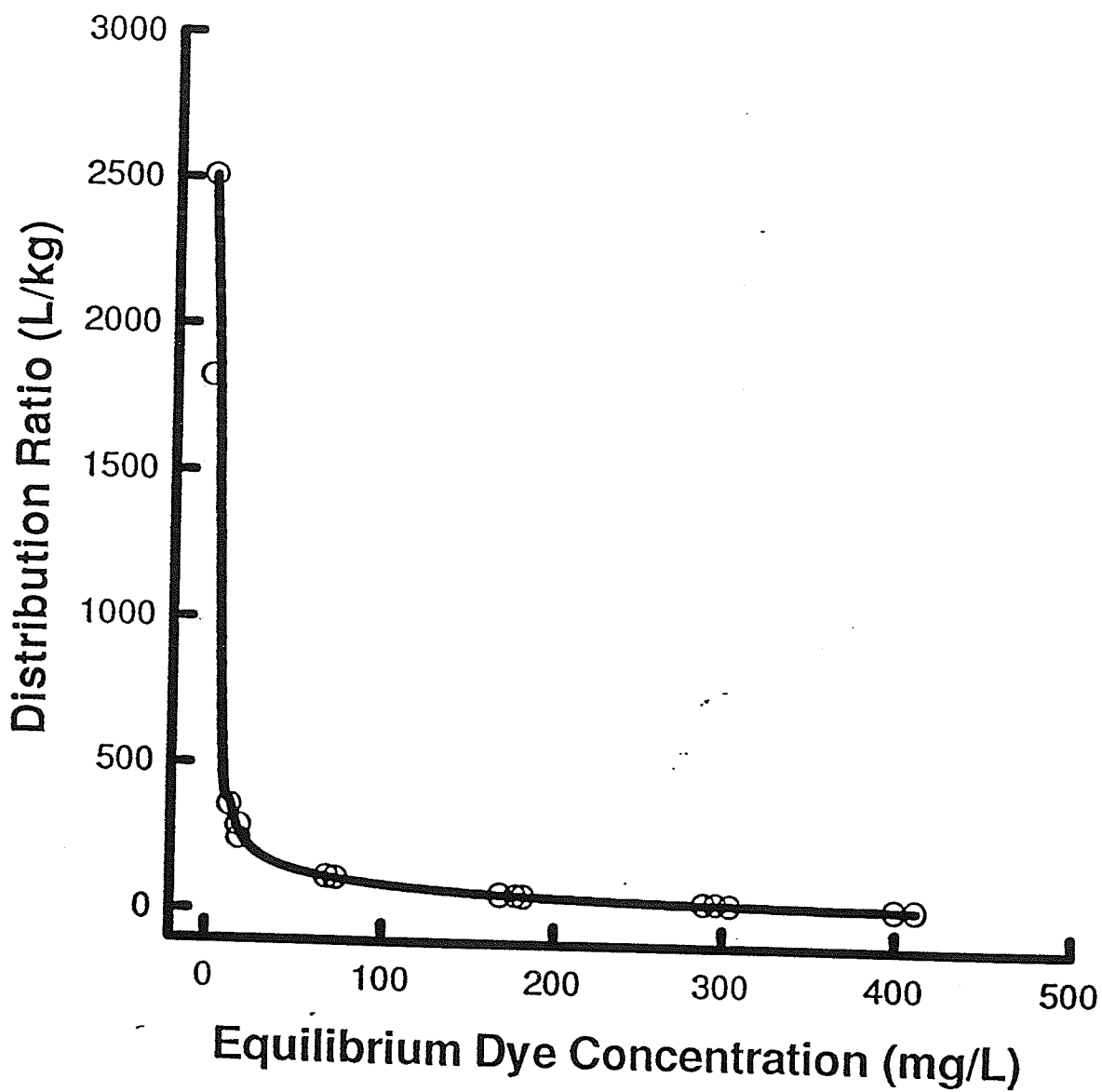
The discovery of an interesting trend was made while constructing the extraction profiles using data from several separate experiments. It appeared that the amount of extraction was somehow linked with the concentration of dye present during an extraction. In order to study the effect of the equilibrium dye concentration on the extraction, two experiments were designed to vary the equilibrium dye concentration; the first varied the initial dye concentration and kept the amount of foam present constant, the second kept the initial amount of dye constant and varied the amount of foam.

A concentrated dye stock solution of 4-phenylazobenzenesulfonic acid, was prepared as previously described. Unlike other experiments in which each sample solution received equal aliquots of stock solution, these sample solutions were prepared by varying the amount of added stock solution, thereby varying the initial dye concentration in the sample solutions from 5 mg/L to 500 mg/L. This experiment was run at a pH which was close to the pH of maximum extraction.





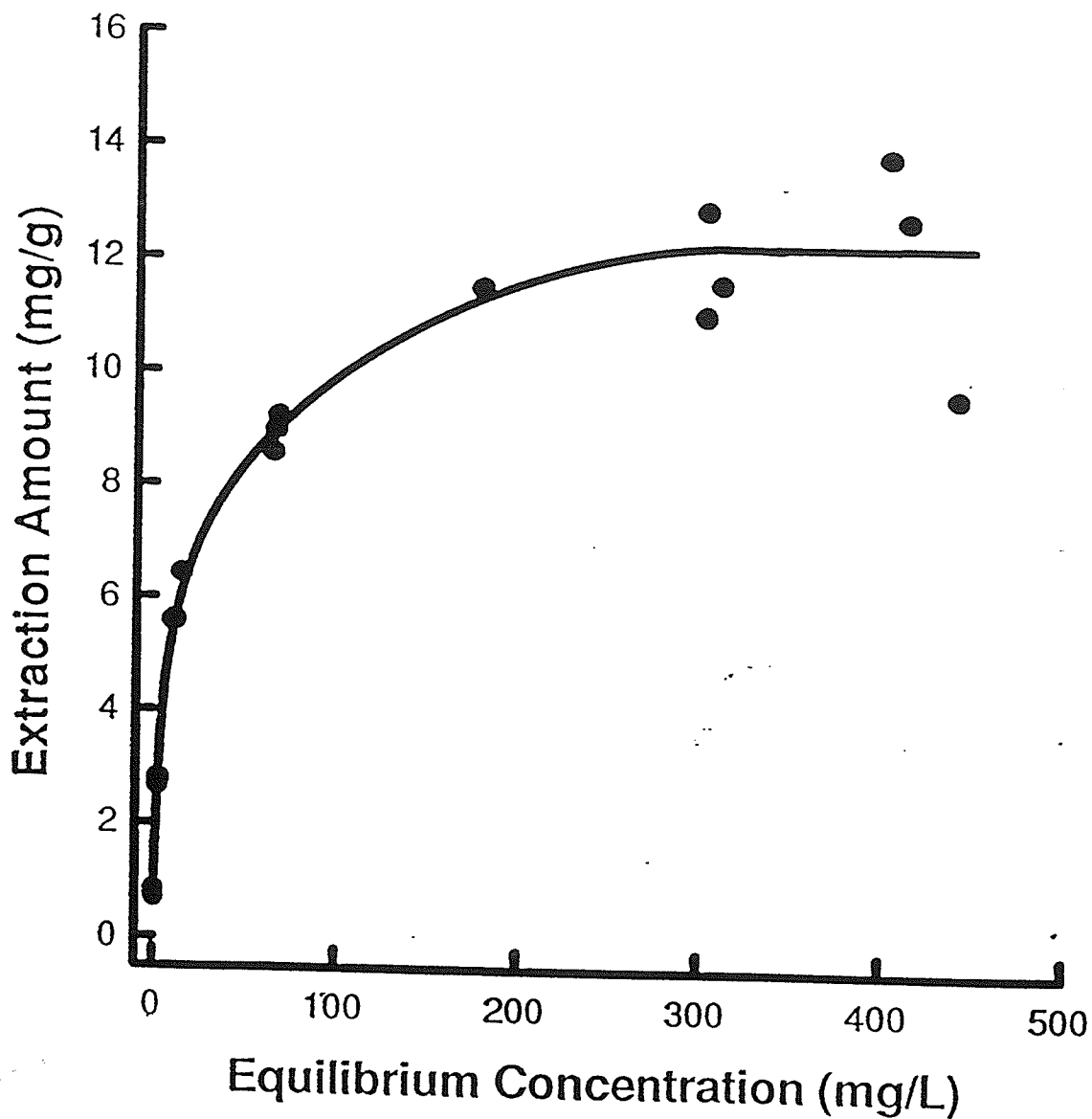
**Figure 19.** The effect of equilibrium dye concentration on the extraction of 4-PABSA with polyether foam. Conditions: 0.1 g foam, 15 mL dye solution ( $\sim 10^{-5}$  M, pH $\sim$  2.5), 24 h shaking time.



