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NOVEL POLYETHYLENE GLYCOL-BASED AQUEOUS BIPHASIC SYSTEMS FOR THE EXTRACTION OF STRONTIUM AND CESIUM

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ABSTRACT

The partitioning behavior of Sr^{2+} and Cs^+ in aqueous biphasic systems formed by the addition of polyethylene glycol (PEG)-2000 to either NaOH, $(NH_4)_2SO_4$, or K_2CO_3 was investigated. Phase diagram data reveal that on a weight percent basis the salting out effects of the three salts increase in the order $(NH_4)_2SO_4 < K_2CO_3 <$ NaOH. In the presence of traditional extractants 12-crown-4, 15-crown-5, or 18-crown-6, only the partitioning of Sr^{2+} from $(NH_4)_2SO_4$ media using 18-crown-6 resulted in the expected 1:1 extractant dependency. All other measured distribution ratios in the presence or absence of extractants and regardless of salt system appear to be governed by cation enthalpy of hydration and system composition. The distribution ratio for cesium, D_{Cs} is greater than D_{Sr} due to cesium's lower enthalpy of hydration. D_M vs. percent salt and percent PEG both reveal an increase in D_M with decreasing salt or PEG.

INTRODUCTION

We are actively pursuing the investigation of metal ion partitioning in polyethylene glycol (PEG)-based aqueous biphasic systems formed by the addition of an inorganic salt to an aqueous PEG solution (1-4). Although some of these systems and those formed by the addition of two dissimilar aqueous polymers have been investigated for biomaterial separations (5,6), our recent review of this area revealed that metal ion separations were virtually ignored (7). This was surprising given the unique advantages of PEG-based aqueous biphasic systems including the absence of an organic diluent and the possibility of cleaner, cheaper, nontoxic separation processes. Thus, we have taken on the challenge of finding and defining those separations that PEG-based aqueous biphasic systems can accommodate, but traditional oil/water techniques are either not applicable or perform poorly.

One such separations problem, currently of high concern and profile, involves the highly alkaline waste storage facilities at Westinghouse Hanford (8). ^{90}Sr and ^{137}Cs in these wastes pose severe radiological and thermal hazards (9). The selective removal of these elements directly from alkaline media is difficult with traditional oil/H_2O systems. We have recently demonstrated, however, that simulants of several of these waste types will induce biphase formation when contacted with aqueous PEG-2000 solutions (10). This is a result of the additive action of biphase forming salts when present in solution together (11), and the relative transparence of other matrix ions. Thus, if appropriate extractants can be developed for the ions of interest, separations may be possible directly from the tank wastes without pretreatment.

A preliminary report on our work investigating crown ethers as extractants for Group 1 and 2 cations from highly alkaline media utilizing a PEG-based aqueous biphasic system has appeared (2). This work demonstrated that extraction based on metal ion recognition is possible from 20% (w/w) NaOH when high concentrations of NO_3^- are present. In the absence of nitrate anion, trends in the distribution of Group 1 and 2 cations appeared to follow trends according to their enthalpy of hydration.

This paper focuses on our continuing efforts to define the fundamental parameters governing metal ion partitioning in PEG-based aqueous biphasic systems. The partitioning of Sr^{2+} and Cs^+ have been investigated from highly alkaline (NaOH), basic (K_2CO_3), and acidic ($(NH_4)_2SO_4$) media in the presence and absence of 12-crown-4, 15-crown-5, and 18-crown-6. The effects of total system composition, crown ether, and matrix ions will be discussed.

EXPERIMENTAL

Reagent grade $(NH_4)_2SO_4$, Na_2SO_4, Na_2CO_3, PEG-2000, 12-crown-4, 15-crown-5, and 18-crown-6 (Aldrich), K_2CO_3, KNO_3, $NaNO_3$, NH_4NO_3, NaOH, and KOH (Fisher), and RbOH (Strem) were used as purchased. All water used was purified by a commercial deionization system.

