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PARTITIONING OF AROMATIC MOLECULES IN AQUEOUS BIPHASIC SYSTEMS

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ABSTRACT

Aqueous biphasic systems (ABS) may be suitable for the separation of aromatic molecules in industrial and environmental settings; hence it is invaluable to have predictive models of partitioning behavior in these systems for design and evaluation purposes. In a continuing study of the partition of small aromatic organic molecules, the distribution of several relatively hydrophilic substituted benzene species is reported. The partitioning behavior of five charged substituted benzene species (phthalic acid, 4-hydroxybenzoic acid, benzoic acid, salicylic acid, and *p*-toluic acid) and one uncharged species (1,3-dinitrobenzene) has been studied in ABS prepared from stock solutions of 40% (w/w) PEG-2000 and increasing concentrations of four water-structuring salts [K_3PO_4, K_2CO_3, $(NH_4)_2SO_4$, and NaOH]. Comparison has been made with published data on the partitioning of these solutes in 1-octanol/water biphasic systems. In general, the partition of these species may be understood in terms of the free energy of hydration of the salt forming the ABS and the dissociation of the charged groups of the distributed solutes.

INTRODUCTION

Although separation processes are common in the chemical industry, little attention has been paid to these processes and their impact on the environment. Systems employed in liquid/liquid separations frequently involve the use of toxic and volatile

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organic compounds (1). Our goal is to apply relatively benign systems for the extraction and separation of small organic molecules in industrial and environmental remediation applications (2). Aqueous biphasic systems (ABS), whose major component in each of the two phases is water, can provide an extraction technology that eliminates the need for volatile organic compounds (3,4). Previous work has demonstrated the quantitative partitioning of a number of uncharged substituted benzene compounds (5), which indicates that ABS extraction processes should have high utility for the recovery, purification, and extraction of these small organic molecules. We have also demonstrated a correlation between the partitioning behavior of the uncharged molecules in PEG/salt ABS and that in 1-octanol/water biphasic systems (5). The correlation observed may be developed as a plausible way to predict the partitioning behavior of uncharged small organic molecules in ABS (5).

We have currently extended our study to include the partitioning of small "charged" aromatic compounds as a function of the salt cation and anion type, the solute charge, and the total salt concentration in polymer/salt ABS formed with polyethylene glycol (PEG) of molecular mass 2000 g/mol. This partitioning behavior may be understood in terms of the Gibbs free energy of hydration of the salt stock solution used to form the biphase, as well as the dissociation of the charged molecule. The distribution data for these molecules in ABS are compared with similar published values for their distribution in 1-octanol/water systems (log P) (6).

EXPERIMENTAL

The chemicals, [K_3PO_4, K_2CO_3, $(NH_4)_2SO_4$, NaOH, and polyethylene glycol], all of reagent grade, were obtained from Aldrich (Milwaukee, WI). Carbon-14 tracer solutions of phthalic acid, 1,3-dinitrobenzene, 4-hydroxybenzoic acid, salicylic acid, *p*-toluic acid, and benzoic acid were purchased from Sigma (St. Louis, MO) and then prepared for use by dilution with benzene, water, or toluene. All water was purified using a commercial deionization system (Barnsted, Dubuque, IA). Standard liquid scintillation analyses were performed using Ultima Gold Scintillation Cocktail (Packard

Instrument Co., Downers Grove, IL) and a Packard Tri-Carb 1900TR Liquid Scintillation Analyzer.

The polymer and salt stock solutions were prepared on a weight percent or molar basis. The compositions given are those of the stock solutions prior to the formation of the equilibrium biphase. Further experimental details may be found in Reference (7). Each liquid/liquid distribution ratio (D) was determined by mixing 1 mL of a 40% (w/w) PEG-2000/water solution with 1 mL of a stock salt solution of known concentration, as indicated in the Results section. The systems thus prepared were Vortex mixed for 2 min and then centrifuged (2000 × *g*) for 2 min. Carbon-14 tracers were diluted to an activity of 0.06–0.08 μCi/μL for use as the "spike" in the partitioning experiments. Tracer quantities (0.12–0.24 μCi) of the appropriate radionuclide were added to the system, which was centrifuged (2 min, 2000 × *g*) and then Vortex mixed (2 min). (The contact time had previously been established as sufficient for equilibrium to be attained in these systems.) The phases were disengaged by centrifugation (2 min, 2000 × *g*) and carefully separated using disposable Pasteur pipettes. Equal aliquots of each phase were taken for standard liquid scintillation analysis. All measurements were made in duplicate.

The reported distribution ratios represent the total concentration of tracer in the upper PEG-rich phase divided by the concentration of the total tracer concentration in the lower salt-rich phase. Since equal aliquots of each phase were analyzed and the activity of the carbon-14 tracer is directly proportional to its concentration, D can be defined as in Eq. 1.

$$D = \frac{\text{activity in counts per minute for PEG - rich phase}}{\text{activity in counts per minute for salt - rich phase}} \qquad (1)$$

RESULTS AND DISCUSSION

Previous investigations we have undertaken on organic molecule partition in ABS indicated a preference for sulfonated aromatic compounds to partition to the PEG-rich phase in PEG/salt ABS (8,9). The current need for the removal of aromatic compounds (e.g., benzene, PCBs, PABs, etc.) from the environment and from industrial effluents, as well as the ready availability of carbon-14-labeled benzene derivatives of controlled substitution, led to the selection of simple substituted benzene molecules for the investigation of their partitioning behavior in ABS. We have previously reported on the distribution of several neutral substituted benzene compounds (5). The current study extends this work to include five charged substituted benzene compounds and one uncharged hydrogen bond acceptor: phthalic acid, 4-hydroxybenzoic acid, 1,3-dinitrobenzene, benzoic acid, salicylic acid, and *p*-toluic acid. The partitioning behavior of these six solutes was studied in ABS prepared from stock solutions of 40% (w/w) PEG-2000 and increasing concentrations of four water-structuring salts: potassium phosphate, potassium carbonate, ammonium sulfate, and sodium hydroxide.

