Partitioning behavior of Group 1 and 2 cations in poly(ethylene glycol)-based aqueous biphasic systems

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Abstract

The partitioning behavior of several Group 1 and 2 cations was investigated in poly(ethylene glycol) (PEG)-based aqueous biphasic systems. All of these metal ions prefer the salt-rich phase over the PEG-rich phase with distribution ratios all well below one regardless of the system investigated. The relative salting-out ability of the individual cations can be directly correlated to their Gibbs free energy of hydration (ΔG_{hyd}). In addition, the relative magnitude of the distribution ratios for these metal ions can also be explained in terms of ΔG_{hyd}.

Keywords: Partitioning; Cations; Metal ions; Poly(ethylene glycol)

1. Introduction

The Group 1 and 2 metal ions are of particular interest from a separations standpoint as several radioisotopes of these metals are present in relatively large concentrations in real-world waste systems. For instance, it is estimated that the major radiological and thermal hazards which are present in the highly alkaline underground radioactive waste storage tanks at the Westinghouse Hanford site are due to the presence of radioactive strontium and cesium isotopes (namely ^{90}Sr and ^{137}Cs) [1]. The presence of these ions in significant concentrations in these high ionic strength waste solutions may interfere with separation processes designed to selectively remove other components such as pertechnetate or the actinides. Given the fact that the separation of Group 1 and 2 cations from alkaline media is difficult using traditional solvent extraction systems, the development of new techniques is desirable.

Aqueous biphasic systems (ABS) formed by the addition of an inorganic salt to a water-soluble polymer offer many unique advantages when compared to traditional oil–water solvent extraction systems for the separation of metal ions. Since both phases are entirely aqueous the use of organic diluents is not necessary to maintain a biphasic system. A variety of non-toxic, inexpensive water-soluble polymers [e.g., poly(ethylene glycol)s (PEGs)] can be utilized in combination with a range of relatively innocuous inorganic salts. In addition, these systems can be fine-tuned to achieve phase separation characteristics that are comparable with traditional systems.

We are investigating the use of PEG-based

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ABS for the extraction of metal ions from high ionic strength solutions containing such anions as OH^-, SO_4^{2-}, CO_3^{2-}, and PO_4^{3-} [2–11]. (We have recently reviewed the limited literature in this area in Ref. [4].) The Group 1 and 2 cations pose an interesting problem in terms of partitioning in ABS in that it is their salts that are often used to form the two-phase system.

We have previously investigated the use of some water-soluble complexants to facilitate extraction of these metal ions from the salt-rich to the PEG-rich phase. Crown ether ligands were an obvious starting point because of their known size selectivity for hard metal ions as well as for their successful use in traditional Group 1 and 2 solvent extraction systems [12,13]. We have demonstrated that simple crown ligands, such as 18-crown-6, can be used to partition these metals from the salt-rich phase to the PEG-rich phase in ABS when large amounts of an extractable counteranion are present [2]. We also demonstrated with this work that traditional ideas of molecular recognition can hold in ABS, although better extractants are needed that not only selectively complex specific Group 1 and 2 metal ions, but also quantitatively partition to the PEG-rich phase.

A better understanding of the partitioning behavior of Group 1 and 2 cations in ABS is needed. From a fundamental viewpoint we are attempting to add to the very limited database of knowledge which exists concerning metal ion partitioning in ABS. From a practical viewpoint the Group 1 and 2 cations are present in large quantities in many real-world waste systems such as the Hanford site tank wastes previously mentioned. These wastes are rich in many phase forming ions such as OH^- and CO_3^{2-}. We have recently shown that an ABS can be formed by simply contacting a simulated Hanford tank waste with an aqueous PEG solution [10]. More excitingly, however, technetium (as TcO_4^-) can be partitioned from this simulated waste almost quantitatively to the PEG-rich phase in the absence of any other added complexants. The fate of the Group 1 and 2 cations also present in the waste streams is not entirely clear, but given the utility of ABS for separations from alkaline

and complex matrices, it is imperative to gain a thorough understanding of how matrix components behave in these systems.

2. Experimental

Poly(ethylene glycol), average molecular mass 2000, K_3PO_4, $(NH_4)_2SO_4$, K_2CO_3, and NaOH were purchased from Aldrich (Milwaukee, WI, USA) and used without further purification. All water was distilled and purified using a Barnstead deionization system. Radiotracer solutions of ^{22}Na, ^{86}Rb, ^{45}Ca, ^{85}Sr, ^{133}Ba (DuPont NEN Research Products, Boston, MA, USA) and ^{45}Ca (Amersham, Arlington Heights, IL, USA) were prepared and stored in dilute nitric acid.