The distribution ratios were measured in aqueous biphasic systems prepared by the addition of equal aliquots of a 40% (w/w) salt stock solution ($(NH_4)_2SO_4$ or K_2CO_3) to a 40% (w/w) PEG-2000 stock solution. The sodium hydroxide systems were prepared in the same manner with a 20% (w/w) NaOH stock solution. The crown ethers used as extractants were diluted to a known molarity with the 40% (w/w) PEG-2000 to give a new PEG stock. Nitrate solutions were prepared so that the cations for each system were the same, e.g., for the NaOH system a quantity of $NaNO_3$ was diluted with the 20% (w/w) NaOH solution to give a new salt stock. Nitrate solutions for the sulfate and carbonate systems were prepared using NH_4NO_3 and KNO_3, respectively. After initial mixing of the two stock solutions, the systems were equilibrated by vortexing for two minutes followed by two minutes of centrifugation.

Tracer solutions of ^{22}Na, ^{45}Ca, ^{85}Sr, ^{86}Rb, ^{133}Ba, and ^{137}Cs were prepared in dilute nitric acid. Tracer quantities of each metal solution were added to the equilibrated systems and each system was again vortexed and centrifuged for two minutes. The upper PEG-rich phase was separated from the lower salt-rich phase and equal aliquots of each phase were removed for radiometric counting. All distribution ratio measurements were carried out at 25°C. The distribution ratios for a given metal ion, D_M were then calculated as:

$$D_M = \frac{\text{Activity in PEG-rich upper phase}}{\text{Activity in salt-rich lower phase}}$$

For the system composition studies, salt and PEG stock solutions of varying concentrations were prepared. 20%, 30%, 40%, 50%, and 60% (w/w) PEG-2000 concentrations were used. 20%, 30%, and 40% (w/w) $(NH_4)_2SO_4$ and 20%, 30%, 40%, and 50% (w/w) K_2CO_3 concentrations were used. To study the effects of varying PEG concentrations, systems were prepared by mixing equal volumes of the 40% salt stocks and the range of PEG solutions. To study the effects of varying salt concentrations, equal volumes of the 40% PEG solution and the range of salt concentrations were used. The distribution ratio measurements were then carried out as reported above. The phase diagrams were determined by turbidity titrations according to the method of Albertsson (5).

RESULTS

Phase Diagrams

Three aqueous biphasic systems were investigated for this report. Each was prepared by mixing equal aliquots of 40% (w/w) PEG-2000 stock solution with a salt stock solution of either 20% NaOH, 40% K_2CO_3, or 40% $(NH_4)_2SO_4$. Figure 1 illustrates the phase diagrams for each system. The positions of the three binodials (system compositions above which result in biphasic behavior and below which the systems are monophasic) reveal that the amount of salt required to form a biphase with a given concentration of PEG-2000 decreases in the order $(NH_4)_2SO_4 > K_2CO_3 > NaOH$ on a weight percent basis. Data by Goddard (11) and results in our laboratory (12) suggest that the position of the binodial is not only affected by the biphase forming anion but also cation effects. In general, we have observed that the