The partitioning of each solute was examined in the four different PEG/salt ABS. Figures 1–6 show the variation in the distribution ratio of the solutes with increasing concentration of added salt stock solution in the four different PEG/salt ABS. In ABS prepared with the salts K_3PO_4, K_2CO_3, and $(NH_4)_2SO_4$, the distribution ratios increase with increasing salt stock solution concentration. However, in the PEG-2000/NaOH system, the solutes phthalic acid (Figure 5) and 4-hydroxybenzoic acid (Figure 6) show a decrease in distribution ratio with increasing concentration of added NaOH salt stock solution. Additionally, Figure 4 indicates that the distribution of salicylic acid remains approximately constant with increasing NaOH concentration, with a distribution ratio of about 1 representing an even distribution between the two phases.

The partitioning behavior of macromolecular and ionic solutes in ABS, for the most part, becomes increasingly one-sided as the difference in composition between the two phases increases (10,11). Although the rate of increase of the partition coefficient appears to ameliorate at the highest concentrations of added salt, the results are in approximate conformity with the relationship in Eq. 2,

$$\ln K = k\Delta w_2 \tag{2}$$

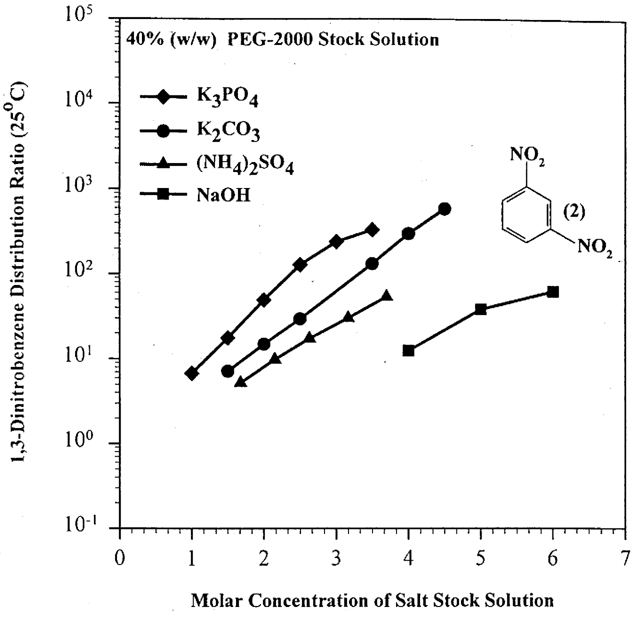

FIGURE 1. Distribution ratios for 1,3-dinitrobenzene in 40% (w/w) PEG-2000/X *M* salt ABS as a function of increasing salt stock solution concentration.

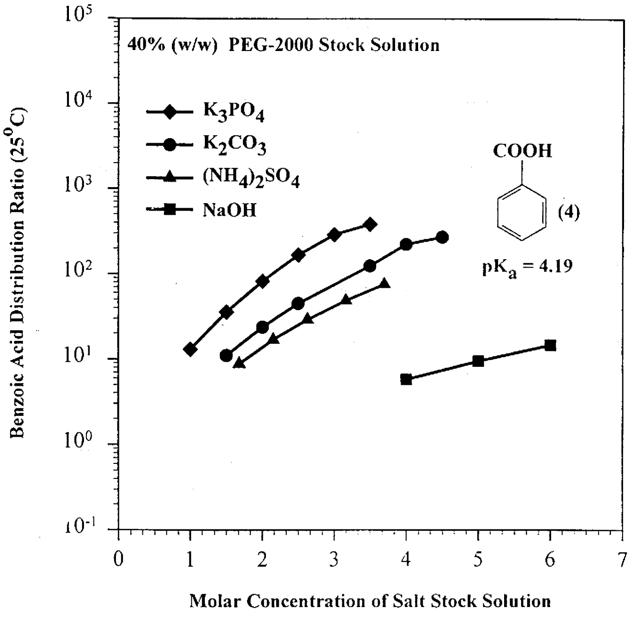

FIGURE 2. Distribution ratios for benzoic acid in 40% (w/w) PEG-2000/X *M* salt ABS as a function of increasing salt stock solution concentration.

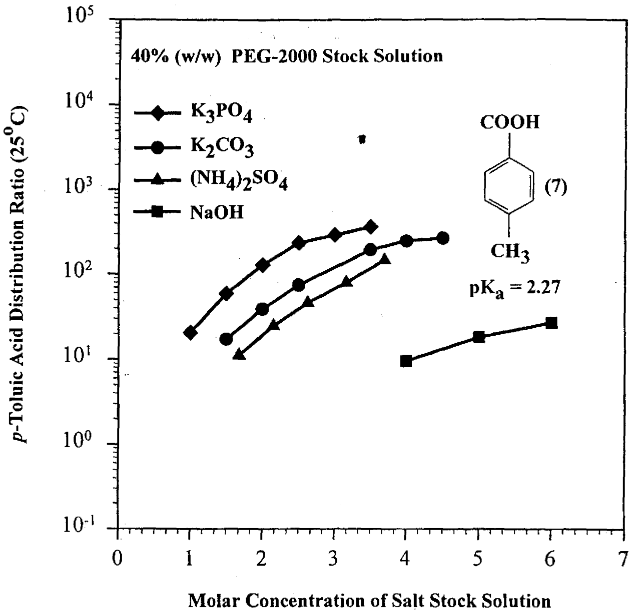

FIGURE 3. Distribution ratios for *p*-toluic acid in 40% (w/w) PEG-2000/X *M* salt ABS as a function of increasing salt stock solution concentration.

