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DISTRIBUTION OF NAPHTHALENE BETWEEN
COMMERCIAL RESINS AND WATER-METHANOL SOLUTIONS

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Distribution of naphthalene between
commercial resins and water-methanol solutions

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Several XAD resins, two of their chemically modified derivatives, and two carbon adsorbents were evaluated by measurement of distribution coefficients using the batch method. Numerical comparison of distribution data and graphical interpretation of these resins were also presented. The distribution differences were explained in terms of resin structure and solvent compositions. Naphthalene was the solute for the study, and methanol the solvent. It was found that Spherocharb, a newly developed carbon adsorbent, had very large distribution coefficient. However, in the application for separation, desorption can conceivably be a problem. Distribution data collected can be a valuable aid in the choice of adsorbent, solvent composition and other operating conditions in separation work.

INTRODUCTION

The development of macroporous resins has found wide application in industrial, scientific, and laboratory areas. Bastos reported the use of Amberlite XAD-2, a high surface area macroporous resin, in toxicological analysis (1,2,3). Burnham et al. (4) and Junk et al. (5) described the application of these resins for separation of organic contaminants in water. Macroporous resins also found application in industry, such as the separation of detergent components, emulsifiers, wetting agents, and so on (6,7).

In separation work, the choice of resin is always an important consideration. The most commonly used commercial resins, supplied by companies such as Rohm and Haas of Philadelphia, vary significantly in their chemical and physical nature. These properties, including chemical structure, surface area, pore size, porosity, and polarity, are some of the determining factors in the efficiency and ultimate success of such work. Several resins and other sorbents have been used to concentrate trace organic impurities prior to their analysis by gas or liquid chromatography. It has been customary to evaluate and compare the resins by giving the overall percentage recoveries of known organic substances added to water. While this is useful information, it provides no direct comparison of the partitioning equilibrium of various solutes between water

and the sorbing resins. In this study, distribution coefficients of naphthalene, a typical aromatic compound, were measured using the common XAD resins, their derivatives, and some carbon adsorbents. It is well-known that knowledge of distribution coefficients greatly aids the choice of operating conditions, avoiding time-consuming trial-and-error process (8). Although distribution coefficients in the present study were measured by the batch method, they can nevertheless be used to estimate solute behavior in ion-exchange or separation chromatography (9). A main part of this study was devoted to the investigation of the effect of solvent composition on distribution coefficient. In semi-aqueous systems, solute behavior is expected to change when the solvent composition varies. The experiments were designed to observe the trend of solute behavior when the solvent composition was varied. Results of several commonly used resins were compared and evaluated.

EXPERIMENTAL

Instrumentation

One hundred milliliter volumetric flasks were used for equilibration. Resins used were cleaned in a Soxhlet extractor with methanol for 12 hours or more, air dried and stored in stoppered bottles.

Equilibrium was arrived at by shaking solution flasks with a Burrell mechanical shaker (Model CC).

Ultraviolet spectra of naphthalene solutions were obtained from a Cary 14 Recording Spectrophotometer.

Determination of naphthalene concentration was done with a Cary 16 spectrophotometer.

Materials

Resins

The mesh size of resins were as received. Nominal mesh sizes were 20-50, except for sulfonated XAD-2, which was 60-120 mesh, and acylated XAD-4 which was approximately 200 mesh. Fine resin particles were eliminated by shaking repeatedly in 10% methanol solution. For sulfonated XAD-2 and acylated XAD-4, which contained some very fine particles, additional processing was necessary. A 2.5 cm. x 30 cm. glass tube was connected to a distilled water tap from the lower opening. Resins were placed in the tube, and the flow

rate of water, was adjusted so that fine particles gradually floated out of the tube.

The weights of resins in the study were dry resin weights. Hydrophobic resins were wetted with a few milliliters of methanol before placing in solution.