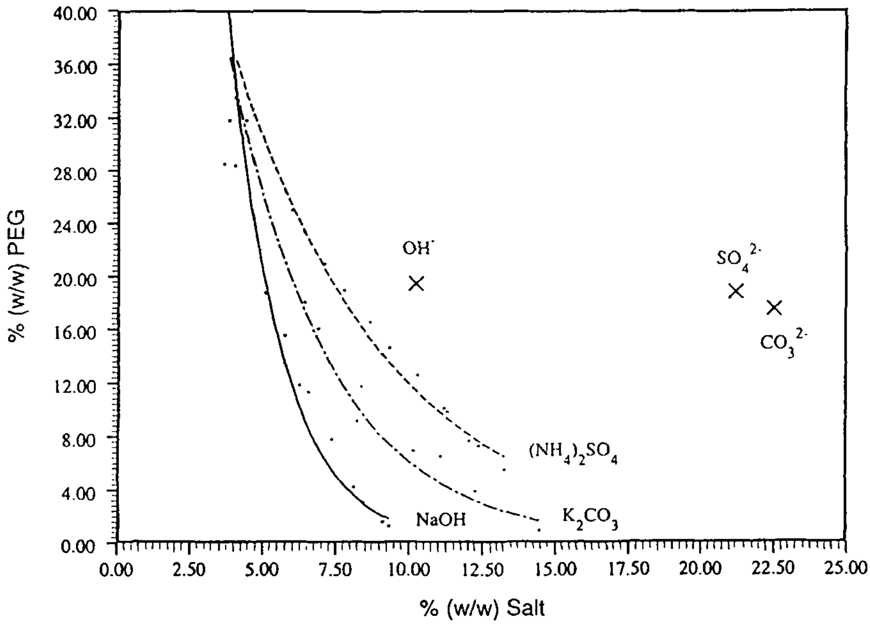

FIGURE 1. Phase diagrams for the three PEG-based aqueous biphasic systems utilized in this study. System compositions above the binodials are biphasic, while those below the binodials are monophasic. The X's represent the total system compositions obtained by mixing equal aliquots of 40% (w/w) PEG-2000 and either 40% $(NH_4)_2SO_4$, 40% K_2CO_3, or 20% NaOH.

higher the cation's enthalpy of hydration, the lower (further to the left) the binodial. Thus KOH and RbOH both give binodials lying farther to the right than NaOH, and sulfate and carbonate salts of the same cation give similar binodials (Figure 2). This is true even when the salts are compared on a mole/liter basis rather than using weight percent.

The overall system composition utilized in studies without crown ethers are given by the X's in Figure 1. The relatively high solubilities of $(NH_4)_2SO_4$ and K_2CO_3 allow system compositions near 20% salt, 20% PEG. The further the system compositions are from the binodial, the more resistant the biphasic systems are to

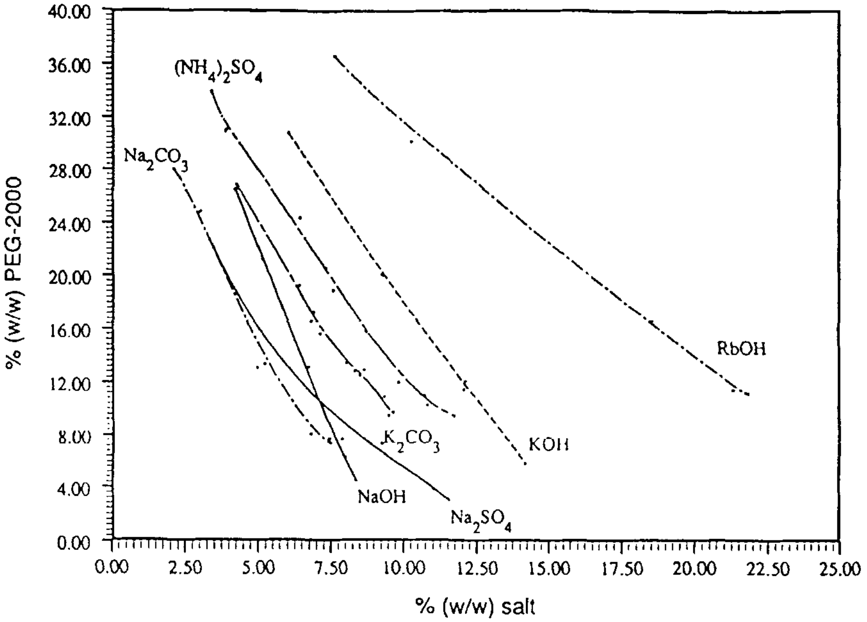

FIGURE 2. Phase diagrams for PEG-2000/salt systems illustrating cation and anion effects on the position of the binodial.

fluctuations in temperature, pH, and matrix ions in solution. In addition, this minimizes the amount of PEG in the salt-rich phase and vice-versa. Unfortunately, there is a compromise as the systems tend to become more viscous and difficult to use as the distance from the binodial increases.