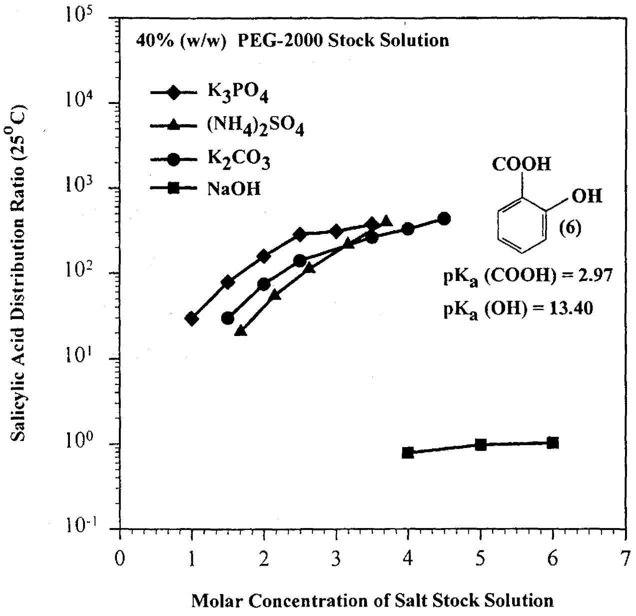

FIGURE 4. Distribution ratios for salicylic acid in 40% (w/w) PEG-2000/X *M* salt ABS as a function of increasing salt stock solution concentration.

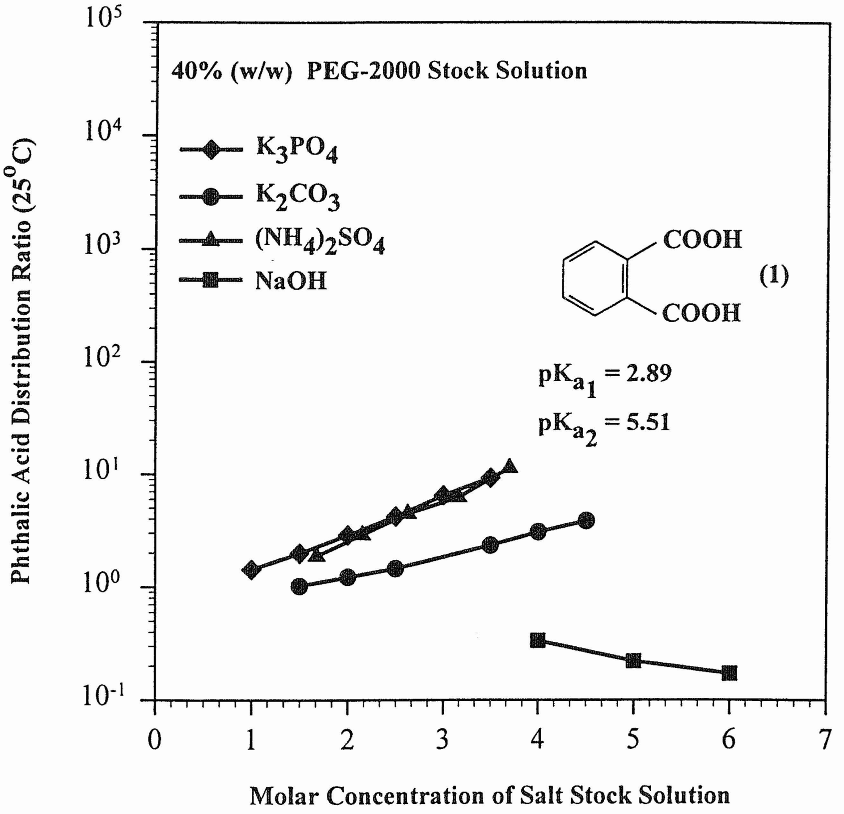

FIGURE 5. Distribution ratios for phthalic acid in 40% (w/w) PEG-2000/X *M* salt ABS as a function of increasing salt stock solution concentration.