The phase diagrams were determined by turbidity titration using the method of Albertsson [14]. The metal ion distribution ratios were performed radiometrically as follows. For each measurement a system was prepared by mixing equal aliquots of a PEG-2000 stock solution and a salt stock solution of the reported concentration. The system was equilibrated by vortex-mixing for 2 min followed by 2 min of centrifugation at 2000 g. A tracer quantity of a radionuclide of the metal ion of interest was added to this equilibrated ABS. This system was then vortex-mixed for 2 min followed by 2 min of centrifugation at 2000 g. The phases were separated and placed into separate containers. Equal aliquots of each phase were removed for standard radiometric analysis. A distribution ratio was then calculated as the activity (counts per minute) in the PEG-rich phase divided by the activity in the salt-rich phase. Although radiometric distribution ratios are usually accurate to within ±5%, due to the complexity of the systems we report a conservative accuracy of ±10%.

3. Results and discussion

The phase diagram is perhaps the simplest tool which can be used to interpret overall behavior in an ABS. The phase diagram gives such useful

information as the relative amounts of biphase forming components needed to maintain a two-phase system, as well as the relative ratios of each component in either phase. How these variables affect the partitioning of metal ions in a given ABS are, however, not well known.

The distribution ratios for a series of Group 1 and 2 cations in sulfate, carbonate, and hydroxide–PEG-2000-based ABS are presented in Table 1. In light of the fact that salts of Group 1 and 2 cations are commonly used to salt-out PEG, it is not surprising that these metal ions prefer the salt-rich phase in an ABS. By examining a series of phase diagrams one can determine the relative salting-out ability of both cations and anions. Intuitively, the better a given species is at salting-out PEG, the more it will prefer the salt-rich phase and the lower its distribution ratio will be.

Phase diagrams for a series of Group 1 (and ammonium) salt–PEG-2000 ABS are presented in Fig. 1. The ability of a given salt to form a biphase when contacted with aqueous PEG has been previously correlated with fundamental thermodynamic parameters such as hydration enthalpy [15]. We have recently begun to investigate the relationship between salting-out ability and Gibbs free energy of hydration (ΔG_{hyd}) [11]. The more water-structuring (and hence the better at salting-out PEG) a given species is, the more negative its ΔG_{hyd}. Thus the relative ordering in salting-out ability of both the cations and anions present can be directly correlated with their ΔG_{hyd} values.

In the Fig. 1 example, it is easy to see that the

Table 1
Distribution ratios for Group 1 and 2 cations in sulfate, carbonate, and hydroxide–PEG-2000 aqueous biphasic systems

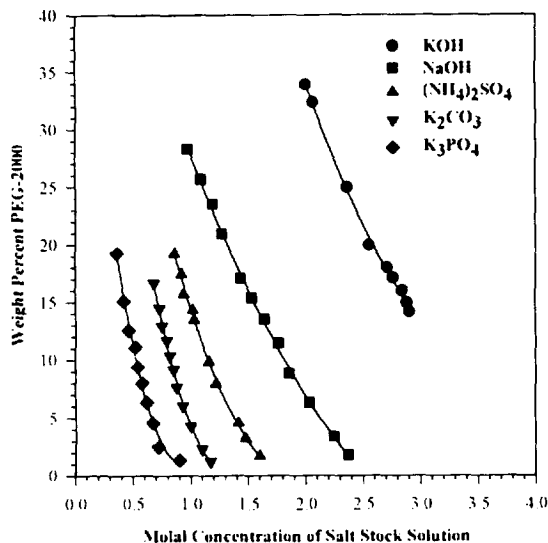|	$(NH_4)_2SO_4$ system	K_2CO_3 system	NaOH system
D_{Na}	0.027	0.017	0.098
D_{Rb}	–	–	0.31
D_{Cs}	0.051	0.049	0.33
D_{Ca}	0.0054	0.0022	0.020
D_{Sr}	0.0074	0.0043	0.022
D_{Ba}	0.012	0.0035	0.045

Fig. 1. Phase diagrams for a number of Group 1 (and ammonium) salt–PEG-2000 aqueous biphasic systems.

salting-out ability of the anions follows the ordering $PO_4^{3-} > CO_3^{2-} > SO_4^{2-} > OH^-$. This ordering directly follows the anions calculated ΔG_{hyd} values (all ΔG_{hyd} data from Ref. [19]; PO_4^{3-}, -2835 kJ/mol $> CO_3^{2-}$, $-1300 > SO_4^{2-}$, $-1145 >$ OH^-, -345). The salting-out effects are additive and the cations have a contribution as well with the same arguments as offered for the anions holding true. When comparing salts having the same anion, the one whose cation has a more negative ΔG_{hyd} value is better at salting-out PEG. Thus from Fig. 1, less NaOH (ΔG_{hyd} of $Na^+ = -365$ kJ/mol) is required to salt-out PEG-2000 compared to KOH (ΔG_{hyd} of $K^+ = -305$ kJ/mol).