NaOH is less soluble and the 20% salt stock used to make each biphase results in a system composition much closer to the binodial. As discussed below, many of the differences in D_M observed between the three systems may be attributable to system composition.

The addition of crown ethers to the PEG phase shifts the binodial to the right (4). Although the change is not dramatic, it does take more salt to form a biphase with a given amount of PEG. The method of preparing the PEG stock solution containing crown ether (diluting a known mass of crown ether to volume with 40%

PEG) itself lowers the absolute amount of PEG present in each biphase. The higher the concentration of crown ether, the lower amount of PEG present. As we will see below this could also affect the distribution ratios observed.

Partitioning Studies

Distribution ratios for Group 1 and 2 cations from all three media in the absence of extractant are given in Table 1. It is readily apparent that the highest D values are obtained from the NaOH system followed (at considerably lower values) by the $(NH_4)_2SO_4$ and then K_2CO_3 media. In the presence of extractant (18-crown-6, 15-crown-5, or 12-crown-4) this same general ordering is observed.

Within each of the different salt systems, the extractant profiles for 18-crown-6 and 15-crown-5 (Figures 3, 4) reveal $D_{Cs} > D_{Sr}$. The difference between D_{Cs} and D_{Sr} is relatively constant except as noted below for the $(NH_4)_2SO_4$ system. The addition of 1 M nitrate salt to each system enhances the distribution ratios but does not dramatically alter the extractant profiles.

Distribution ratios have been obtained for 18-crown-6 and 15-crown-5 (D_{CE}) in NaOH and $(NH_4)_2SO_4$ media. For given concentrations of crown ether in the presence of nitrate salts, the D_{CE} values cluster around one (2, 4).

The method of preparing each system containing a crown ether extractant affects the absolute amount of PEG-2000 present. To study the effects of increasing or decreasing PEG and salt concentrations, distribution ratio measurements were conducted as a function of percent PEG and percent salt. Due to the low workable solubility range of NaOH, this study was conducted for the $(NH_4)_2SO_4$ and K_2CO_3 media only. The results are depicted in Figures 5 and 6. In general as the percent salt or percent PEG increases the distribution ratios decrease.

DISCUSSION

In previous work investigating the partitioning of Group 1 and 2 cations in the NaOH system with 18-crown-6 and 15-crown-5 (2), we observed a strong correlation

TABLE 1. DISTRIBUTION RATIOS IN THE ABSENCE OF CROWN ETHER

	System:		
	$(NH_4)_2SO_4$	K_2CO_3	NaOH
D_{Na}	0.027	0.017	0.098
D_{Rb}	-----	-----	0.31
D_{Cs}	0.051	0.049	0.33
D_{Ca}	0.0054	0.0022	0.020
D_{Sr}	0.0074	0.0043	0.022
D_{Ba}	0.012	0.0035	0.045

