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Metal ion separations in polyethylene glycol-based aqueous biphasic systems: correlation of partitioning behavior with available thermodynamic hydration data

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Abstract

Solvent extraction, utilizing an oil–water mixture (e.g., chloroform–water) and a suitable complexant, is a proven technology for the selective removal and recovery of metal ions from aqueous solutions. Aqueous biphasic systems (ABS), formed by mixing certain inorganic salts and water-soluble polymers, or by mixing two dissimilar water-soluble polymers, have been studied for more than 40 years for the gentle, non-denaturing separation of fragile biomolecules, yet ABS have been virtually ignored as a possible extraction technology for metal ions. In this report we review our metal ion partitioning work and discuss the three major types of partitioning: (1) those rare instances that the metal ion species present in a given solution partitions to the PEG-rich phase without an extractant; (2) the use of halide salts which produce a metal anion complex that partitions to the PEG-rich phase; and (3) the use of a water-soluble extractant which distributes to the PEG-rich phase. In addition, we correlate the partitioning behavior we observed with available thermodynamic data for metal ions and their complexes.

Keywords: Aqueous two-phase systems; Partitioning; Polyethylene glycol; Metals

1. Introduction

Aqueous biphasic systems (ABS) consist of two immiscible phases formed when certain water-soluble polymers are combined with one another or with certain inorganic salts in specific concentrations. As two-phase systems they are suitable for carrying out liquid–liquid separations of various solutes such as biomolecules, metal ions, and particulates [1–5].

Traditional solvent extraction employs an organic

solvent and an aqueous solution as the two immiscible phases. The ability to utilize a number of different diluents, extractants, and aqueous phases makes solvent extraction a powerful separations method possessing a number of favorable characteristics including rapid extraction kinetics for many separations, the adaptability of the method to a wide variety of solutes, and back extraction or stripping of the solute and recycling of the solvent and/or diluent are often feasible [6]. Further, liquid–liquid extraction is capable of large volume throughput and is amenable to large-scale separations, and can be engineered for high selectivity and efficiency by the use of multistage contactors.

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In spite of these numerous advantages, there are several drawbacks to traditional oil–water solvent extraction. Even with today's environmental standards a number of extraction systems still utilize toxic and flammable organic diluents. When the diluent is coupled with a highly selective extractant the cost of the solvent system can become very expensive. (Not to mention the costs of safely designing a system to operate with a volatile or flammable diluent.) Finally, partitioning of a polar or charged solute from an aqueous phase into an organic medium requires dehydration, the extent of which depends upon the organic solvent. In some separations schemes this is trivial, while in others, particularly for the separation of metal ions, it is of paramount importance.

In ABS the major component in each of the two phases is water, and because of this non-denaturing environment these systems have been widely employed in biological separations for over 40 years. A number of reviews on the bioanalytical uses of and theory of bioseparations are available [1–4,7,8]. Prior to our work, only a limited number of papers reporting metal ion separations in aqueous biphasic systems were published [9–16] with a single review comprehensively summarizing these results [17].

A number of different water-soluble polymers may be utilized in ABS, with polyethylene glycols (PEGs), dextrans, and ficolls receiving the most attention. An even wider variety of polymer–salt combinations exists usually with Na^+ , K^+ , or NH_4^+ salts of mono- through trivalent anions like OH^- , CO_3^{2-} , SO_4^{2-} , and PO_4^{3-} .

The partitioning of solutes in ABS is affected by numerous variables. The type and molecular mass of the polymer(s) and the type of salt (both the cation and anion are important) are amongst the most important variables, as are their respective concentrations. (The phase-forming components must be present in sufficient quantities to create heterogeneous aqueous phases.) Other important variables include system pH, temperature, and the addition of neutral and charged species which may be used to modify partitioning character.

ABS retain all of the practical advantages of liquid–liquid extraction and also have a number of unique advantages due, in large part, to their aqueous nature. Polyethylene glycol-based aqueous biphasic systems (PEG-ABS) are virtually nontoxic and non-

flammable, all components are commercially available in bulk quantities and are inexpensive, and the systems have reasonable phase separation characteristics [18–20] and can even be used with traditional solvent extraction equipment [2,8]. One of the most important advantages of aqueous biphasic systems is that partitioning takes place between two aqueous phases, therefore the effects of solute dehydration on the extraction process are diminished. When metal ions distribute to the PEG-rich phase only a subtle reorganization of the hydration sphere may be required, whereas in traditional solvent extraction near-complete dehydration may be necessary.