Solutions

Care was taken to ensure that the final methanol content of the solutions was as desired, which was 10% to 50% methanol. For the batch of Sphero carb, 60% to 100% methanol solutions were used because of the much greater adsorption character of the resin. The concentration of naphthalene solutions used was from 2 ppm to 12 ppm. The chemicals used were reagent grade. Naphthalene was collected from sublimation of stock naphthalene crystals.

Equilibration

Impurity determination

The absorbances of distilled water from laboratory distilled water tap and permanganate-treated tap were compared at 220 nm. No difference in absorbance was evident. The distilled water tap in our laboratory was then considered satisfactory for use in the present work.

Absorbance variation

During the experiments, it was noted that solutions of identical naphthalene concentration, but different in

water-methanol ratio, show varying absorbances. To determine if the variation was consistent, absorbance values of XAD resins were tabulated and a plot of the average absorbance versus % methanol was made.

Equilibration

The literature value of $\lambda_{\max}$ for naphthalene is 221 nm. Spectra of naphthalene solutions run on the Cary 14 showed $\lambda_{\max}$ at 220 nm. All measurements of U.V. absorbances were then made at 220 nm.

A calibration curve of absorbances versus concentration was made for naphthalene concentrations from 0.05 ppm to 0.35 ppm.

Approximately 0.1 g. portions of XAD-2 resin were weighed accurately and placed in 100 ml. volumetric flasks. Exactly 5 ml. methanol were pipetted into the flasks, which were allowed to stand for 15 minutes. A 10 ppm naphthalene solution was made up in such a way that when 40 ml. were pipetted into the flasks with the wet resins, the final water to methanol ratio was 9:1.

The naphthalene solution was introduced into three flasks, two with the resin, and one without. The latter served as the starting solution. Its absorbance, measured after shaking, was taken as that of the starting solution. A blank was prepared by introducing 40 ml. of methanol-water solution containing no naphthalene into a flask with wetted

resin. The final composition of the blank was also 10% methanol. The flasks were stoppered and mounted onto a Burrell mechanical shaker, and shaken for 24 hours.

After equilibration, the flasks were taken off the shaker and allowed to stand for 15 minutes. Solutions in the flasks were then transferred into quartz cells for measurement at 220 nm. with micro-pipettes.

Equilibration of solution was done at least in duplicates. All measurements were made with blanks as references.

Similar procedures were used for solutions that were 20%, 30%, 40%, and 50% in final methanol content. An example of the preparation of the solutions is shown in Table 1.

Distribution coefficients were calculated for each methanol composition from absorbance values. Plots of $\log D$ versus % methanol were made.

The experiment was repeated using XAD-4, 1, 7, 8, sulfonated XAD-2, acylated XAD-4, Amberlite XE-340, and Spherocarb. In the experiment of Spherocarb, naphthalene solutions were 60% to 100% methanol.

Table 1. Preparation of equilibrating solutions

ml. MeOH for wetting solution	Preparation of naphthalene solution in 250 ml. volu- metric flasks		Total volume of MeOH in final solution (ml)	Total volume of final solution (ml)	% MeOH in final solution
	ml. MeOH used	ml. MeOH in 40 ml. solution			
2	13.75	2.2	4.2	42	10
5	25.0	4.0	9.0	45	20
5	53.125	8.5	13.5	45	30
5	81.25	13.0	18.0	45	40
5	109.38	17.5	22.5	45	50

RESULT AND DISCUSSION

Absorbance Maximum

Ultraviolet spectra of several naphthalene solutions with different concentration and methanol content showed that maximum absorbance occurred at $\lambda = 220$ nm. (Figure 1).

Calibration Curve

Absorbances of naphthalene solutions from 0.05 to 0.35 ppm were plotted against concentration. A linear plot was obtained (Figure 2). In the following calculations, the assumption was made that the concentration of naphthalene would be proportional to absorbance in the low concentration range.