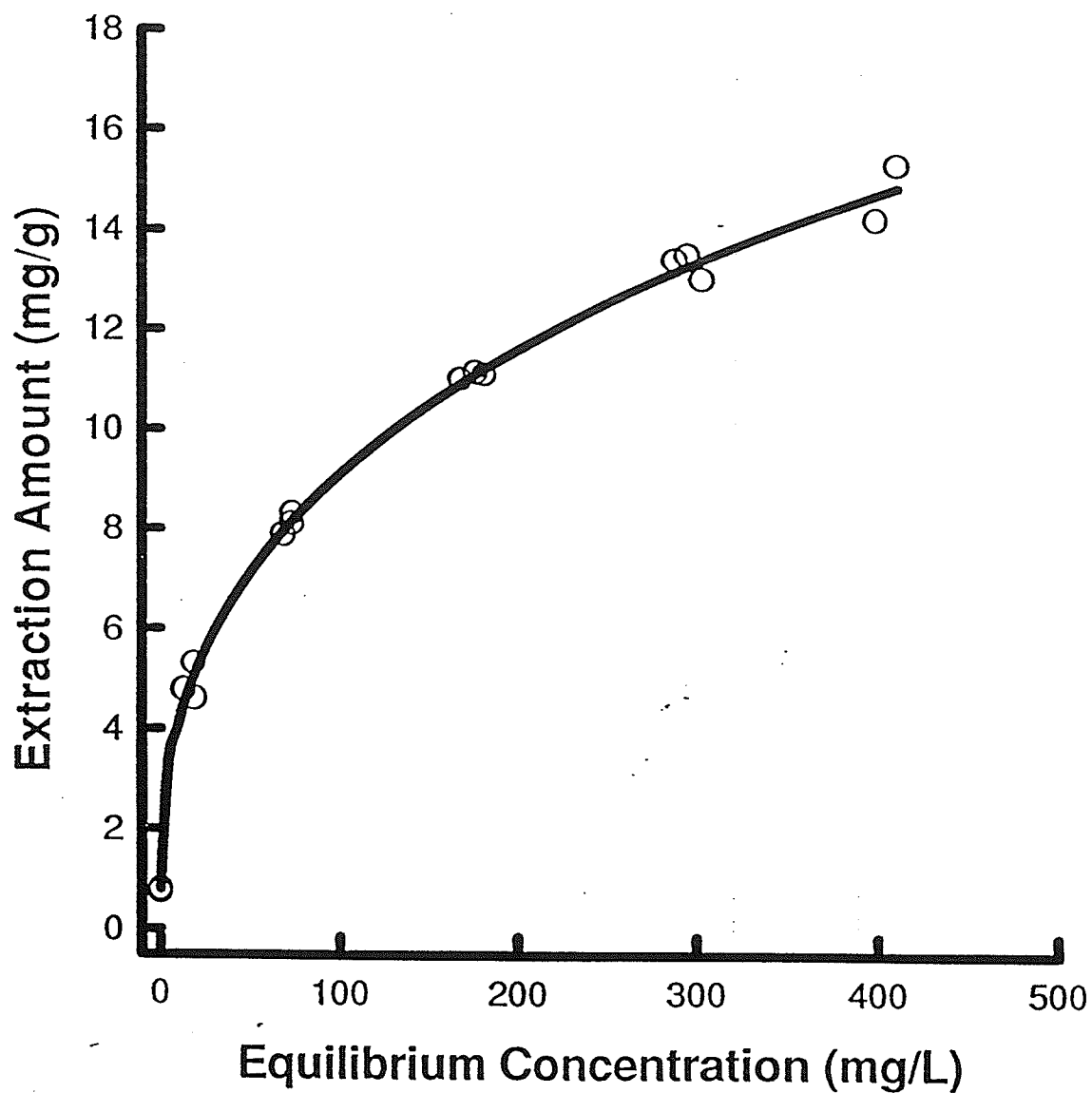
**Figure 20.** The effect of equilibrium dye concentration on the extraction of 4-PABSA with polyester foam. Conditions: 0.1 g foam, 15 mL dye solution ( $\sim 10^{-5}$  M, pH $\sim$  2.5), 24 h shaking time.

The results of this experiment showed that the distribution ratio is very dependent on the equilibrium dye concentration. Figures 19 and 20 show the results using polyether and polyester foam respectively. Initially, it was thought that this behaviour might be an indication that the foam was reaching capacity, i.e. the foam was becoming saturated with dye. To examine this, data was used to plot the actual amount of dye being sorbed per gram of foam. Figures 21 and 22 show that while the polyether foam appears to approach its capacity, estimated to be approximately 12 mg of 4-PABSA per gram of foam, the polyester does not appear to approach capacity. Additionally, the experiments showing the greatest dependence on dye concentration occur under conditions well below this saturation level. It was therefore concluded, that the dependency of the sorption on equilibrium dye concentration was not related to the capacity of the foam.