Metal ion extraction in aqueous biphasic systems usually fits into one of three major categories: (1) extraction by the PEG-rich phase alone; (2) extraction of negatively charged metal complexes of inorganic anions; and (3) extraction using a water-soluble complexant. The majority of metal ion separations carried out thus far are from category three, and examples from category one are extremely rare, with TcO_4^- as the primary example [19,20]. Use of thiocyanate and halide anions to form anionic metal complexes has received scattered attention in aqueous two-phase separations [17,21]. To date, however, only a single preliminary communication by our group presents a systematic study of metal halide complex anion partitioning in PEG-based aqueous biphasic systems [22]. In this contribution, we will review our metal ion partitioning work and correlate partitioning behavior with available thermodynamic data for the metal ions and their complexes.

2. Experimental

PEG-2000 was purchased from Aldrich (Milwaukee, WI, USA) and used as received. NH_4Cl , NH_4Br , NH_4I , $(\text{NH}_4)_2\text{SO}_4$, NaOH , Na_2SO_4 , Rb_2SO_4 , Cs_2SO_4 , Na_2CO_3 , Na_2SeO_4 , Na_2CrO_4 , Na_2SO_3 , and K_2CO_3 were of reagent quality and used without further purification. All water was purified using commercial deionization systems.

^{109}Cd (New England Nuclear; Boston, MA, USA) was purchased, transformed to the nitrate salt and stored in 2–5 M HNO_3 prior to use. ^{212}Pb was obtained as part of the ^{228}Th decay chain and

purified by extraction chromatography. The final chemical form of the Pb^{2+} radionuclide was a nitrate salt in 2–5 M HNO_3 . ^{36}Cl (New England Nuclear) was used as H^{36}Cl and ^{129}I (New England Nuclear or Isotope Products Laboratories; Burbank, CA, USA) was utilized as its sodium salt. ^{99}Tc (Amersham; Arlington Heights, IL, USA) was purchased and used as an aqueous NaTcO_4 solution.

All PEG-2000 and salt stock solutions were prepared on a weight percent, molal, or molar basis. The systems containing extractants were prepared by diluting the NH_4X ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) extractant to volume with the salt stock solution. This approach results in a net decrease in the concentration of phase-forming salt present in the uptake experiment. The effect is trivial at low extractant concentrations but potentially significant at higher extractant concentrations. The compositions referred to in Section 3 are for pre-equilibrium stock solution concentrations.

The distribution ratios were determined in the following manner. Equal aliquots (750–1000 μl) of PEG-2000 stock solution and salt stock solution were combined. The systems were pre-equilibrated by vortex-mixing for 2 min followed by 2 min of centrifugation (2000 g). Tracer quantities of the radionuclide of interest were added and the system centrifuged then vortex-mixed for 2 min. (The contact time was experimentally determined to be sufficient for these systems to reach equilibrium.) The phases were disengaged by 2 min of centrifugation and were carefully separated. Equal aliquots of each phase were then submitted for standard liquid scintillation or γ -radiometric analyses. The radiometric distribution ratio (D) is defined as the counts per minute (cpm) in the upper PEG-rich phase divided by the cpm in the lower salt-rich phase. Radiometrically determined distribution ratios are generally accurate to $\pm 5\%$; however, due to the complexity of these ABS, a conservative accuracy of $\pm 10\%$ is reported.

The discussion relating the Gibbs free energy of hydration to the charge-to-size ratio of the complex halide anions required calculation of the volume of the anions, which was carried out in the following manner. Crystallographic coordinates for Cd^{2+} halide complexes [23–25] were put into the SYBYL [26] modelling suite of programs and the volume of the anionic complex determined using its volume-

calculating algorithm. A search of the Cambridge Crystallographic Database [27] showed only polymeric lead halide species, so a tetrahedral geometry was approximated and modelled by defining tetrahedral angles and energy minimizing the bond distances. The charge of the anion was then divided by the volume (in arbitrary units) to yield the charge-to-size ratio.