As mentioned previously, the distribution ratio of a given ionic species can be directly related to its relative salting-out ability in a given ABS. Species that are chaotropic (such as pertechnetate) feature ΔG_{hyd} values whose magnitudes are smaller (i.e. they are less negative). These species are thus excluded from the very ordered hydrogen bonding environment present in the salt-rich phase and reside in the PEG-rich phase. Conversely, those species which are water-structuring orient water molecules favorably which aids in the salting-out of PEG. As a result these species

reside in the salt-rich phase. With these facts in mind we chose to investigate the relationship between distribution ratio and ΔG_{hyd} in a variety of ABS in hopes of better understanding metal ion partitioning in these systems.

A plot of Group 1 and 2 metal ion distribution ratios vs. ΔG_{hyd} is presented in Fig. 2. This figure demonstrates that within a given family of metals, the distribution ratio is linearly related to the metals relative ΔG_{hyd} value. This can be explained by examining the metal ions' interaction with surrounding water molecules. Again, the more favorable a species' interaction is with surrounding water molecules (reflected by an increasingly negative ΔG_{hyd} value) the lower its distribution ratio. The opposite of this is again true and species which have increasingly less negative ΔG_{hyd} feature higher distribution ratios. This finding allows one to predict the relative ordering of distribution ratios for a given series of metals.

The correlations presented above were all investigated from ABS which are formed using Group 1 salts. We are currently studying the partitioning of these metal ions from a variety of salt systems which are not necessarily based on Group 1 or 2 salts. We believe that these correlations will hold true regardless of the nature of

the salt used thus enabling us to predict metal ion partitioning behavior in all salt-based ABS.

Another variable which effects metal ion distribution ratios in ABS is overall system composition. Increasing the concentration of either salt or PEG in an ABS is equivalent to moving toward longer tie line lengths on the phase diagram. This results in a system which features increasingly less mixing of components (i.e. less PEG in the salt-rich phase and less salt in the PEG-rich phase).

The change in relative PEG concentration between the two phases (ΔPEG) has previously been used to explain neutral solute partitioning in ABS [16–18]. We have previously shown that this behavior is also true when dealing with metal ions [8–10]. Species which distribute preferentially to the salt-rich phase (such as Group 1 and 2 metals) exhibit distribution ratios that decrease linearly with either increasing PEG or salt concentration [3]. On the other hand, species that prefer the PEG-rich phase (such as pertechnetate) increase linearly under the same conditions [8–10]. These findings may make it possible to fine-tune the separation characteristics for a given system. If for instance, pertechnetate is to be partitioned in the presence of Group 1 or 2 matrix ions, a system composition can be chosen which maximizes the TcO_4^- distribution ratio while minimizing the partitioning of the other species.

4. Conclusions

This work has demonstrated that the partitioning behavior of the Group 1 and 2 cations in ABS can be directly correlated with fundamental thermodynamic data. Group 1 and 2 metal ion distribution ratios decrease with increasingly more negative ΔG_{hyd} values. This is a result of the same interactions with surrounding water molecules which are responsible for two-phase formation in these systems. One possible novel application of this finding may be the prediction of ΔG_{hyd} values for metal ions which are difficult to measure (e.g., Fr^+ or Ra^{2+}) by measuring their distribution ratios in ABS.

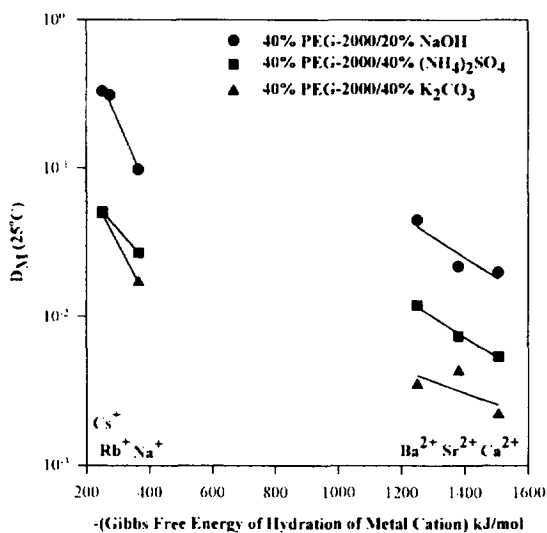Fig. 2. Distribution ratio vs. negative Gibbs free energy of hydration (ΔG_{hyd} values from Ref. [19]).

Although some of the findings presented in this study may seem elementary in nature, they are important due to the lack of explanations present in the literature regarding metal ion partitioning in ABS. The work presented here enables us to predict the relative ordering of Group 1 and 2 partitioning in PEG-based ABS by simply examining fundamental thermodynamic data. While these metal ions themselves do not partition to the PEG-rich phase in ABS, it is hoped that correlations such as the ones presented in this study will help to further develop separation schemes for metal ions in the presence of these matrix ions. It is also hoped that these ideas may lead to predictive models which may be applied not only to metal ions, but to other species (such as organic extractants) as well. The development of such tools are imperative if ABS are to be exploited to their full potential for metal ion separations and this goal is currently being pursued in our research effort.

Acknowledgement

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