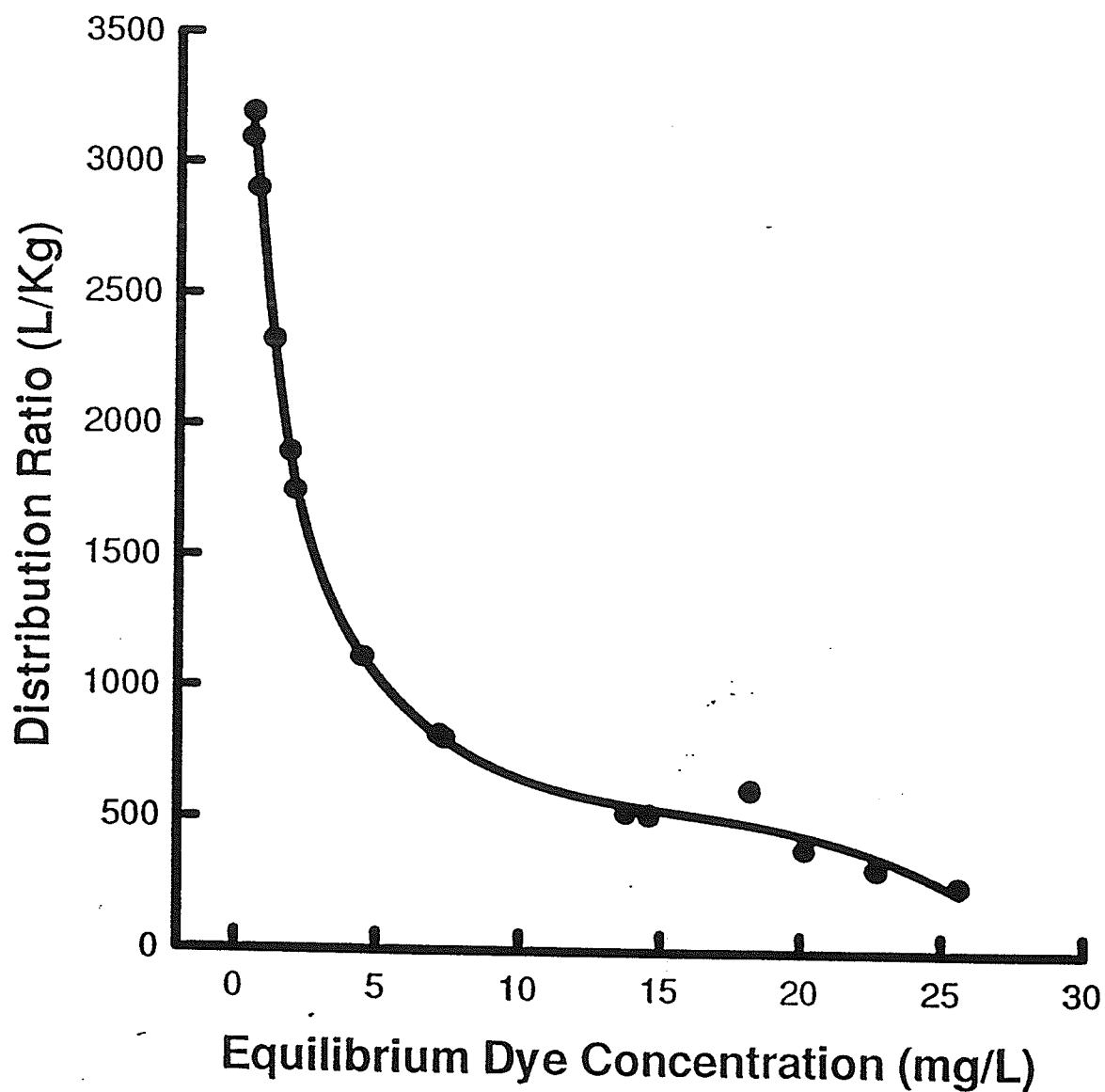
These findings seem to be confirmed by the results of the experiments where the foam weight was changed. Instead of using the normal 0.08 - 0.12 g of foam, the amount of foam used in this experiment was varied from 0.01 g to 0.32 g. In this experiment, the pH and initial dye concentration were the same for all the samples. The results of the extractions, shown in figures 23 and



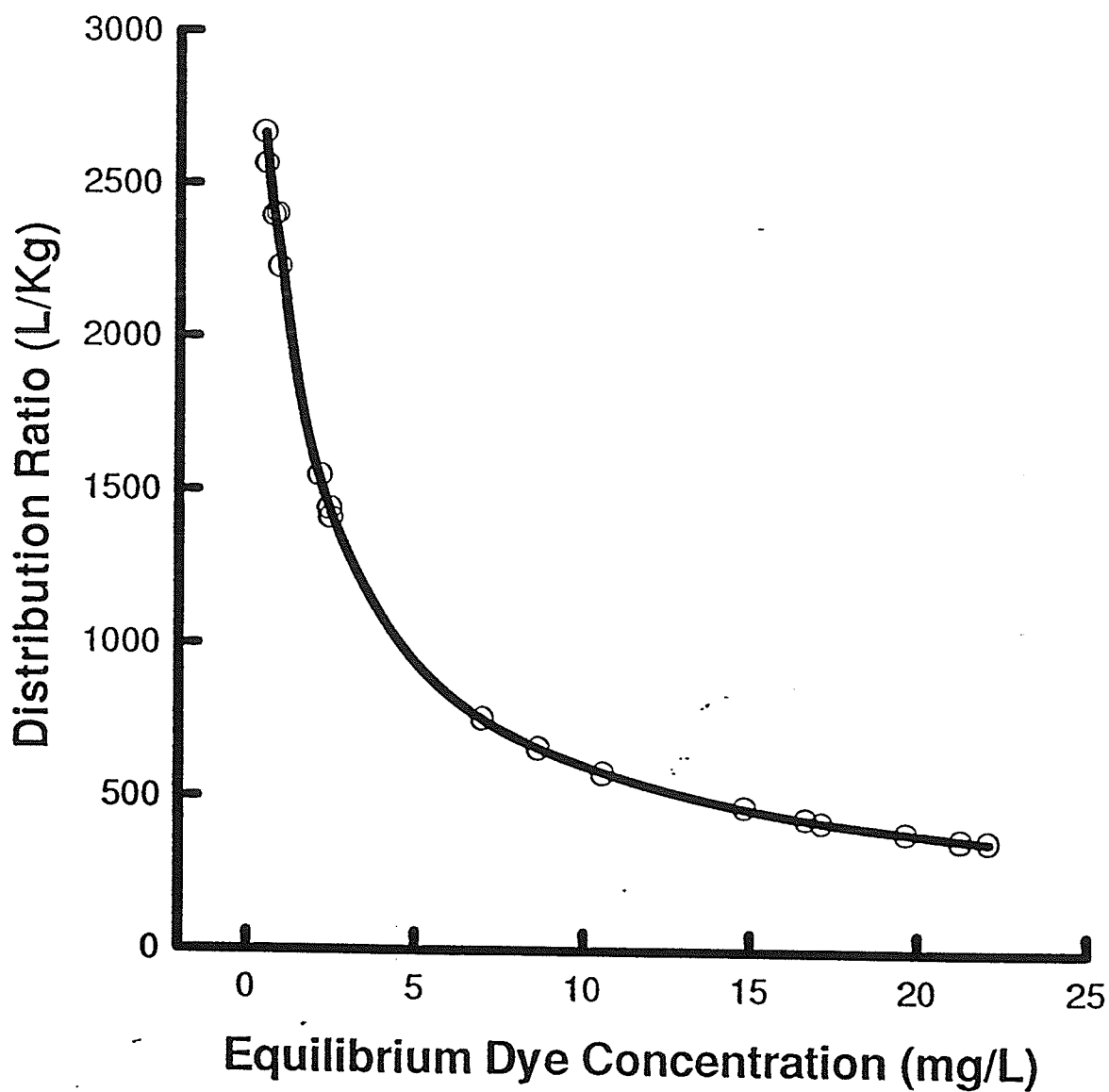
**Figure 21.** The amount of 4-PABSA extracted per gram of polyether foam. Conditions: 0.1 g foam, 15 mL dye solution ( $\sim 10^{-5}$  M, pH $\sim$  2.5), 24 h shaking time.



**Figure 22.** The amount of 4-PABSA extracted per gram of polyester foam. Conditions: 0.1 g foam, 15 mL dye solution ( $\sim 10^{-5}$  M, pH $\sim$  2.5), 24 h shaking time.