3. Results and discussion

3.1. Category 1: partitioning to the PEG-rich phase without an extractant

We discovered that the large, relatively soft pertechnetate anion, TcO_4^- , partitions to the PEG-rich phase in a variety of PEG-ABS in the absence of an extractant [5,19,20]. This result is exciting because of the many current needs for improved technetium separations ranging from purification of $^{99\text{m}}\text{Tc}$ in nuclear medicine [28–31] to the removal of the environmentally mobile $^{99}\text{TcO}_4^-$ from nuclear waste repositories [32,33]. As a result of its favorable partitioning characteristics and the need for new separations technologies for this element, we have been investigating in detail the nature of the interactions of pertechnetate with PEG-based ABS.

TcO_4^- , because it partitions to the PEG-rich phase in the absence of an extractant, provides a convenient probe of system composition. The distribution ratios of pertechnetate in a series of Group 1 sulfate-ABS based on PEG-2000 are presented in Fig. 1. The trends in distribution ratios follow from the relative salting-out ability of the salts. Na_2SO_4 salts-out PEG better than $(\text{NH}_4)_2\text{SO}_4$ [34] and thus at a given concentration, D_{Tc} values are higher from Na_2SO_4 than $(\text{NH}_4)_2\text{SO}_4$. In addition, as the concentration of a given salt increases, the distribution ratios for pertechnetate increase.

It is clear from the literature that increasing the incompatibility between the PEG-rich and salt-rich phases increases the affinity of a solute for a particular phase [7,35–37]. Since TcO_4^- prefers the PEG-rich phase, the distribution ratios increase as the phase incompatibility increases (which results in an increase in the difference in PEG (or salt) concentration in each phase). A linear relationship

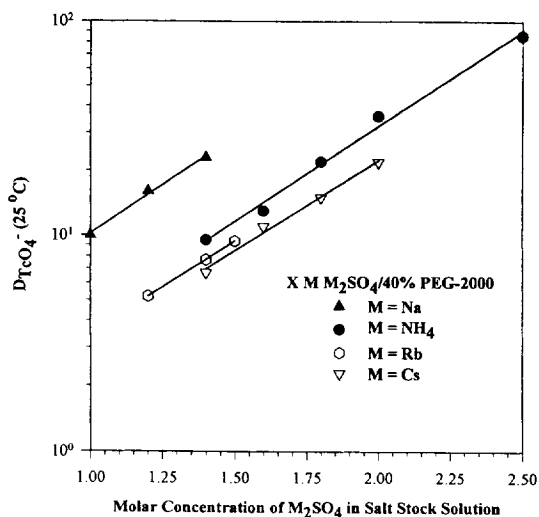


Fig. 1. Log/linear plot of the pertechnetate distribution ratios vs. the molar concentration of M_2SO_4 stock solution used to prepare the ABS with 40% PEG-2000.

between $\log D$ for neutral solutes and the difference in PEG concentration between the phases has been noted previously in the literature [7,35–37].

While the results for TcO_4^- are consistent with other partitioning studies reported in the literature, it is less clear why the partitioning occurs at all and perhaps more importantly, how to predict in advance the partitioning behavior from a variety of PEG-ABS. We have begun to address the need for predictive tools by correlating our partitioning data with fundamental thermodynamic parameters of hydration, assuming that the major interactions that govern partitioning involve interactions of the solutes with water.

In Goddard's paper describing the salting-out of PEG with various salts [34], the relative salting-out ability was reported to depend on ionic charge, hydration radius, and specific interactions between the salt and PEG. The ability of an anion to salt-out PEG was also correlated to the anion's lyotropic number. Lyotropic number, hydration radius, charge-to-size ratio, and charge can all be related to an ion's Gibbs free energy of hydration (ΔG_{hyd}), thus we have chosen to investigate the relationship between ΔG_{hyd} and our partitioning results. A convenient tabulation of ΔG_{hyd} for a variety of cations and anions has been recently published by Marcus [38].

We are using the calculated values of ΔG_{hyd} from this report.

As has already been stated, the results in Fig. 1 follow from the relative salting-out ability of the various sulfate salts. What is perhaps less clear is that the distribution ratios for pertechnetate can be correlated with the ΔG_{hyd} of the salt cations used to form the biphasic. In Fig. 2, $\log D_{Tc}$ for a given molar concentration of salt stock solution is plotted against the negative Gibbs free energy of hydration of the salt cation. Of the given cations, Na^+ has the largest $-\Delta G_{hyd}$, salts-out PEG the best, and has the highest pertechnetate distribution ratio. The sodium cation is the most "water-structuring" of the cations used and thus creates the largest phase incompatibility and the largest difference in PEG and salt concentrations between the phases, resulting in the highest D_{Tc} 's. Cation effects are obviously an important feature in designing an appropriate ABS and must be taken into consideration in any model used to predict distribution ratios.