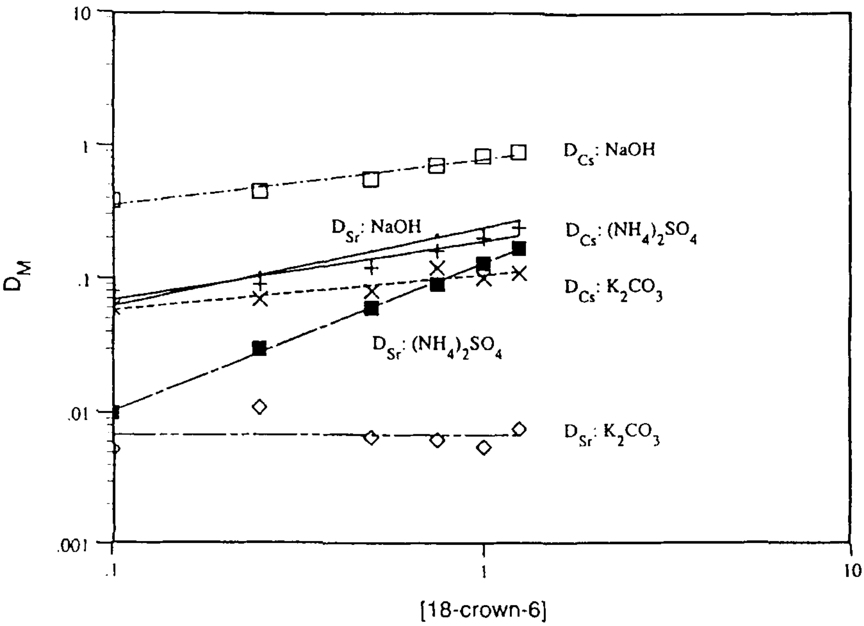

FIGURE 3. Extractant profiles for Sr^{2+} and Cs^{+} vs. [18-crown-6] from all three systems studied.

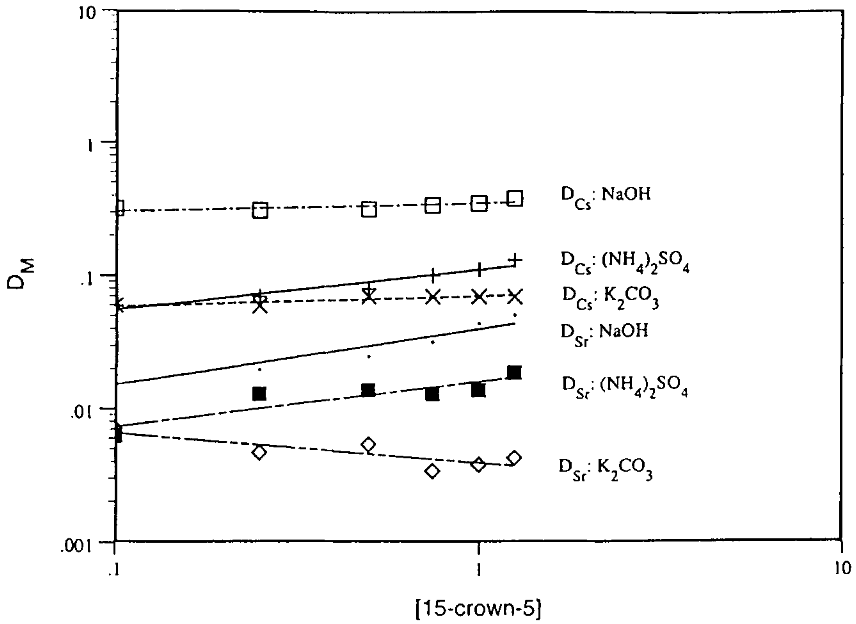

FIGURE 4. Extractant profiles for Sr^{2+} and Cs^{+} vs. [15-crown-5] from all three systems studied.

between log K (for formation of an M^{n+}/18-crown-6 complex) and D_M, but only when the concentrations of NO_3^- anion reached 2 M. At lower nitrate anion concentrations or in the presence of 15-crown-5, the distribution ratios were in the order $Ca^{2+} < Na^{+} < Sr^{2+} < Ba^{2+} < Rb^{+} \approx Cs^{+}$. That work pointed toward further study to correlate total system composition with partitioning behavior and to understand the fundamental parameters of the partitioning process for metal ions.