**Figure 23.** The effect of equilibrium dye concentration on the extraction of 4-PABSA with polyether foam. Conditions: 0.01 - 0.32 g foam, 15 mL dye solution ( $\sim 10^{-5}$  M, pH $\sim$  2.5), 24 h shaking time.



**Figure 24.** The effect of equilibrium dye concentration on the extraction of 4-PABSA with polyester foam. Conditions: 0.01 - 0.32 g foam, 15 mL dye solution ( $\sim 10^{-5}$  M, pH $\sim$  2.5), 24 h shaking time.

24, were very similar to those found in the experiments which varied the initial dye concentration.

To explain these results two models were evaluated; one involves the solvent extraction mechanism and how it is affected by the ionic strength of the solution, the other, called the dual-mode sorption model<sup>33</sup> involves the solvent extraction mechanism and the adsorption mechanism.

*Ionic Strength:* Examining the solvent extraction model shown below, we can better understand what might be occurring.

$$\begin{aligned}
 & \text{HA}_{\text{aq}} \rightleftharpoons \text{HA}_{\text{org}} \\
 K_d = & \frac{a_{\text{HA}\cdot\text{org}}}{a_{\text{HA}\cdot\text{aq}}} = \frac{[\text{HA}_{\text{org}}]f_{\text{HA}\cdot\text{org}}}{[\text{HA}_{\text{aq}}]f_{\text{HA}\cdot\text{aq}}} = D \frac{f_{\text{HA}\cdot\text{org}}}{f_{\text{HA}\cdot\text{aq}}} \quad (3)
 \end{aligned}$$

Where HA is a neutral dye species,  $K_d$  is the distribution coefficient,  $a_{\text{HA}}$  is the activity of the dye in the corresponding phase, and  $f_{\text{HA}}$  is the activity coefficient of the dye in the corresponding phase.

In this model there is an equilibrium between the neutral



species in the aqueous phase and the neutral species in the organic phase, in this case the foam. This equilibrium can be expressed as a ratio of the activities of the dye in each phase, which in turn can be expressed as the distribution ratio multiplied by the ratio of the activity coefficients of the dyes in each phase. It is usual to assume for dilute solutions that the activity coefficients are both near unity and constant<sup>30</sup>. Therefore the distribution coefficient  $K_d$  is approximately equal to the distribution ratio and it is generally assumed that solvent extraction is concentration independent.

The problem then is to explain the extraction results using this solvent extraction model. One plausible explanation involves the assumption made regarding the activity coefficients. From equation 3 it can be seen that if either of the activity coefficients were not constant, the distribution ratio,  $D$ , would have to change since  $K_d$ , the distribution coefficient, is a thermodynamic constant. One thing that would change the aqueous activity coefficient of the dye, is the ionic strength of the solution.

Although it has been shown that the extraction is largely of neutral species, the species involved are actually zwitterions.

Therefore it might be possible that changing the concentration of the dye would also change the ionic strength of the solution, although no information regarding such effects was found in the literature. As the ionic strength of the solution increases, the activity coefficient of the dye in solution would decrease<sup>30</sup>. Again, looking at equation 3, it can be seen that this would cause the ratio of the activity coefficients to increase. Since  $K_d$  is a thermodynamic constant, the distribution ratio would have to decrease as the aqueous activity coefficient decreased. This is the exact behaviour observed in these experiments. While there is some doubt as to whether such small increases in dye concentration could affect its activity coefficient, additional strength is added to this argument by the salt concentration results discussed later.

Based on this model, as a solution approaches infinitely dilute conditions, the distribution ratio should become a closer approximation of the distribution coefficient and the maximum distribution ratio for an extraction should become more constant. However, even when the equilibrium dye concentration approaches the limits of detection, the distribution ratio showed no signs of levelling off, therefore no estimation of  $K_d$  can be made.

*Dual-Mode Sorption:* Dual-mode sorption is the second model used to try and explain the dependence of the extraction on the equilibrium dye concentration. In this model, the sorbed dye is classified into two groups; the absorbed dye (solvent extraction mechanism), and the adsorbed dye (surface adsorption described by the Langmuir equation). This model is mathematically represented as

$$C_{org} = C_{ab} + C_{ad} = K_d C_{aq} + \frac{SK_L C_{aq}}{1 + K_L C_{aq}} \quad (4)$$

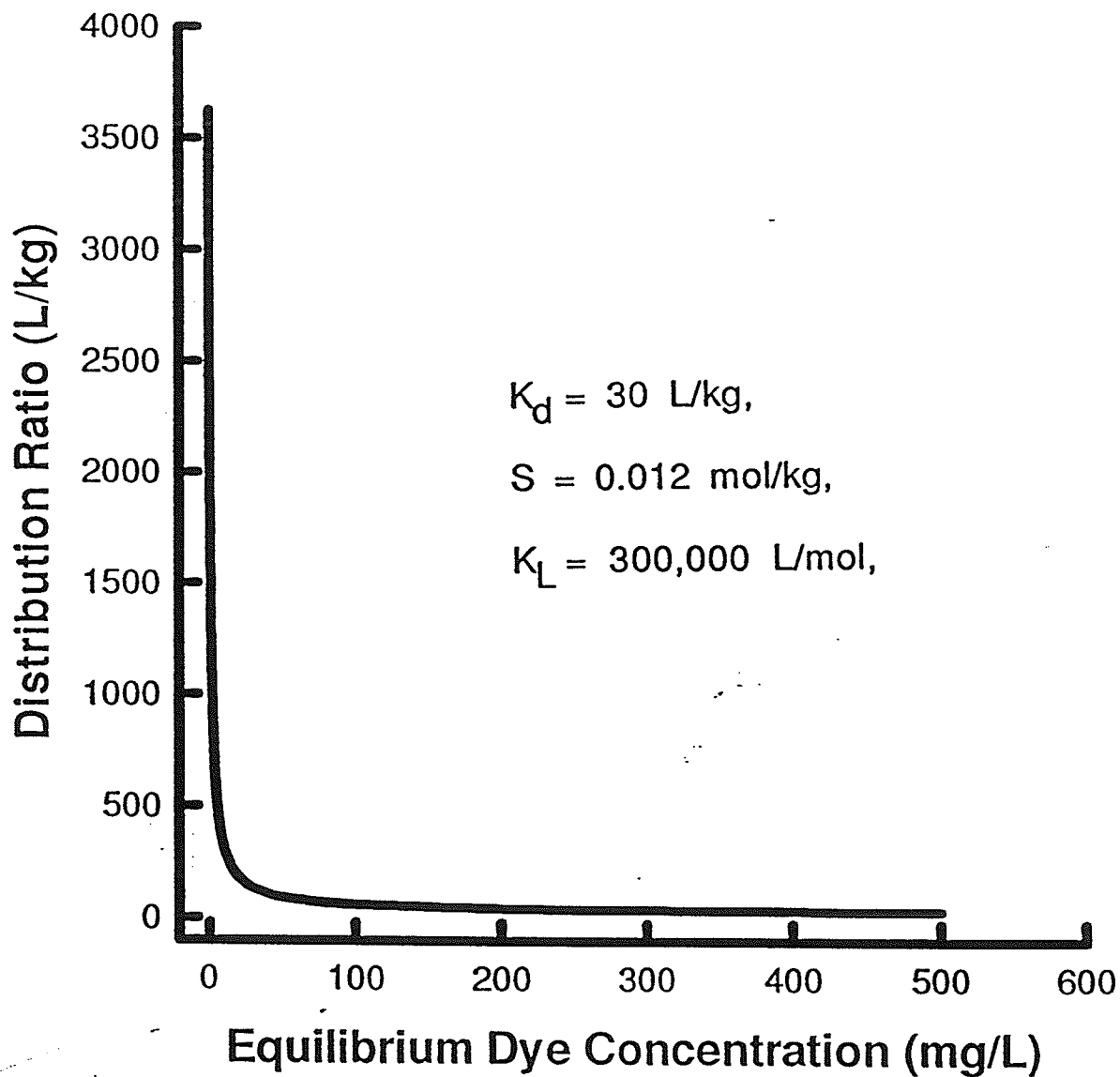
where  $C_{org}$  and  $C_{aq}$  are the equilibrium dye concentrations on the polyurethane foam and in solution;  $C_{ab}$  and  $C_{ad}$  are the equilibrium dye concentrations on the foam as an absorbed species and as an adsorbed species;  $S$  is the saturation value for the Langmuir adsorption;  $K_d$  is the distribution coefficient; and  $K_L$  is the Langmuir constant.