Anions are known to affect the structure of water more than cations, thus a salt's anion determines whether an ABS will form. Water-structuring anions typically salt-out PEG, while chaotropic anions do not. Fig. 3 presents the correlation of D_{Tc} versus $-\Delta G_{hyd}$ for several divalent anions at a given salt

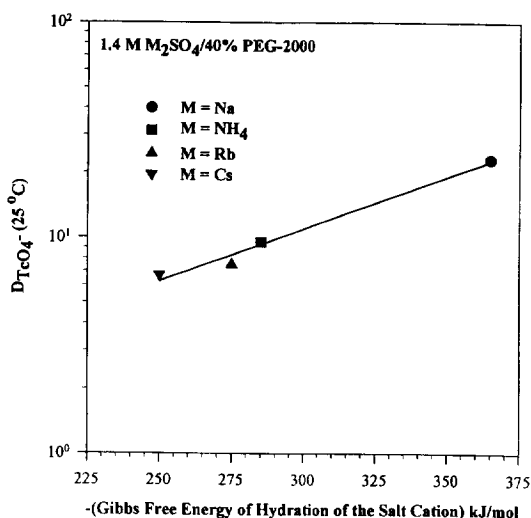


Fig. 2. Pertechnetate distribution ratios vs. the negative ΔG_{hyd} of the M_2SO_4 cation.

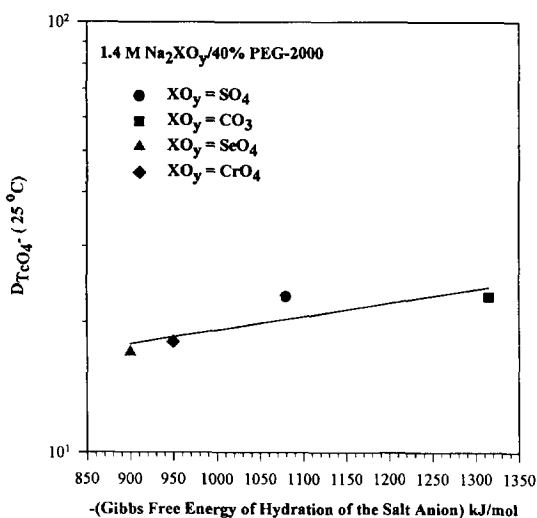


Fig. 3. Perchnetate distribution ratios vs. the negative ΔG_{hyd} of the Na_2XO_y anion.

and PEG concentration. Again, a reasonably linear correlation is observed.

If the distribution ratios can be correlated to the ΔG_{hyd} for the cation or the anion, what about the combined ΔG_{hyd} for a given stock solution? Fig. 4 plots the log D_{Tc} for a series of ABS prepared by mixing equal aliquots of 40% PEG-2000 and increasingly concentrated $(NH_4)_2SO_4$ stock solutions against the total $-\Delta G_{hyd}$ for the stock solution. This value was calculated by summing the molar ionic

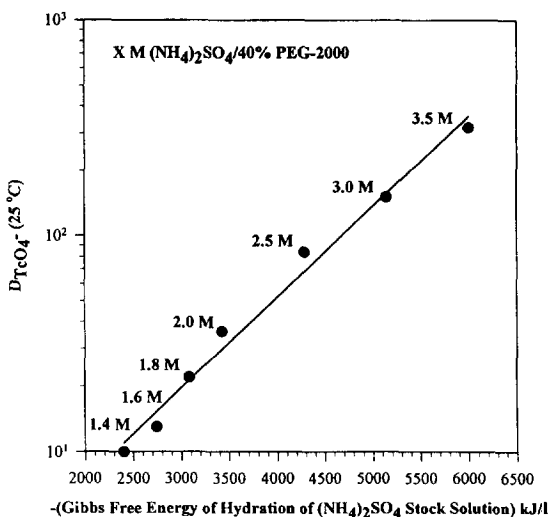


Fig. 4. Perchnetate distribution ratios vs. the negative total ΔG_{hyd} for several $(NH_4)_2SO_4$ stock solutions used to prepare an ABS with 40% PEG-2000.

concentration times the ΔG_{hyd} of the individual ions. Again, a reasonably linear correlation is observed.