In the present study, the higher D values from NaOH media than from $(NH_4)_2SO_4$ and K_2CO_3 can now be explained from analysis of system composition (Figure 1) and distribution vs. percent PEG or percent salt data (Figures 5, 6). The total system composition used for the NaOH system is significantly lower in total salt concentration and much closer to the binodial than that of either $(NH_4)_2SO_4$ or K_2CO_3

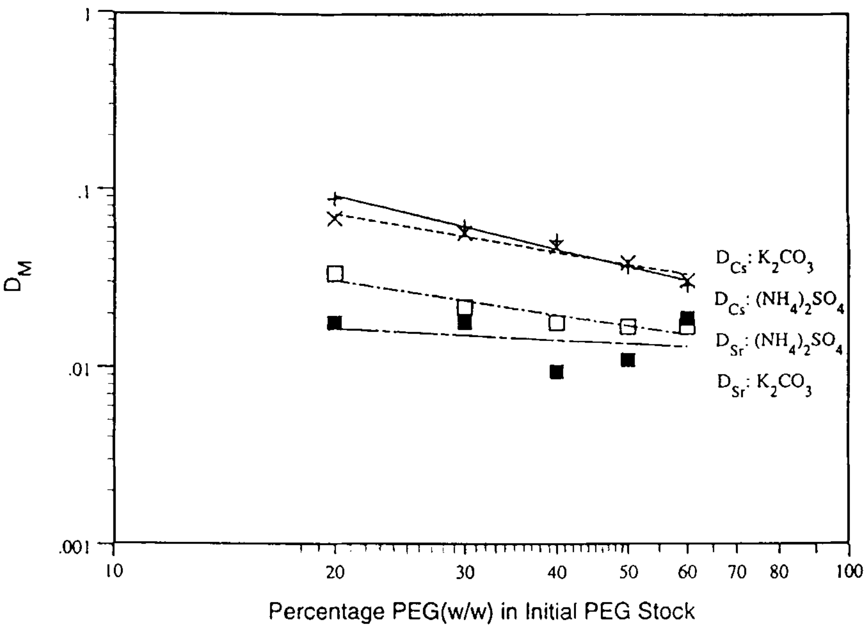

FIGURE 5. D_M vs. percent PEG-2000 for systems prepared by mixing equal aliquots of 40% $(NH_4)_2SO_4$ or 40% K_2CO_3 with PEG stock solutions of decreasing weight percent PEG.

biphasic systems. Figure 6 shows that D_M increases as percent salt decreases. Since on a weight percent basis the NaOH system requires the least amount of salt to induce a biphase, its metal ion partitioning characteristics are superior to either $(NH_4)_2SO_4$ or K_2CO_3. Noting the close similarity of the $(NH_4)_2SO_4$ and K_2CO_3 system compositions, this may also explain the relatively similar D_M results for these media (in the absence of extractant).

While the distribution ratios obtained for Sr^{2+} are all low (Figures 3, 4), several interesting trends in the extractant profiles are noted. First, 15-crown-5 is relatively ineffective in all three media with lower D_{Sr} values than observed for 18-crown-6. In the highly alkaline NaOH, both 15-crown-5 and 18-crown-6 have similar extractant