Equation 4 can be solved for the distribution ratio,  $D$ , as:

$$D = K_d + \frac{SK_L}{1 + K_L C_{aq}} \quad (5)$$

From equation 5 it is now obvious that the distribution ratio is not independent of the dye concentration. Using the values (obtained by estimation),  $K_d = 30$  L/kg,  $S = 0.012$  mol/kg, and  $K_L = 300,000$  L/mol, a graph of equation 5, shown in Figure 25, is almost identical to that observed in figures 19 and 20. From equation 5 it can be seen that as the concentration of the dye increases, the contribution to  $D$  from the adsorption component becomes minimal, and  $D$  approaches the value of  $K_d$ . As the concentration approaches zero,  $D$  should approximate  $K_d + SK_L$ . No levelling off of  $D$  was observed as  $C_{aq}$  approached zero; however, as  $C_{aq}$  increased, a levelling off of  $D$  was observed. Therefore according to this model, the data obtained suggests that the absorption coefficient,  $K_d$ , is much smaller than previously thought.

To test these findings, future studies should focus on soluble non-ionic dyes or other organic compounds. This should eliminate any effect on the ionic strength of the solution but



**Figure 25.** Graphical representation of the dependence of the distribution ratio on equilibrium dye concentration according to the dual-mode sorption model.

should not affect the amount of adsorption occurring.

### **Effect of Salt Addition**

It has been common for researchers to use the addition of various salts to the sample matrix to gain information on the mechanism of extraction. The effect of salt concentration on the extraction has been used to demonstrate "salting-out". This phenomenon is used to improve liquid-liquid extractions, by adding a salt to the aqueous layer which forces more non-ionic solute into the organic layer. The ability to produce a salting-out effect is generally thought to be evidence of a solvent extraction mechanism. The relative effect of various salts in increasing an extraction is also used as evidence of which mechanism is operating. For solvent extraction, the extraction should increase as the charge density of the cation increases. For example, with salts of the alkali metals, lithium, sodium, and potassium, the extraction should be greatest in the presence of the  $\text{Li}^+$  and least for  $\text{K}^+$ . However for the cation chelation mechanism<sup>21</sup>, the sequence of effect is expected to follow that of the crown ether, 18-crown-6, which is the reverse of the above. Both salt concentration and order of effect were addressed in this study.

*Effect of Various Salts:* The effect of the addition of various salts on the extraction of 4-PABSA was studied using salts of the alkali metal series from lithium to cesium, as well as with the chloride salts of  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ . The salt concentration was arbitrarily chosen to be 0.6 M (60 mL of 1 M salt stock solution was diluted to 100 mL) and a solution pH of  $\sim 2.5$  was chosen to be close to the extraction maximum. Table 7 shows a summary of the results.

The extraction efficiency of the alkali metal salts using polyether foam was found to increase to potassium ( $\text{Li}^+ \approx \text{Na}^+ < \text{K}^+$ ), and then decrease to cesium ( $\text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ ). This order would seem to suggest that the extraction is proceeding via the cation chelation mechanism, while the order of the remaining salts ( $\text{NH}_4^+ > \text{Ca}^{2+} > \text{Al}^{3+}$ ) supports the solvent extraction model<sup>23</sup>. However there are several reasons to doubt the cation chelation model; namely, the order of the alkali salts is the same using either polyester- or polyether-type polyurethanes, and, most importantly, all of the salts added decreased the extraction instead of increasing it.

As previously stated, it is either difficult or impossible for

**Table 7.** The effect of the addition of various salts on the extraction of 4-PABSA.

Salt Added	Distribution Ratio (L/kg)	
	Polyester	Polyether
None	950 ± 150	1100 ± 200
LiCl	110 ± 15	170 ± 25
NaCl	110 ± 5	155 ± 14
KCl	170 ± 20	260 ± 30
RbCl	140 ± 5	218 ± 16
CsNO <sub>3</sub>	65 ± 11	80 ± 10
NH <sub>4</sub> Cl	124 ± 6	192 ± 11
CaCl <sub>2</sub>	75 ± 5	93 ± 17
AlCl <sub>3</sub>	93 ± 9	93 ± 7

Conditions: 0.1 g foam, 15 ml dye solution ( $10^{-5}$  M dye, 0.6 M salt, pH~2.5), 24 h shaking time.