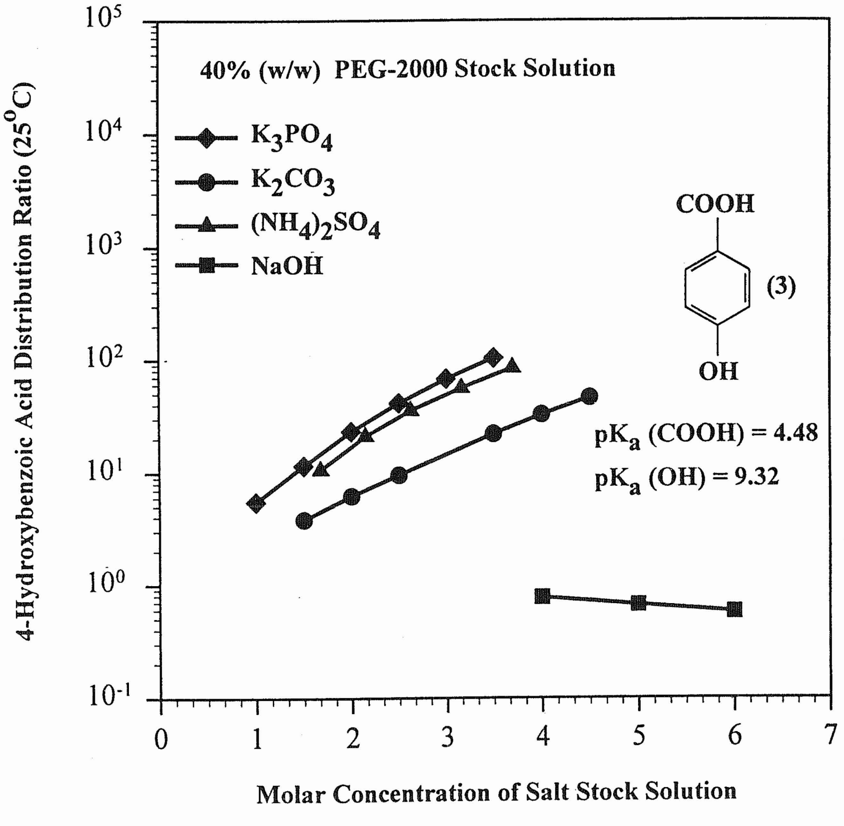

FIGURE 6. Distribution ratios for 4-hydroxybenzoic acid in 40% (w/w) PEG-2000/X *M* salt ABS as a function of increasing salt stock solution concentration.

where K is the partition coefficient, k is a constant, and Δw_2 is the difference in concentration between the phases of one of the phase forming components (12–14).

Figures 1-6 also show that (with some exceptions, as discussed) at a given concentration of salt, the partition coefficient is higher in systems comprising the following anion series of salts: $PO_4^{3-} > CO_3^{2-} > SO_4^{2-} > OH^-$. The partition coefficient at a given salt concentration, for all solutes and salt systems, follows the Hofmeister or lyotropic series of the salt. This relationship has also been shown to underlie the phase separation of PEG in the presence of salts (15). These effects have been related to the increasing magnitude of the negative free energy of hydration (ΔG_{hyd}) of these salts, particularly in studies utilizing the pertechnetate anion as the partitioned solute (4,10,16,17).

Table 1 shows that, in general, the neutral substituted benzenes have higher distributions than the charged species in both 1-octanol/water and PEG-2000 ABS, except for benzene and 1,3-dinitrobenzene whose partitioning characteristics are similar to those of salicylic acid and *p*-toluic acid. Phthalic acid, with its two carboxylic acid groups (pK_a = 2.89 and 5.51), has the lowest distribution in the three basic ABS (K_3PO_4, K_2CO_3, NaOH). 4-Hydroxybenzoic acid (carboxyl pK_a = 4.48) has the next lowest distribution in these systems, closely followed by benzoic acid (pK_a = 4.19). It is noteworthy that the pK_a of the hydroxyl group of 4-hydroxybenzoic acid is relatively low (9.32) compared with that of salicylic acid. It is possible that this group is fully dissociated at the pH levels of these systems. Also of interest is the fact that, for both these species (4-hydroxybenzoic acid and phthalic acid), the distribution ratio is less than one and decreases with salt concentration in the PEG-2000/NaOH ABS. Of the charged solutes, *p*-toluic and salicylic acid have the highest distribution ratios in the basic ABS, which in the former case is indicative of the influence of a methyl group and in the latter, may be that intramolecular hydrogen bonding between the adjacent hydroxyl and carboxyl groups results in a higher distribution ratio than is displayed by 4-hydroxybenzoic acid.

The partition behavior of these species in the acidic ammonium sulfate systems is somewhat different, however, due to the much lower pH levels of these ABS compared with the alkali metal salt systems [$(NH_4)_2SO_4$, pH ~ 5.5; K_3PO_4, K_2CO_3, NaOH, pH >

TABLE 1. 1-OCTANOL/WATER PARTITION COEFFICIENTS (P) AND PEG/SALT DISTRIBUTION RATIOS (D) FOR THE TEN SOLUTES STUDIED

Solute[a]	pK_a	P	D 1.5 *M* K_3PO_4	D 3.0 *M* K_3PO_4	D 2 *M* K_2CO_3	D 4 *M* K_2CO_3	D 1.7 *M* $(NH_4)_2SO_4$	D 3.2 *M* $(NH_4)_2SO_4$	D 5 *M* NaOH
1. Phthalic acid	pK_1, 2.89 pK_2, 5.51	5.4	2.0	6.4	1.2	3.0	1.9	6.2	0.22
2. 1,3-Dinitrobenzene		31	18	240	15	300	5.2	30	38
3. 4-Hydroxybenzoic acid	pK_1, 4.48 pK_2, 9.32	38	12	68	6.2	33	11	56	0.66
4. Benzoic acid	4.19	74	36	290	24	220	8.8	48	9.5
5. Benzene		130	43	340	37	270	11	88	96
6. Salicylic acid	pK_1, 2.97 pK_2, 13.40	180	79	310	74	330	21	220	1.0
7. *p*-Toluic acid	2.27	190	60	290	39	250	11	79	18
8. Toluene		540	91	1200	76	780	15	140	140
9. Chlorobenzene		690	130	1900	130	1300	28	300	220
10. Dichlorobenzene		2800	250	3200	190	3100	41	450	450
11. Trichlorobenzene		10000	480	9800	340	7900	45	790	750

[a] Numbers correspond to those shown in Figure 10

13). Thus, in Figures 5 and 6 the partition of phthalic acid and hydroxybenzoic acid in the $(NH_4)_2SO_4$ system is displaced above that of the partition of the same solutes in the K_2CO_3 system, a contradiction of the statements made above that the distribution of the solutes follows the lyotropic series of salts. The pK_a values for these solutes (see Table 1 and Figures 5 and 6) are much closer to the pH of the system, and thus a proportion of the distributed molecules carries less charge than in the more basic PO_4^{3-}, CO_3^{2-}, and OH^- systems. Therefore, the distribution ratio is a measure of the distribution of the charged and uncharged species, and the results show that the charged species has a lower distribution value than that of the uncharged species.