In taking this one step further, it should be possible to calculate a total ΔG_{hyd} for salt stock solutions of different cations and anions and see a similar correlation. This is exactly what we observe in Fig. 5. Regardless of whether the anion is SeO_4^{2-} , SO_3^{2-} , SO_4^{2-} , or CO_3^{2-} , or whether the cation is Na^+ , NH_4^+ , or K^+ , or whether the salt stock solutions have different concentrations, D_{Tc} is linearly correlated to the total Gibbs free energy of hydration of the salt stock solution for a given concentration of PEG stock solution.

We have been careful in this study to keep the cations and anions studied of the same valence. It is not yet clear, for example if the above arguments will hold when comparing salts of hydroxide or phosphate, although we are actively investigating this area. It is also important to know the speciation of the ions when making these comparisons. Phosphate salts for example may exist in solution as phosphate, hydrogen phosphate, dihydrogen phosphate, or some combination of the three and each has a different ΔG_{hyd} .

The use of ΔG_{hyd} is not restricted to the salts used to form an ABS, but may also be predictive of the behavior of ionic solutes. Fig. 6 plots the distribution

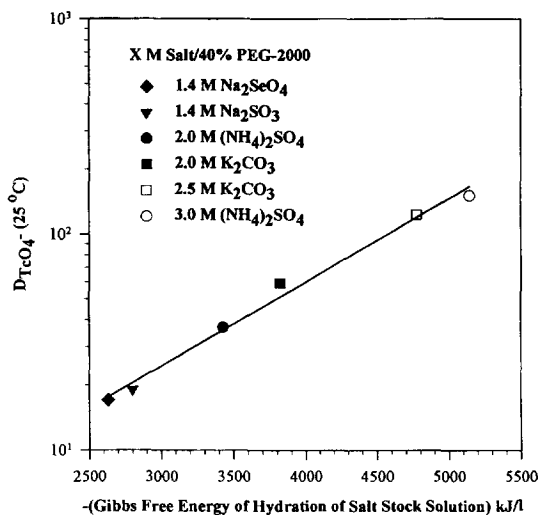


Fig. 5. Perchnetate distribution ratios vs. the negative total ΔG_{hyd} for several salt stock solutions used to prepare an ABS with 40% PEG-2000.

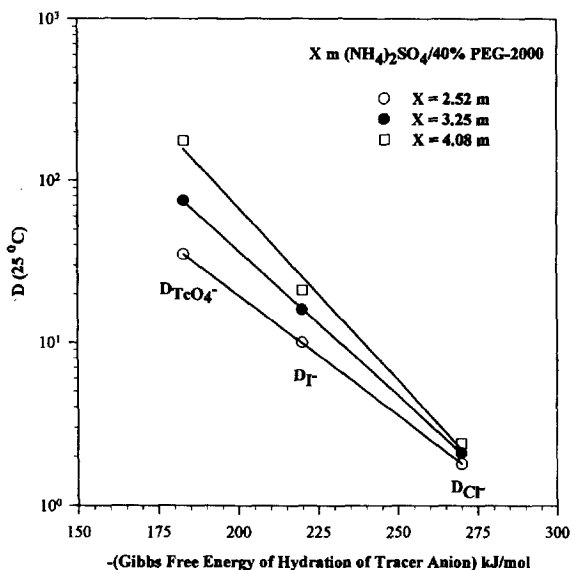


Fig. 6. Distribution ratios for three chaotropic anions in three different $(\text{NH}_4)_2\text{SO}_4/\text{PEG-2000}$ ABS vs. their negative ΔG_{hyd} .

ratios for three chaotropic ions versus their $-\Delta G_{\text{hyd}}$. The three lines represent partitioning studies carried out at three different molal concentrations of $(\text{NH}_4)_2\text{SO}_4$. (The value of ΔG_{hyd} for TcO_4^- was interpolated from those given for MnO_4^- and ReO_4^- in Ref. [38].) The less negative the value of ΔG_{hyd} , the more chaotropic (water-destructuring) the ion is and the more it prefers the hydrogen-bonding environment of the PEG-rich phase.