Absorbance Variation

For comparison, absorbance values of all the naphthalene solutions of XAD resins were adjusted to 1.067 ppm, and were plotted against % methanol. A linear relationship was observed (Table 2 and Figure 3). From these data, it was obvious that solutions of similar concentration did not have the same absorbances. The increase in absorbance when methanol content of the solution increases suggests that methanol is the contributing factor. It is conceivable that impurities in the methanol, such as acetone, which at

Figure 1. Absorbance maximum of 0.35 ppm naphthalene solution

Figure 2. Calibration curve of naphthalene solution at $\lambda = 220$ nm

Table 2. Summary of absorbances of 1.067 ppm naphthalene solutions

Resin	Methanol Content of Solution				
	10%	20%	30%	40%	50%
XAD-2	.729	.754	.763	.773	.802
XAD-4	---	.720	.738	.772	---
XAD-1	.730	.760	.782	.803	---
XAD-7	.737	.733	.741	.746	.754
XAD-8	.709	.734	.750	.788	.804
Avg.	.726	.740	.755	.774	.787

Figure 3. Absorbance of 1.067 ppm naphthalene versus % MeOH at 220 nm

low levels were not significant, contributed to the absorbance increase at higher methanol content. However, all measurements were done with reference that should have cancelled out the effect. It is interesting that such a phenomenon exists.

Calculation

Distribution coefficients were calculated according to the formula

$$D = \frac{\text{mg. naphthalene on resin/g. resin}}{\text{mg. naphthalene in soln./ml. soln.}}$$

The weights of resin were dry resin weights. Absorbance values of solutions after equilibrium had been reached were taken as the amount of naphthalene left in the solution. The difference between this and the absorbance of starting solution gave the amount of naphthalene adsorbed onto the resin. The assumption was made here that absorbance would be proportional to concentration. Distribution coefficients for the resins studied are shown in Table 3.

When log D was plotted versus the percentage of methanol, linear relationship was found in all cases (Figures 4,5,6).

Table 3. Summary of distribution coefficients

Resin	Naph. Conc. (ppm)	D				
		10%	20%	30%	40%	50%
XAD-2	10	216,000	96,100	34,300	8,310	2,440
XAD-4	10	234,000	120,000	34,700	9,640	2,500
XAD-1	12	59,000	33,000	14,700	4,900	1,730
XAD-7	12	11,100	5,280	2,430	952	359
XAD-7	2	14,200	6,920	2,770	964	335
XAD-8	12	6,960	3,230	1,240	518	183
Acylated XAD-4	4	184,000	106,000	35,100	9,020	2,530
Sulfonated XAD-2	4	15,800	6,730	2,800	939	335
XE-340	4	90,100	79,400	28,100	12,300	5,600
<hr/>						
Resin	Naph. Conc. (ppm)	D				
		60%	70%	80%	90%	100%
Sphero carb 15		790,000	122,000	41,400	17,100	6,040

Figure 4. Effect of methanol content on distribution coefficient of naphthalene

Figure 5. Effect of methanol content on distribution coefficient of naphthalene

Figure 6. Effect of methanol content on the distribution coefficient of naphthalene

Effect of Starting Concentration

To determine whether distribution values remained the same when different solute concentrations of the starting solution were used, batch equilibration using XAD-7 were run at 2 ppm and 12 ppm (Table 3). The results indicated no significant difference in using naphthalene solutions that differed six-fold in concentration. Since all solutions in this study were within the range tested, it was concluded that starting solution concentration did not have any effect on the measurement of distribution coefficient using the present method.