In common with other authors, the partitioning in ABS of these small aryl organics may be compared with similar data pertaining to the partition of the same or similar species in aqueous/organic systems (12,14,18–22). From the distribution of benzene and toluene in the current ABS, the free energy of transfer of a methylene group may be calculated from Eq. 3,

$$-\Delta G_{CH_2} = 2.303RT\log D \tag{3}$$

where R is the gas constant, T is the absolute temperature, and D is the distribution coefficient in a given system (23). This value may be compared with that obtained from the distribution of different solutes in a wide variety of biphasic systems, as shown in Table 2. The discrepancy between the current value for the 1-octanol/water system and that given in Table 2 (24) probably results from its calculation from a homologous series of solutes rather than from the distribution of a single species as studied here. Nevertheless, the data given in Table 2 clearly show that the relative hydrophobicities of the phases of PEG/salt ABS as measured by the free energy of transfer of a methyl group are in reasonable agreement with similar values obtained by others (14,24). Table 2 also shows that the free energy of transfer of a methyl group to the PEG-rich phase of an ABS is evidently tunable over a wide range. The apparent hydrophobicity, as measured in this way, may range from values that are approximately equivalent to those determined for benzene/water aqueous/organic systems to free energy of transfer values

TABLE 2. FREE ENERGY OF TRANSFER OF A CH_2 GROUP FROM THE AQUEOUS TO THE ORGANIC PHASE OF AN ORGANIC-WATER SOLVENT TWO-PHASE SYSTEM AND FROM A SALT-RICH TO A PEG-RICH PHASE OF A PEG/SALT ABS

Organic/water	$-\Delta CH_2$ (kcal/mol CH_2)	PEG/salt	$-\Delta CH_2$ (kcal/mol CH_2)
Hexane	1.1010 ± 0.043[a]	40% (w/w) PEG-2000/ 1.0 M K_3PO_4	0.354
Chloroform	0.846 ± 0.24[a]	40% (w/w) PEG-2000/ 3.5 M K_3PO_4	0.818
Benzene	0.842 ± 0.066[a]	40% (w/w) PEG-2000/ 1.5 M K_2CO_3	0.458
Octanol	0.727 ± 0.017[a]	40% (w/w) PEG-2000/ 4.5 M K_2CO_3	0.854
Octanol	0.816	40% (w/w) PEG-2000/ 1.7 M $(NH_4)_2SO_4$	0.192
Methyl isobutyl ketone	0.722 ± 0.015[a]	40% (w/w) PEG-2000/ 3.7 M $(NH_4)_2SO_4$	0.345
Xylene	0.644 ± 0.092[a]	40% (w/w) PEG-2000/ 4.0 M NaOH	0.144
Octane	0.768 ± 0.053[a]	40% (w/w) PEG-2000/ 6.0 M NaOH	0.396
n-Butanol	0.542 ± 0.058[a]	19.4% (w/w) PEG-1500/ 16.1 % (w/w) $MgSO_4 \cdot 7H_2O$	0.216[b]
Methyl ethyl ketone	0.433 ± 0.006[a]	7.81% (w/w) PEG-8000/ 14.1% (w/w) $K_2HPO_4 \cdot 3H_2O$	0.158[b]

[a] Reference (24).

[b] Reference (14).

that are very much less than those found between the aqueous/organic phases of methyl ethyl ketone/water biphasic systems.

Figures 7–10 show the relationship between published values of the 1-octanol/water partition coefficient (6) and the distribution values obtained in two selected systems from each of the four different PEG-2000/salt systems for the five charged solutes and one uncharged solute employed in this study and to the five uncharged solutes employed in our previous study (5). (The slopes, intercepts, and correlation coefficients of the plots shown in Figures 7–10 may be found in Table 3.) For the systems composed of K_3PO_4 and K_2CO_3, inclusion of the charged solutes has somewhat weakened the correlation as compared (through the correlation coefficient) with our previous study, which employed only neutral solutes (5). For the PEG-2000/$(NH_4)_2SO_4$ system, the degree of correlation is about the same. This is not surprising since the comparison, with regard to the charged species, in the case of the K_3PO_4 and K_2CO_3 systems is being made between largely charged moieties in the ABS and log P values determined for, or adjusted to, the neutral species in each case for the 1-octanol/water systems (6). Thus, in the case of the $(NH_4)_2SO_4$ ABS, some, at least, of the charged species are not fully dissociated (see pK_as for each species in Table 1 and Figures 1–6).

In the case of the NaOH system, the correlation with log P after including the new charged species with the neutral species from the previous study is nonexistent, although, as shown in Figure 10, the previous correlation for the neutral species clearly stands out. What is abundantly clear from Figure 10 is that the new neutral species included in this study, dinitrobenzene, **2**, partitions in perfect accord with the previous neutrals employed. Equally noticeable is the poor correlation with 1-octanol/water log P distribution coefficients of all the charged species included in the present study. Their partition coefficients are much lower in this system than would have been predicted from their log P values, based on the partition of neutral species.