3.2. Category 2: extraction of negatively charged metal complexes of inorganic ions

Soft metal ions with relatively high formation constants for anionic halide or pseudohalide complexes can be partitioned from a salt-rich to the PEG-rich phase in ABS [17,22]. Fig. 7 graphs the data for two representative ions, Cd^{2+} and Pb^{2+} . In the absence of a halide extractant, the distribution ratios are low (0.066 and 0.10, respectively), corresponding to the large negative value of ΔG_{hyd} for these ions. Addition of a halide extractant, however, increases D_M in the order $\text{Cl}^- < \text{Br}^- < \text{I}^-$. In addition, the distribution ratios for Cd^{2+} are higher than those observed for Pb^{2+} .

The efficacy of the halide extractants appears to be

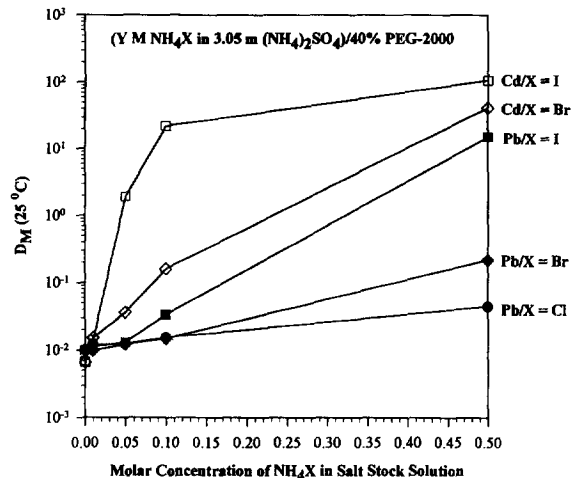


Fig. 7. Metal ion distribution ratios vs. the molar concentration of NH_4X in the salt stock solution.

related to their relative softness. The larger halides are more polarizable and form stronger complexes with soft metal ions [39,40]. This is also reflected in the ΔG_{hyd} for these ions; the softest, most polarizable I^- ion has the smallest absolute value of ΔG_{hyd} . We assume then that the metal halide complex anions, surrounded by the polarizable iodide ions, are chaotropic and thus partition to the PEG-rich phase.

This partitioning process must proceed via two steps. First, the stability constants for the formation of the complex ion must be large enough in the ABS matrix for formation of the appropriate ion, then, the complex metal ion, now chaotropic, partitions to the PEG-rich phase. A plot of distribution ratios as a function of $\log K$ values for the formation of MX_4^{2-} is presented in Fig. 8. Although not necessarily linear, there is a general increase in D as $\log K$ increases. This trend, however, could simply be due to the increasing chaotropic nature of the MX_4^{2-} ions as X goes from Cl^- to I^- . The softest I^- ion forms the strongest complexes with Cd^{2+} and Pb^{2+} compared to Br^- or Cl^- . The same characteristics that lead to stronger metal complexes also result in more water-destructuring character.

In lieu of reliable values of ΔG_{hyd} for the MX_4^{2-} ions, it is possible to test our hypothesis on the increasing chaotropic nature of the ions by correlating the distribution ratios with charge density of the MX_4^{2-} ions (Fig. 9). If we make the crude approxi-

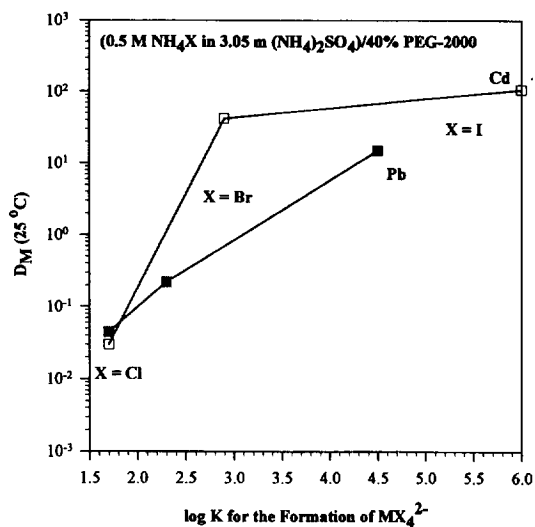


Fig. 8. Metal ion distribution ratios vs. log K values [39,40] for the formation of MX_4^{2-} .