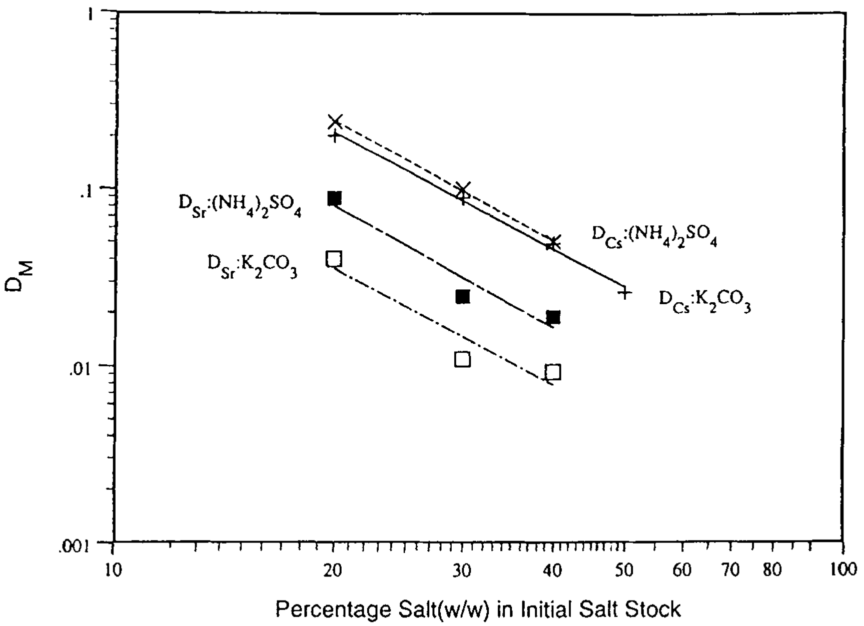

FIGURE 6. D_M vs. percent salt for systems prepared by mixing equal aliquots of 40% PEG-2000 with $(NH_4)_2SO_4$ or K_2CO_3 salt stock solutions of decreasing weight percent salt.

dependence profiles with the latter shifted to slightly higher D_{Sr} values. Sr^{2+} partitioning in the NaOH system thus appears to be motivated by changes in the system composition and is independent of any Sr^{2+} crown ether interaction.

The Sr^{2+} distribution results from K_2CO_3 and $(NH_4)_2SO_4$, however, appear to be dependent upon 18-crown-6. The 18-crown-6 dependencies for Sr^{2+} (Figure 3) exhibit a slope of 0.0 from K_2CO_3 and a slope of 1.1 from $(NH_4)_2SO_4$. These data supply reasonable evidence for a crown ether complexation effect based on the following: The log K values (13) for M^{n+}/18-crown-6 interactions in water are Sr^{2+} = 2.72, K^+ = 2.03, and NH_4^+ = 1.23. From K_2CO_3 media, tracer quantity Sr^{2+} must compete for free 18-crown-6 with a very effective competitor (K^+) present in much higher concentrations, consequently Sr^{2+} appears to have no dependence on 18-

crown-6. However, when the matrix cation is an ineffective competitor (e.g., NH_4^+) the Sr^{2+} distribution profile exhibits a slope of 1.1 suggesting 18-crown-6 complexation. At this point it is not possible to determine what role changes in system composition play.

Cesium ion partitioning does not seem to exhibit a true crown ether effect with either 12-crown-4, 15-crown-5, or even 18-crown-6. The smaller crown ethers give relatively flat extractant dependencies. The extractant profiles for 18-crown-6 all exhibit small rises in D_M as the concentration of crown ether increases consistent with the rise in D_M as percent PEG decreases, but not consistent with crown ether complexation. The low log K (0.99) for the Cs^+/18-crown-6 interaction in water (13) would argue that Cs^+ cannot effectively compete with other matrix ions for crown ether complexation.

In the absence of a definitive correlation in D_M vs. [crown ether] (except for Sr^{2+} from $(NH_4)_2SO_4$) some other explanation must be developed for the observed results. The answer may lie in the hydration enthalpy data for Group 1 and 2 cations (14). Goddard (11) has noted, and our phase diagram data tend to confirm (Figure 2), that the higher the hydration enthalpy of both cations and anions the greater the tendency to form a biphasic solution with aqueous PEG. Inclusive of that is the observation that the higher the hydration enthalpy the less salt is required for biphase formation. Intuitively then, the lower the enthalpy of hydration the higher the solubility in the PEG-rich phase and the higher the D_M.

To test this in our systems, D_M data for several Group 1 and 2 cations in all three media under investigation were taken. Figure 7 plots D_M versus enthalpy of hydration for Ca^{2+}, Sr^{2+}, Ba^{2+}, Na^+, Rb^+, and Cs^+. It is immediately evident that within each group there is a strong correlation between D_M and ΔH_{hyd} (e.g., 92% for Group 2 cations and 99% for Group 1 cations in NaOH; 99% for Group 2 cations in $(NH_4)_2SO_4$). This, qualitatively at least, explains the higher D_M's consistently observed for Cs^+ over Sr^{2+}. It also helps to confirm that a different mechanism (presumably Sr^{2+}/18-crown-6 complexation) is operating in the $(NH_4)_2SO_4$ system since D_{Sr} nearly reaches D_{Cs} at 1.25 M 18-crown-6 (Figure 3).