The species that most nearly conform to expectations, based on the partitioning of neutral species in the PEG-2000/NaOH system, are benzoic acid, **4**; and *p*-toluic acid, **7**; which are distinguished by a single carboxylic acid function. Those that least conform to such expectations are phthalic acid, **1**; 4-hydroxybenzoic acid, **3**; and salicylic acid, **6**;

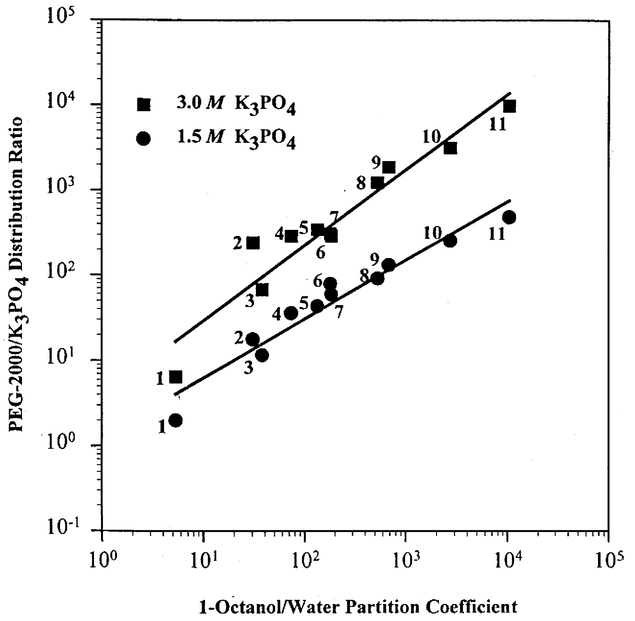

FIGURE 7. Correlation between the distribution ratios (D) in the 40% (w/w) PEG-2000/K_3PO_4 ABS and the 1-octanol/water partition coefficients (P) for the solutes defined in Table 1.

suggesting that the extra charge imparted by the possession of an additional carboxylic acid group, or a hydroxyl moiety that can be dissociated in the NaOH system, may be of importance. That the reduced D value in the NaOH system was not due to solute degradation was confirmed by partitioning phthalic acid in PEG-2000/phosphate following dissolution in 5 *M* NaOH, after which an essentially unchanged D was obtained (1.63 compared with the previous value of 1.99).

The relationship between the partition coefficient in ABS for the K_3PO_4, K_2CO_3, and $(NH_4)_2SO_4$ systems may be approximately described by the equivalent relationships in Eqs. 3 and 4,

$$\ln K = C + E \cdot n_c \tag{4}$$

$$\ln K = B + m \log P \tag{5}$$

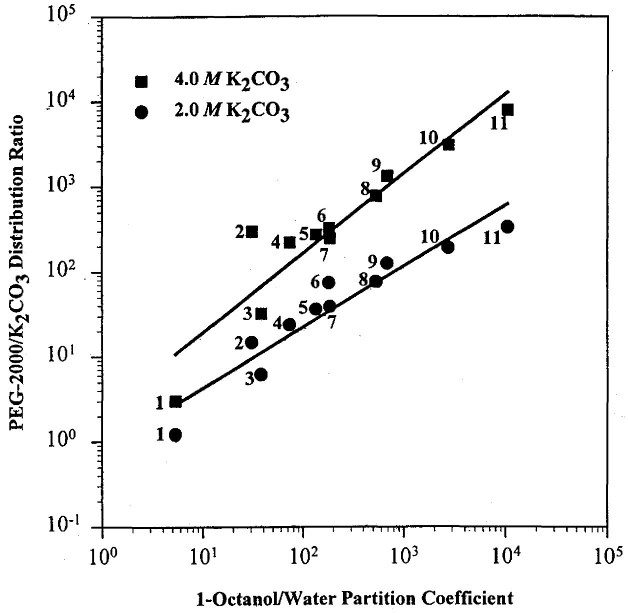

FIGURE 8. Correlation between the distribution ratios (D) in the 40% (w/w) PEG-2000/K_2CO_3 ABS and the 1-octanol/water partition coefficients (P) for the solutes defined in Table 1.

where K is the ABS partition coefficient and, in Eq. 4 (18–20), E is a constant related to the free energy of transfer of a methylene group between the phases and C is a constant that has been related to the differing hydration properties of the two-phases (18). In Eq. 5 (14), B and m represent constants that have been related to the intrinsic hydrophobicity of the phase system as in Eq. 6.

$$\log P_0 = -B/m \tag{6}$$

This parameter denotes the value of the solute 1-octanol/partition coefficient above which solutes will partition to the PEG-rich phase of an ABS and below which they will partition to the lower salt-rich phase (14). Values of m, B, and log P_0 for the present

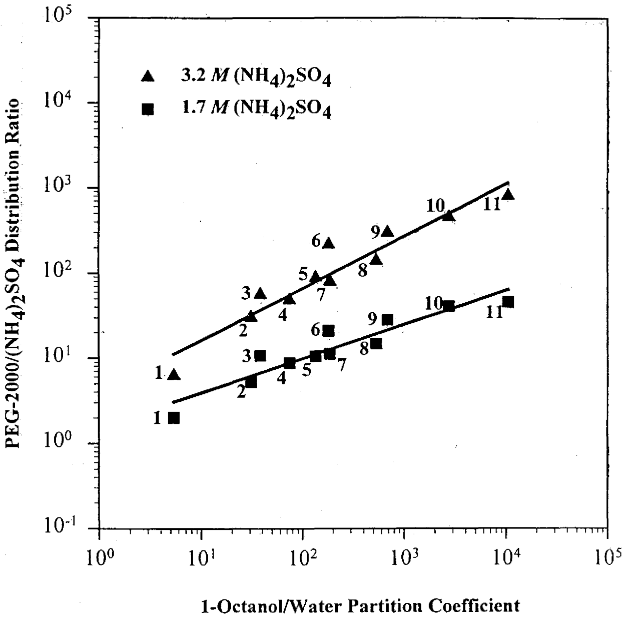

FIGURE 9. Correlation between the distribution ratios (D) in the 40% (w/w) PEG-2000/$(NH_4)_2SO_4$ and the 1-octanol/water partition coefficients (P) for the solutes defined in Table 1.

series of solutes at a selection of different salt concentrations in each ABS are shown in Table 3.