Effect of Resin Structure

Adsorption of solute by macroporous resin is primarily by Van der Waal's forces (7,10), which bind the solute to a solid surface. Depending on the types of sorbate, other factors such as hydrophobic bonding, dipole-dipole interaction and hydrogen bonding may also be important. A general view is that hydrophobic molecules, or portions of molecules are attracted to hydrophobic surfaces on the resin, and hydrophilic materials to hydrophilic surfaces. Therefore, the polarity of a resin is a main factor in solute adsorption. Partitioning between resin and solvent phase is in fact influenced by the relative polarities of resin, solute, and solvent (11,12,13). One way of describing

the polarity of a resin is by means of the dipole moment associated with the surface. The dipole moments of some of the Amberlite adsorbents are shown in Table 4 (7). Comparison of the distribution values of these four resins shows the effect of polarity. XAD-2 and XAD-4, with dipole moments of only 0.3, are very nonpolar. The nonpolar solute naphthalene is strongly adsorbed onto these resins by Van der Waal's forces. XAD-7 and XAD-8, being more polar, adsorb naphthalene to a lesser extent.

Other physical characteristics of a resin that are important in solute partition are surface area, pore size, and porosity. Properties of Amberlite resins and carbon adsorbents are shown in Table 5 (7,14,15).

The adsorption in this study involves primarily Van der Waal's forces which bind sorbate onto the surface of the resin. Therefore, the higher the surface area, the greater the extent of adsorption. XAD-4 has the same polarity as XAD-2, and both are polystyrene in nature. The slightly higher distribution coefficients of the former can be attributed to its larger surface area. However, this effect is less pronounced than the comparison of XAD-7 and XAD-8. They are both acrylic esters, with similar dipole moments. Here, the surface area of XAD-7 is more than three times that of XAD-8. Hence, the distribution values of the former are seen to be much larger than the latter.

Table 4. Inherent dipole moments of functional groups

Absorbents	Dipole Moments
XAD-2	0.3
XAD-4	0.3
XAD-7	1.8
XAD-8	1.8

Table 5. Typical properties of some adsorbents

Resin	Chemical Nature	Porosity Volume (%)	Surface Area (m^2/g)	Average Pore Diameter ($\text{\AA}$)	Nominal Mesh Size
XAD-1	Polystyrene	37	100	200	20 to 50
XAD-2	Polystyrene	42	300	90	20 to 50
XAD-4	Polystyrene	51	780	50	20 to 50
XAD-7	Acrylic Ester	55	450	90	20 to 50
XAD-8	Acrylic Ester	52	140	235	20 to 50
Spherocarb	Carbon	---	1,200	15	80 to 100
XE-340	Carbon	20	400	150	20 to 50

The general effect of pore size is simply that the absorbent must possess pores of a sufficient diameter so that the material to be adsorbed can migrate through the pores to the adsorbing surfaces within the resin. However, in this study, the size of the adsorbate, naphthalene, is sufficiently small so that pore size should not contribute significantly to its free passage.

The effect of porosity of an adsorbent on the partition of a solute can also be related to the distribution data. Porosity of the polystyrene resins decreases in the order of XAD-4>XAD-2>XAD-1 (Table 5). Distribution values of the three resins show the same trend. For the polyacrylic resins, XAD-7 has larger distribution coefficients than XAD-8, corresponding to their porosity difference.

Effect of Solvent

The unfavorable entropy of solution of nonpolar molecules in water is produced by an orientation of water molecules around the organic species. This tendency has been called "iceberg" formation (10). The result of this ordering of water molecules is a large decrease in the entropy of the system. In the adsorption of the organic matter on the resin surface, the "icebergs" are broken up with an accompanying large entropy gain. This entropy is the main driving force of adsorption from aqueous

solution in many cases. The distribution coefficients for all resins in this work showed a logarithmic decrease as the methanol content of the solvent increased. Apparently, the degree of adsorption of naphthalene from the more nonpolar solvents became smaller because less entropy gain was available. This tendency can also be seen in the polarity of the solvent. The dielectric constants of water and methanol are 80 and 33 at room temperature. For lower alcohols, distribution values decrease with decreasing dielectric constant of the solvent (16). As methanol content of the solvent increased, the dielectric constant of the solvent as a whole decreased, thus shifting the distribution in favor of the solvent phase.