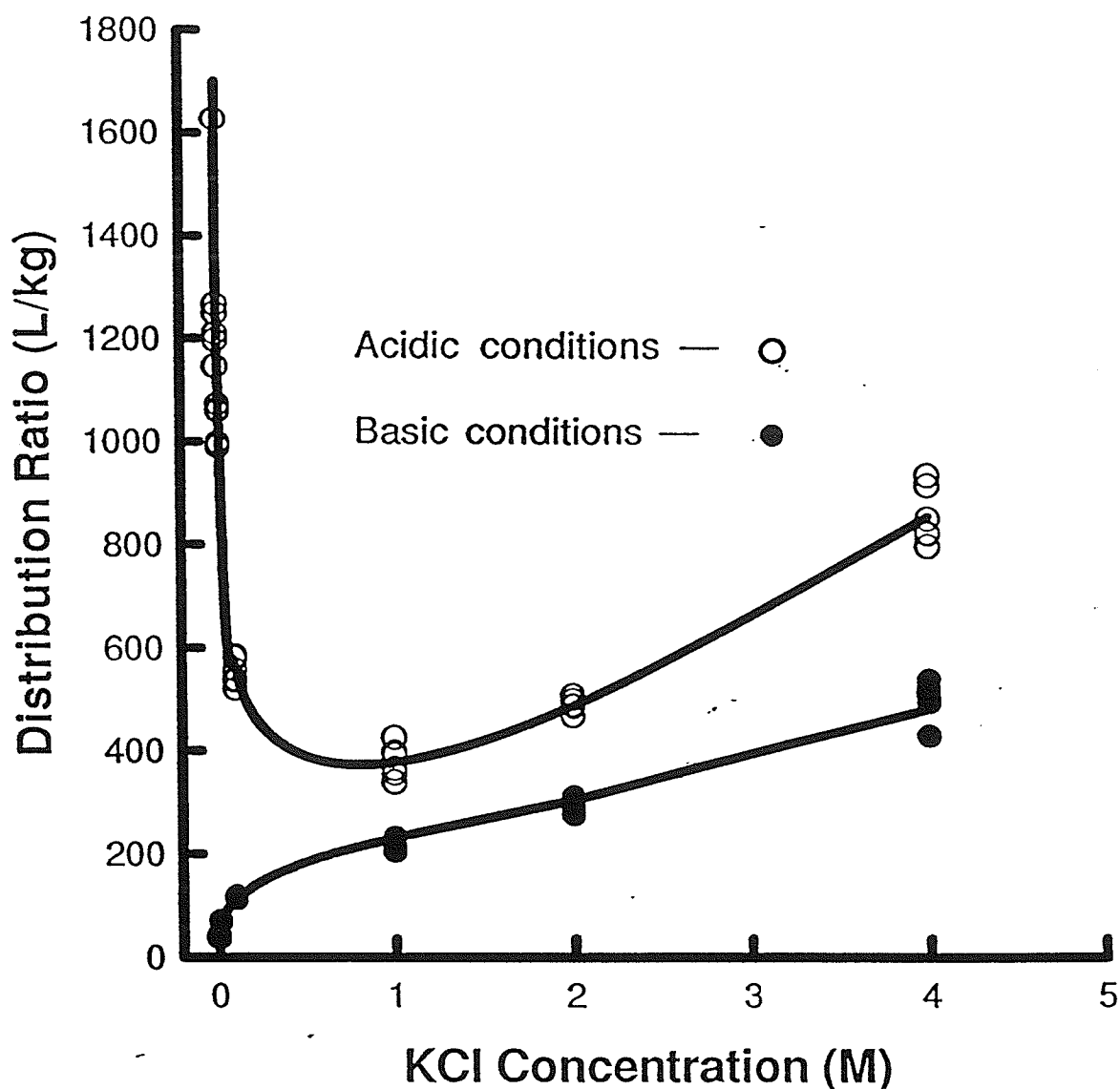


polyester-type polyurethane to assume the helical structure necessary for the cation chelation mechanism. Therefore, since the same salt order effects occur when using either foam, the argument for cation chelation is weakened. In addition, in this case the effect of the cesium cation cannot be directly compared to the others. Only  $\text{CsNO}_3$  was evaluated and the others were as chloride salts. Later, a comparison of the effect of  $\text{NaCl}$  and  $\text{NaNO}_3$  showed that there was much less extraction when using the nitrate salt. Finally, and possibly most significantly, the addition of any of the salts decreased the extraction. The significance of the order of extraction efficiencies of the salts was totally based on the expectation that any increase in concentration of any of the salts should increase the extraction. Clearly an effect other than those previously reported is occurring. One possible explanation is that the dye chelates or forms ion pairs with the cations of the added salts. This might explain the observed order of extraction, and the complex that would be formed might be sufficiently solvated in the aqueous solution to reduce the extractions. Another possible explanation involves the ionic strength of the solution as discussed later.

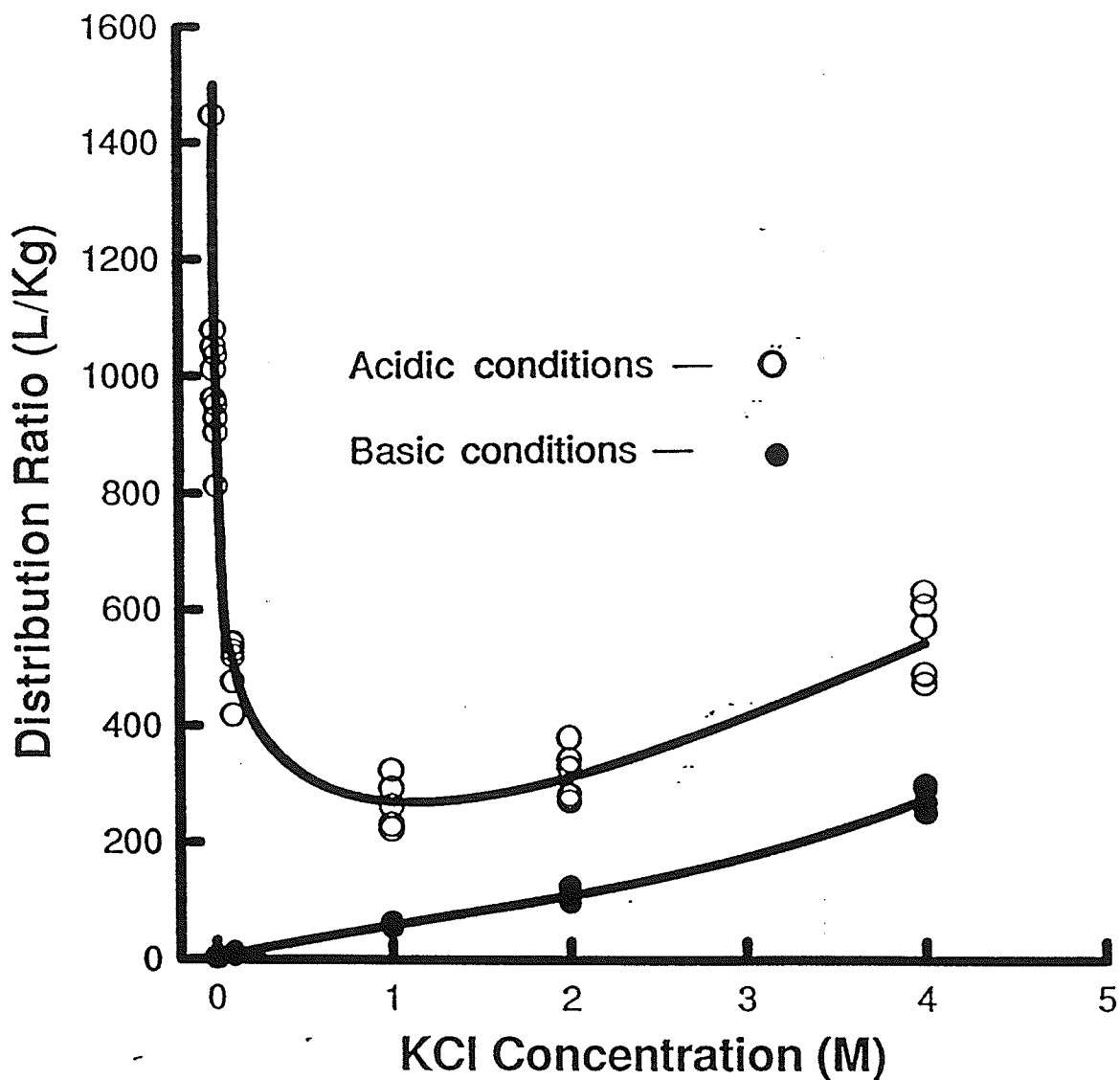
These results are not unique to 4-PABSA or the experimental

conditions. The experiments using 4-PABSA were repeated using 4'-(4-hydroxyphenylazo)benzenesulfonic acid, and 4'-(4-aminophenylazo)benzenesulfonic acid. The results showed that the relative effects of the salts, while somewhat different in magnitude, followed the same order observed with 4-PABSA. In addition to these experiments, the effect of pH on the ability of the salts to affect the extraction was examined using three alkali metal salts, LiCl, KCl, and CsCl. Using the same conditions described above, the effects of the three salts on the extraction of 4-PABSA were determined with solutions having four different pH values of approximately 1, 3, 7, and 9. As before with the different dyes, the results, while differing in magnitude, did not show a change in the order in which the salts affected the extraction, i.e.  $\text{Li}^+ < \text{K}^+ > \text{Cs}^+$ .