In studies of PEG/$(NH_4)_2SO_4$ ABS differing in the molecular masses of PEG employed to form the ABS, it was shown (18) that the free energy of transfer of a methylene group between the phases (E in Eq. 4) is dependent only on the PEG concentration difference between the phases of the ABS. By contrast, the hydration parameter (C of Eq. 4) was found to depend on both the PEG concentration difference between the phases and the molecular mass of PEG comprising the ABS. In order to make a similar comparison, we have previously defined a parameter M/M_0 (5) which relates the concentration of salt used to form the experimental ABS (M) to that which would approximately be required (M_0) to form a system close to the critical point of the

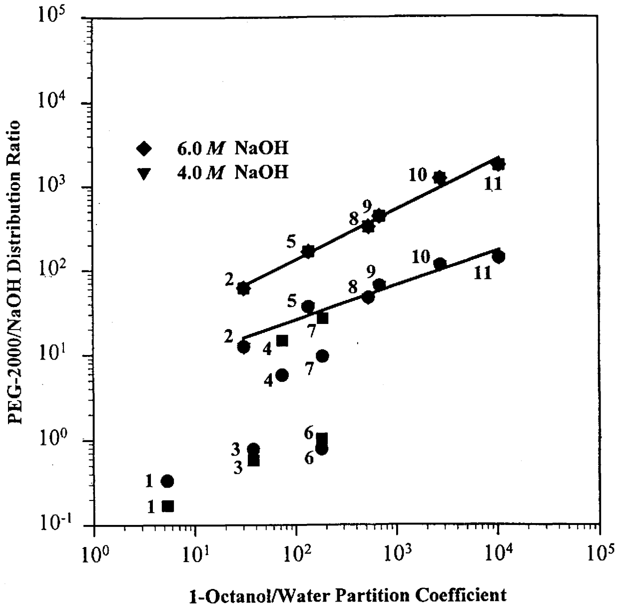

FIGURE 10. Correlation between the distribution ratios (D) in the 40% (w/w) PEG-2000/ NaOH and the 1-octanol/water partition coefficients (P) for the solutes defined in Table 1.

TABLE 3. CORRELATION COEFFICIENTS FOR THE DISTRIBUTION RATIO (ABS) VS PARTITION COEFFICIENT (1-OCTANOL/WATER) RELATIONSHIP

Salt stock solution	M/M_0[a]	D vs. P correlation coefficient	Slope, (m)	Intercept, (B)	Log P_0
1.5 *M* K_3PO_4	1.8	0.94	0.69	0.11	-0.15
3.0 *M* K_3PO_4	3.6	0.92	0.89	0.58	-0.65
2.0 *M* K_2CO_3	1.8	0.90	0.72	-0.08	0.12
4.0 *M* K_2CO_3	3.6	0.87	0.93	0.35	-0.38
1.7 *M* $(NH_4)_2SO_4$	1.0	0.90	0.40	0.18	-0.44
3.2 *M* $(NH_4)_2SO_4$	2.0	0.91	0.61	0.60	-0.98
4.0 *M* NaOH	1.1	0.67	0.81	-0.84	1.0
6.0 *M* NaOH	1.7	0.68	1.2	-1.3	1.0

[a] See text.

ABS (see Reference (5) for a more-detailed explanation of this parameter). This parameter is closely proportional to other measures of the relative divergence of the compositions of the coexisting phases of the ABS such as tie line length (11) and system stability (25), but does not require the determination of the compositions of the equilibrium phases of the ABS for its estimation.

Figure 11 shows the relationship between the slope of the correlation between log D and log P with increasing concentration of the salt stock solution expressed as M/M_0 for the ABS composed of K_3PO_4, K_2CO_3, and $(NH_4)_2SO_4$. The results show that the correlation between log D and log P (or the free energy of transfer between the phases) is, for the most part, dependent only on the relative difference in concentration between the phases. Thus, the resolution of these biphasic systems increases with increasing concentration of the added salt stock solution. At the highest concentrations of added salt in each system, it is evident that this tendency declines. However, there appears to be a distinction between the PEG-2000/$(NH_4)_2SO_4$ ABS and the K_2CO_3 and K_3PO_4 systems, as revealed by the partitioning of the charged solutes, which was not shown in the previous study utilizing uncharged solutes (5). This is because the slope, m, has increased due to the inclusion of the charged solutes with lower distribution coefficients in the K_3PO_4 and K_2CO_3 ABS, whereas the same species partitioned nearer neutrality in the $(NH_4)_2SO_4$ system and had less effect on the slope as mentioned above.

Figure 12 shows that the intercept B, which has been termed the relative hydration parameter (18) of the log D/log P correlations, is dependent not only on the concentration of added salt stock solution but also on the salt type used to form the biphase. It is interesting to note that the PEG-2000/$(NH_4)_2SO_4$ is again distinguishable from the K_2CO_3 and K_3PO_4 ABS by its steeper slope. The dependence of the free energy of transfer (m in Eq. 5) on the difference in composition of the two equilibrium phases and the hydration parameter (B in Eq. 5) on both composition and salt type means that the parameter log P_0 is also variable with salt type and concentration, as may be judged from Table 3. This implies that salts having less negative ΔG_{hyd} values are capable of resolving more hydrophilic species than salts having more negative ΔG_{hyd} values.