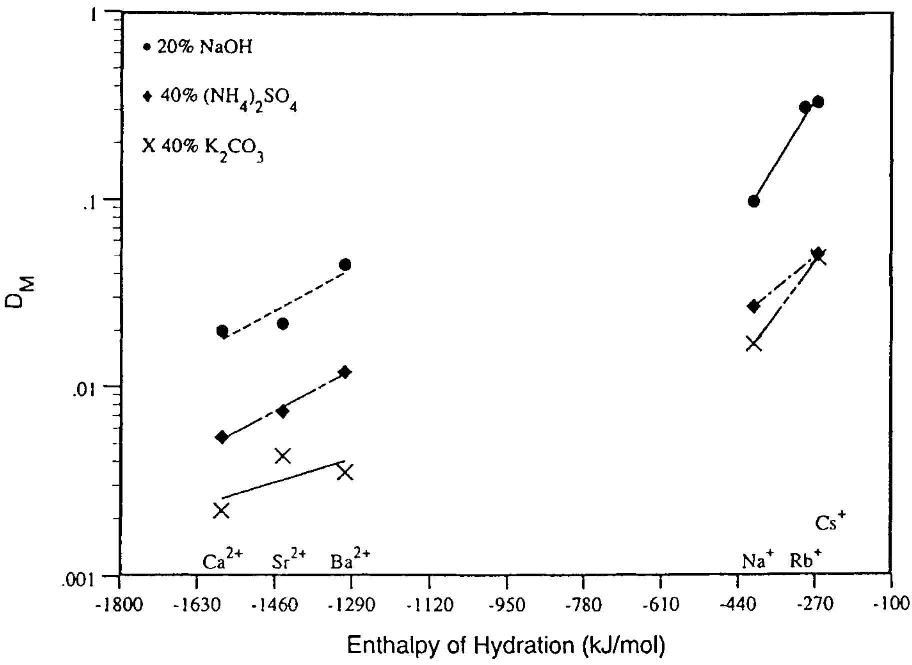

FIGURE 7. D_M vs. enthalpy of hydration for selected Group 1 and 2 cations. Partitioning studies were carried out in the three systems under study in the absence of an extractant.

It is not yet clear whether the correlation observed between D_M and enthalpy of hydration is just between members of a single group or whether this is a general trend for all metal ions. We are currently involved in further research to determine the applicability of using enthalpy of hydration to determine D_M for a variety of metal ions and aqueous biphasic systems.

CONCLUSIONS

This study has demonstrated that partitioning via metal ion recognition is possible in PEG-based aqueous biphasic systems. D_{Sr} vs. concentration of 18-crown-

6 showed excellent correlation for the extraction of a 1:1 complex from $(NH_4)_2SO_4$ media. This study has also shown that, in the absence of a good extractant, the driving force behind Cs^+ or Sr^{2+} partitioning is the enthalpy of hydration of the aqueous metal ion.

At this point, the single most important obstacle to selective partitioning of Sr^{2+} or Cs^+ from aqueous biphasic systems is a familiar one. A macrocyclic ligand with good binding characteristics and selectivity, and which has a high affinity for the PEG-rich phase, must be found or prepared. This task is complicated by the fact that it is not a simple matter of building in hydrophobicity to an existing ligand as in traditional oil/water extraction. The macrocycle for aqueous biphasic systems must be both water soluble and prefer the hydrogen bonding environment present in the PEG-rich phase.

It is clear that while the potential for novel and exciting separation processes exists, a tremendous amount of study is still necessary to understand the fundamental parameters governing aqueous biphasic extraction. Once we have achieved this understanding, the search for suitable extractants and optimal system compositions for specific applications can begin in earnest.

ACKNOWLEDGEMENTS

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