*Salt Concentration:* The effect of salt concentration on the extraction of 4-PABSA was examined using various concentrations of KCl. These experiments were conducted under acidic conditions, close to the pH of maximum extraction, and under basic conditions, where no extraction occurs without salt addition. The results of the experiments with polyether- and polyester-type foams are shown in figures 26 and 27 respectively.



**Figure 26.** The effect of potassium chloride concentration on the extraction of 4-PABSA with polyether foam. Conditions: 0.1 g foam, 15 mL dye solution ( $\sim 10^{-5}$  M, 0.001 - 4 M KCL), 24 h shaking time.



**Figure 27.** The effect of potassium chloride concentration on the extraction of 4-PABSA with polyester foam. Conditions: 0.1 g foam, 15 mL dye solution ( $\sim 10^{-5}$  M, 0.001 - 4 M KCL), 24 h shaking time.

It was known from experiments earlier in this study, that the amount of extraction from a 0.6 M salt solution was less than from solutions without salt. Figures 26 and 27 show that under acidic conditions, salt concentrations much less than 0.6 M have a large effect on the extraction efficiency. The behaviour observed is similar to that with increasing dye concentration, and can be explained in the same way. As the salt concentration increases, the ionic strength of the solution will increase. At moderate ionic strengths ( $<0.1$ ) the activity coefficient of the dye in the aqueous phase will decrease<sup>30</sup>. Again, because the distribution coefficient is a thermodynamic constant, any change in an activity coefficient necessitates a change in the distribution ratio, in this case a decrease. At higher ionic strengths ( $>0.1$ ) the activity coefficient could start to increase<sup>30</sup> which would result in the increase in extraction as observed.

The behaviour observed in basic solutions is quite different from that found with acidic solutions. In this pH range there is originally no extraction without salt present; upon the addition of salt there is an increase in extraction. These results are similar to the salting-out effect referred to earlier, where upon addition of a salt the extraction of a non-ionic solute would increase.

However at the basic pH of the experiment, only charged species should exist. In this case it is possible the potassium ion could associate with either the negatively charged sulfo-group or with the pair of electrons on one or both of the nitrogens of the azo-group. These possible associations would yield neutral species which could be extractable, as was observed.

### **Foam Degradation**

Foam from three of the polyether groups (2,3,4) were used to evaluate the effect of the colour of the foam (assumed to be a sign of degradation) on its extraction properties. In general terms group 3 foam was the lightest, group 4 was the darkest, and group 2 was between the two. The evaluation involved the general extraction procedure using Ethyl Orange solutions. Both "neutral" and acidic conditions were used in the evaluation. The results, shown in Table 8, clearly show the significance of the colour of the foam on its extraction behaviour. It appears that the darker the foam the less able it is to extract Ethyl Orange from the aqueous solution. In an attempt to reproduce the "browning" of the foam, small amounts of the three grades of foam were heated in Pyrex beakers at 100°C for 20 h. This foam was then

**Table 8.** Effect of foam degradation on the extraction of Ethyl Orange.

Foam Group	Maximum Distribution Ratio, (L/kg)			
	Before Heating		After Heating	
	Acidic	Neutral	Acidic	Neutral
Group 3	5000 ± 1000	1600 ± 600	∞	∞
Group 2	1800 ± 200	390 ± 20	∞	∞
Group 4	690 ± 70	120 ± 10	10500 ± 700	3000 ± 500

Conditions: 0.1 g foam, 15 ml dye solution ( $10^{-5}$  M dye), 24 h shaking time.

reevaluated as above, the results of which are also shown in Table 8. It appears quite clear that however the original colour is produced, it is not from heat, at least not in those conditions tested. Despite this, the increased extraction properties of the foam after heating may prove helpful to future researchers. Other possible sources of degradation, such as ozone or exposure to ultraviolet light, were not pursued.

The discovery of the relevance of foam colour immediately raises questions on the future reproducibility of the results found using the polyether-type foam. If the colour of the foam so greatly affects the extraction properties, one blend of foam may have marked differences in its extraction ability from another blend. The reproducibility of the results was tested using two batches of foam: foam from group 1, and foam from a separately prepared blend of polyether foam (group 5). The foam in group 5 was prepared from the same supply of polyether sheets, and was cleaned using the same cleaning procedures. After cleaning when selecting foam for grinding, only pieces "lighter" in colour were chosen. After grinding, the foam was homogenized by manual mixing. Using the general extraction procedure with 4-PABSA, the extraction behaviour of the group



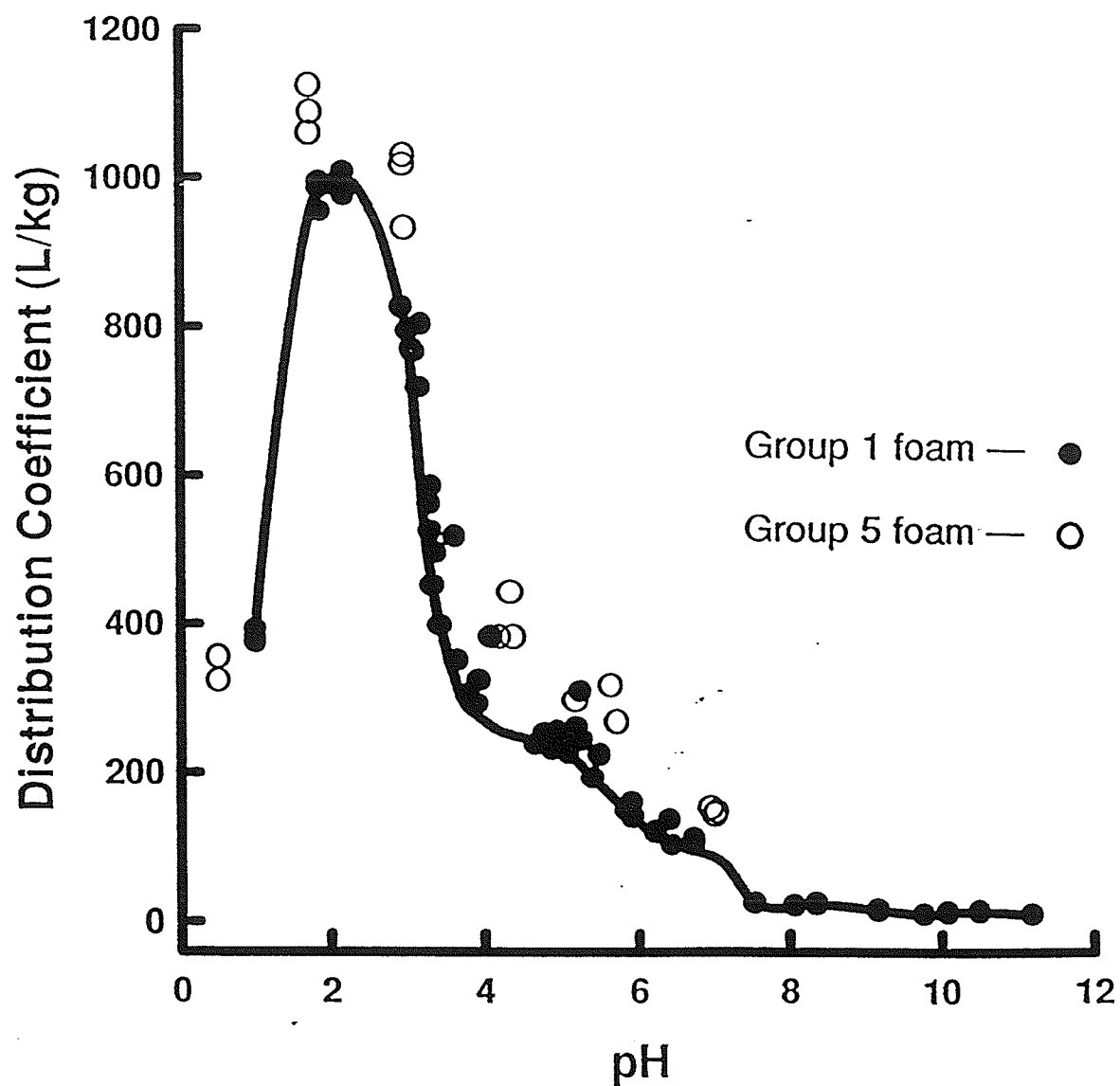


Figure 28. Comparison of the extractions of 4-PABSA, using two batches of polyether foam. Conditions: 0.1 g foam, 15 mL dye solution ( $\sim 10^{-5}$  M), 24 h shaking time.