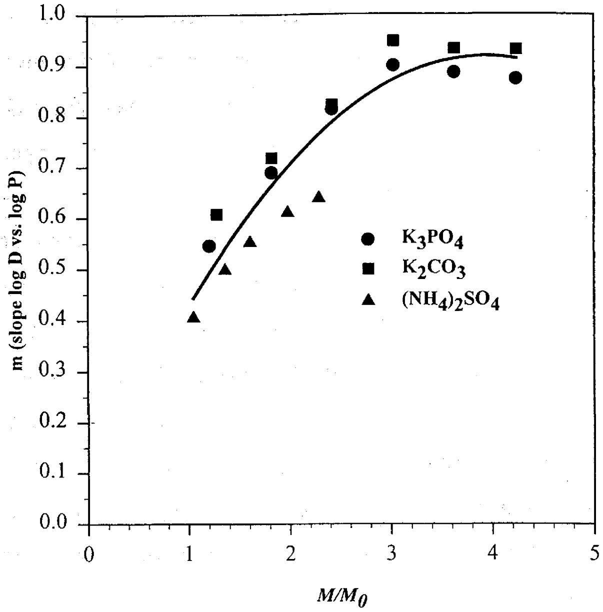

FIGURE 11. Slope (m) of the correlation between the distribution ratios (D) in the 40% (w/w) PEG/salt ABS and the 1-octanol/water partition coefficients (P) as a function of the normalized salt composition parameter, M/M_0, for the PEG-2000 ABS with K_3PO_4, K_2CO_3, and $(NH_4)_2SO_4$.

CONCLUSIONS

The quantitative partitioning of a number of charged and uncharged substituted benzene species has been examined in ABS composed of PEG-2000 and several different salts. Distribution values ranging from close to 1 to more than 10,000 have been observed. In general, inclusion of an acidic charged moiety reduces the partition coefficient over the uncharged or more hydrophobicly-substituted parent (compare benzoic acid/benzene and toluic acid/toluene or the chloro-substituted species). In a similar study of carboxylic acid-substituted benzenes (26), it was found that at high pH values the distribution coefficient of the carboxylic acid was higher than that of the corresponding alcohol (3,5-dintrobenzoic acid/3,5-dinitrobenzyl alcohol and 3-

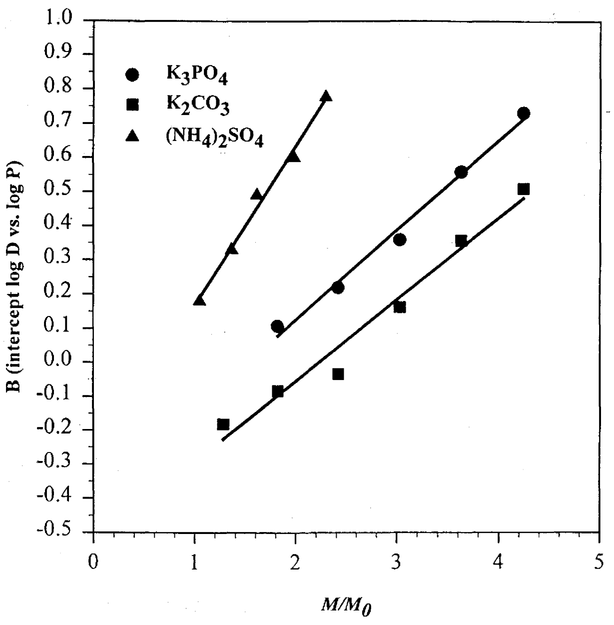

FIGURE 12. Intercept (B) of the correlation between the distribution ratios (D) in the 40% (w/w) PEG/salt ABS and the 1-octanol/water partition coefficients (P) as a function of the normalized salt composition parameter, M/M_0, for the PEG-2000 ABS with K_3PO_4, K_2CO_3, and $(NH_4)_2SO_4$.

nitrobenzoic acid/3-nitrobenzyl alcohol), tending to imply, perhaps, that inclusion of a carboxylic acid function would increase the partition coefficient of the substituted parent when the opposite is, in fact, the case. These results are also confirmed here where the inclusion of a hydroxyl moiety alongside the acidic function, in general, also reduces the distribution coefficient compared with the singly substituted acidic function (compare 4-hydroxybenzoic acid/benzoic acid). However, when the substitution of the hydroxyl is at the ortho position rather than para to the carboxylic acid function and intramolecular hydrogen bonding can occur, the resulting species is more hydrophobic (compare salicylic acid with 4-hydroxybenzoic acid). This cannot occur with phthalic acid, where the bulky carboxylic acid groups are out of plane to the ring and the doubly substituted carboxylic acid has the lowest distribution of all the species in the present study.

The current study demonstrates that published log P values provide a facile means for the estimation of distribution coefficients in ABS where the pH levels of these systems result in the partitioned molecules remaining largely neutral. For particular species, and where this is not the case, considerable divergence of log P and log D values is possible. The current research is being continued to determine the effects of further group contributions on observed partitioning behavior. This information will be invaluable in contributing to the current understanding of the driving forces behind solute partitioning in ABS. With this information, we hope to be able to develop predictive models for the behavior of more complex molecular species (e.g., dyes, PCBs, PABs, etc.) of importance in pollution control and environmental remediation and thereby evaluate the efficacy of ABS for the analysis and separation of these ubiquitous and important classes of molecules.

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