Effect of Chemical Modification

Comparison of distribution data between XAD-2 and sulfonated XAD-2 showed a dramatic decrease of solute adsorption for the latter. Previous papers had shown that sulfonation of macroporous resin did not hinder or destroy the polymer matrix (17), and the pores were accessible to solutes in the solution (18). Therefore, the increased polarity of the sulfonated resin must have been the contributing factor. The acylation of XAD-4 did not change the polarity of the resin as sulfonation did, and the distribution coefficients of the acylated XAD-4 were quite comparable to those of the parent resin.

Carbon Adsorbents

Amberlite XE-340 is a carbonaceous adsorbent that is chemically intermediate between a polymeric adsorbent and granular activated carbon (10). Distribution data showed its effectiveness to be comparable to XAD-2 and XAD-4. However, the results of Sphero carb, a high surface area carbon molecular sieve, which is designed for gas analysis, was surprisingly high (Figure 6). The outstanding factor is probably its extremely large surface area ($1200 \text{ m}^2/\text{g}$), and, being a carbon adsorbent, its great affinity for non-polar organic species.

SUMMARY

Several XAD resins, two of their chemically modified derivatives, and two carbon adsorbents were evaluated by measurement of distribution coefficients using the batch method. Numerical comparison of distribution data and graphical interpretation of these resins were also presented. The distribution differences were explained in terms of resin structure and solvent compositions. Naphthalene was the solute for the study, and methanol the solvent. It was found that Spherocarb, a newly developed carbon adsorbent, had very large distribution coefficient. However, in the application for separation, desorption can conceivably be a problem. Distribution data collected can be a valuable aid in the choice of adsorbent, solvent composition and other operating conditions in separation work.

LITERATURE CITED

1. G. Ibrahim, S. Andryauskas, and M. L. Bastos, J. Chromatogr., 108, 107 (1975).
2. M. L. Bastos, D. Jukofsky, E. Saffer, M. Chedekel, and S. J. Mulé, J. Chromatogr., 71, 549 (1972).
3. S. J. Mulé, M. L. Bastos, D. Jukofsky, and E. Saffer, J. Chromatogr., 63, 289 (1971).
4. A. K. Burnham, G. V. Calder, J. S. Fritz, G. A. Junk, H. J. Svec, and R. Willis, Anal. Chem., 44, 139 (1972).
5. G. A. Junk, J. J. Richard, M. D. Grieser, D. Witiak, J. L. Witiak, M. D. Arguello, R. Vick, H. J. Svec, J. S. Fritz, and G. V. Calder, J. Chromatogr., 99, 745 (1974).
6. Rohm and Haas Company, Independence Hall West, Philadelphia, PA., Technical Bulletin IE-75, April 1972.
7. Rohm and Haas Company, Independence Hall West, Philadelphia, PA., Technical Bulletin IE-172, Feb. 1975.
8. F. W. Cornish, Analyst, 83, 634 (1958).
9. J. S. Fritz and D. J. Pietrzyk, Talanta, 8, 143 (1961).
10. R. L. Gustafson, R. L. Albright, J. Heisler, J. A. Lirio, and O. T. Reid, Jr., I & EC Prod. Res. & Dev., 7, 107 (1968).
11. W. Brown, Chimica Scripta, 2, 25 (1972).
12. W. Brown, J. Chromatogr., 59, 335 (1971).
13. E. Takahagi and S. Seno, J. Chromatogr., 108, 354 (1975).
14. Rohm and Haas Company, Independence Hall West, Philadelphia, PA., Preliminary Technical Notes, Amberlite XE-340, ca. 1971.

15. Analabs Inc., North Haven, Connecticut, Analabs Brochure 1976.
16. J. S. Fritz and H. Waki, Anal. Chem., 35, 1079 (1963).
17. J. R. Millar, D. G. Smith, W. E. Marr, and T. R. E. Kressman, J. Chem. Soc. London, 218 (1963).
18. B. Chu and D. M. Tan Creti, J. Phys. Chem., 71, 1943 (1967).

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