was evaluated. The resulting extraction profile is shown in Figure 28. On the basis of these results and other experiments repeated using the same foam, it can be said that the two foam groups have effectively the same extraction behaviour. However, because of the subjective nature of the foam selection, these results show only that the foam blends can be reproduced by the same experimenter and future comparisons may not necessarily be valid.

### **Alternative Compounds**

In addition to the azo dyes used for the majority of the experiments, alternative compounds were considered for use, some of which were experimentally evaluated. Two main groups of compounds were considered, mono-azo dyes similar to those in Table 2 but not containing a sulfo-group, and simple aromatic benzoic acids. These compounds were selected for comparison to the results already obtained, specifically to those substances with similar functional groups. A list of both groups appears in Table 9. No results are shown because meaningful results were never obtained.

**Table 9.** List of alternative compounds considered for study.

Benzoic Acids	Azo Dyes
Benzoic acid	Azobenzene
o-aminobenzoic acid	4-phenylaniline
m-aminobenzoic acid	4-nitroazobenzene
p-aminobenzoic acid	4-phenylazphenol
p-toluic acid	Sudan Orange
4-tertbutylbenzoic acid	Methyl Yellow
4-fluorobenzoic acid	4-phenylazodiphenylaniline
4-chlorobenzoic acid	
4-bromobenzoic acid	
p-anisic acid	
4-hydroxybenzoic acid	
4-nitrobenzoic acid	
4-carboxybenzoic acid	

The problems encountered with these compounds can be classified into three categories, solubility, extractability and reproducibility. The mono-azo dyes without sulfo-groups are not water soluble and therefore 10 % ethanol solutions were used for extractions. The results of these experiments were often the complete extraction of the organic compound, which did not allow for comparisons of functional group effect. The large extent of extraction was thought to be due to the hydrophobicity of the substances. While this may show the great importance of hydrophobicity to the extraction mechanism, its relevance to real world samples is questionable since any compound that hydrophobic would have likely diffused into or onto some other substance before the water was sampled. However this information may be of use for future chromatographic uses. The benzoic acids, while water soluble, rarely gave reproducible results. Extraction results were always low with the maximum distribution ratios below 300 L/kg.

One interesting result that was obtained while exploring alternative compounds, involved the extraction of Aniline Yellow. Dye from two different sources was used in the extractions, one from the Chem Service biological stain kit (BS-100), the other

from the Aldrich chemical company. The two dyes, although both were called Aniline Yellow, behaved quite differently. The first difference noted for the dyes was their water solubility. The dye from Aldrich required heating and stirring to dissolve even the smallest amounts, while the dye from the stain kit was readily soluble. As well, there was a large difference in the extraction results for the dyes. The aniline yellow from Aldrich behaved the same as the other alternative azo dyes examined, that is, complete extraction regardless of the solution pH. The extraction profile of the dye from the stain kit was similar to those found earlier in the thesis, following a  $pK_a$  type curve with little or no extraction in basic solutions and increasing in the acidic conditions.

The two dyes were examined using thin layer chromatography in a mixed solvent of n-butanol:ethanol:water (50:10:15). As expected, the dye from Aldrich had a much larger  $R_f$  value than that of the stain kit dye, although both remained as single spots on the TLC plate. It seems obvious that the Aniline Yellow from Chem Service was in a different form or has somehow been changed, most likely to increase its water solubility. The possibility that one is merely a salt of the other has been

considered but does not seem likely. The dyes in salt form which were used for the bulk of the thesis work showed no such extraction behaviour when compared to the non-salt dyes. In the past<sup>23</sup> TLC has been used to make implications regarding the suitability of the dye for use in these types of studies. Researchers based suitability on a dye showing only one component on the TLC plate; in this case that alone would not be effective. These results raise questions on the reliability of the other dyes used from the BS-100 kit. However, for the experiments in this study no direct conclusions were made from the results obtained and therefore this is of no immediate concern.

## Conclusions

The study of the extraction of twelve closely related mono-azo dyes shows that these compounds are extracted as neutral zwitterions and their extraction may involve a number of mechanisms. When anionic species are present below a pH of 8, there is some evidence to support some form of an ion-exchange mechanism. Even when this mechanism is thought to be operating, its contribution to the overall extraction seems to be small. The extreme sensitivity of the extraction to dye concentrations which was found can be explained using either a solvent extraction model or a dual-mode sorption model.

The solvent extraction model requires that very small increases in the dye concentration will have large effects on the ionic strength of the solution. While doubtful, this idea is supported by the salt concentration experiments done under acidic conditions. Those results however, may be explained by the chelation of, or ion pairing with, the cation by the dye, producing an unextractable dye species. This explanation would not apply to non-ionic species which might explain why the effect was not reported by previous researchers.

The dual-mode sorption model adequately describes the behaviour observed; however, this model implies a much greater role of adsorption than previously considered. In addition, such a model would not be unique to the substances studied and raises questions as to why this effect was not reported earlier.

Unfortunately information regarding the order in which the salts affect the extractions is inconclusive. The conclusions of previous researchers, regarding the order of the effect, have been based on the salts increasing the extraction. In the experiments done for this study, any addition of a salt decreased the extraction. This behaviour is contradictory to both the cation chelation mechanism and the solvent extraction mechanism. Again, these results might be explained by chelation or ion-pairing. Chelation of the cation by the dye could also account for the order of the effect of salts which seems to be related to the size of the cation.

The inability to obtain the distribution coefficient for the extractions of the dyes, has limited our ability to make the comparisons between dyes that are necessary to study the effect



of various functional groups. Despite this limitation the results show that there can be large differences in the extractions due to the presence and position of functional groups on the ring structure of the dyes. The cause of these differences and other extraction behaviour is not fully understood and needs further study.

Previous researchers have relied heavily on the solvent extraction model to explain the extraction of organic compounds. However, given the large surface area of a foamed polymer it seems logical that adsorption would play a role in extractions of all kinds. This being the case, it is likely that the dual-mode sorption model would better describe the process. The distribution ratio, while useful for describing the results of extractions, is not adequate for comparisons between extractions. Once the dual-mode sorption mechanism is confirmed in future experiments, further studies should be able to assign amounts of extraction to absorption or adsorption, and measure the extraction constants. Using those values researchers can then begin to make the comparisons necessary to study the mechanisms of extraction and the roles of the functional groups of the analytes.

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