mation that ΔG_{hyd} is related to charge density and becomes more negative as charge density increases, we have a reasonable explanation for the trend in D_M versus halide. A drawback to this explanation is that it does not relate, for example, iodide complexes of different metal ions, thus at present, it is difficult to explain the relationship between complexes of different metal ions. However, the exclusion of the

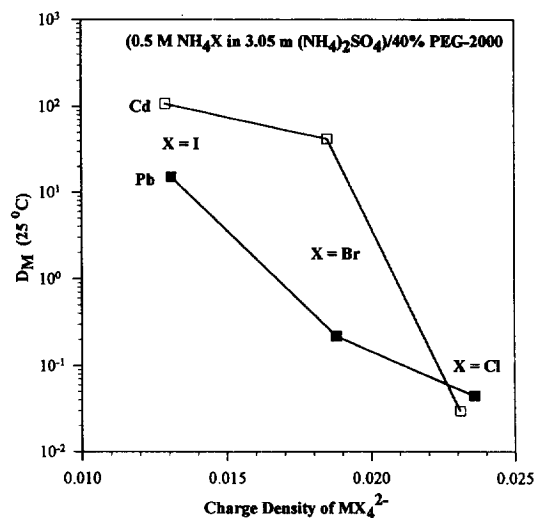


Fig. 9. Metal ion distribution ratios vs. the charge density of MX_4^{2-} .

increasingly water-structuring halide complexes from the salt-rich phase affords a reasonable explanation of the observed partitioning data and is in keeping with the current models of solute partitioning in ABS. Choice of extractant must then consider: (1) is the resulting metal complex likely to form in the ABS matrix? and (2) how chaotropic will the resulting complex be? We are currently investigating a variety of soft to border-line soft metal ions and we are including pseudohalides to further our understanding of this category of partitioning behavior.

3.3. Category 3: extraction using a water-soluble complexant

Hard metal ions require a different approach for extraction. In traditional oil–water solvent extraction, complexing ligands are often necessary to coordinate the metal ion and give it a hydrophobic shell prior to partitioning to an organic solvent. To utilize this approach in PEG-ABS, water-soluble complexing ligands are required. Earlier work from our laboratories has shown that metal ion recognition can be used to selectively extract hard metal ions [41,42]. 18-Crown-6 was used as an extractant to study the partitioning of several Group 1 and 2 ions in an ABS formed by the addition of 20% NaOH to 40% PEG-2000. In the absence of crown ether, the distribution ratios are all very low, with their general order of partitioning following their relative ΔG_{hyd} values [43]. Upon addition of 18-crown-6 and an extractable anion (NO_3^-), a positive correlation was found between the log K (formation constants for the M^{n+} / 18-crown-6 complexes in water) values, the distribution ratios, and the effective ionic radii [41].

We have also been able to extract actinide ions by the addition of dye extractants [18]. This work and that by Spivakov et al. [9–11] have shown that water-soluble dyes that partition quantitatively to the PEG-rich phase, and which form strong complexes with certain actinide ions, can effectively extract the actinides from high ionic strength media. Unfortunately, the dyes used thus far are expensive and highly toxic, leading us to search for more effective ways to partition these ions.

In the absence of extractants, the partitioning of actinides also follows the same trends in hydration parameters. We have shown, for example, a good

correlation between D_{An} and the standard enthalpy of formation of the actinide aquo ions [44]. The availability of reliable, single-source values for ΔG_{hyd} of these ions has hampered our efforts to fully characterize this correlation.

Gibbs free energy of hydration is certainly not a universal parameter to predict distribution ratios. This is especially apparent in this category where few studies have been carried out to determine the thermodynamics of the interaction of ligand–metal complexes with water. It may be possible, however, to correlate the partitioning behavior with a hydrophobicity parameter of the type obtained by looking at the complex partitioning between octanol and water. We are currently pursuing these investigations.

4. Conclusions

In order to move PEG-ABS for metal ion separations out of the laboratory and into the field, we must have predictive tools for the partitioning behavior observed. In addition, it will be necessary to introduce traditional solvent extraction scientists to the many variables associated with this technology. Both of these steps will require a better understanding of the major factors governing metal ion partitioning in PEG-ABS. The work reported here has shown a strong correlation between fundamental parameters of hydration and the observed distribution ratios, but this is only a small step towards a true understanding of the processes involved. Our future research will be aimed at achieving this understanding.

Acknowledgments

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