The crown ether extraction of group 1 and 2 cations in polyethylene glycol-based aqueous biphasic systems at high alkalinity

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<u>Abstract</u>. The crown ethers 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5) and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) have been utilized to study the partitioning of Group 1 and 2 cations between aqueous layers in an aqueous biphasic system formed by the salting out of PEG-2000 (polyethylene glycol of 2000 average molecular weight) with NaOH. Partitioning to the PEG-rich phase is generally only achieved by the addition of high concentrations of $NaNO_3$. In the presence of NO_3^-, the metal ion partitioning results correlate with the log K values for 18-crown-6 complexation in H_2O. This trend does not hold for 15-crown-5.

INTRODUCTION

Traditional liquid/liquid extraction is based on the partitioning of one or more metal ions between a water immiscible organic solution (usually an aliphatic or aromatic hydrocarbon) and an aqueous phase. In certain situations these traditional systems are not applicable and perform poorly, e.g., extractions involving alkaline media. Aqueous mixtures of two dissimilar polymers or of a polymer and an inorganic salt are also known to separate into two distinct immiscible aqueous layers, each of which consists of 80% or more water on a molar basis (ref. 1). Because of the presence of high concentrations of water in each phase, solutes do not have to be dehydrated for partitioning to occur and water soluble extractants may be utilized.

While these systems have been used for over forty years for the separation of biomaterials such as proteins and blood cells (ref. 2), surprisingly little research has gone into using these biphasic systems for the separation of metal ions (ref. 3-12). (We have recently published a review of this literature and our early work in the field (ref. 13).) We became interested in this field as a result of our work on the complexation chemistry of low molecular weight PEGs with salts of the lanthanides (ref. 14-17), La, Y, Th (ref. 18), U (ref. 19,20), Bi (ref. 21,22), Pb (ref. 23), Gd (ref. 23), and Hg (ref. 24). The observation of biphasic systems formed by the addition of a PEG solution and an inorganic salt solution led us to the literature and eventually to initiate a research program to study metal ion partitioning in aqueous biphasic systems.

Beyond the obvious benefits of learning about a new area of chemistry, aqueous biphasic systems based on PEGs offer the potential for cleaner, cheaper separations. The PEGs are water soluble, inexpensive, nontoxic, and biodegradable. Toxic, flammable diluents are eliminated, thus improving the safety of the process, while at the same time drastically reducing overall hazardous waste generation. In addition, these systems allow metal ion separations not accessible with traditional extraction systems.

We have recently utilized these aqueous/aqueous systems to extract a variety of metal ions from the salt-rich to PEG-rich phase either 1) by the addition of a

water soluble complexant which preferentially distributes to the PEG-rich phase (ref. 25), 2) by the addition of an inorganic complexing anion (ref. 26), or 3) via extraction into the PEG-rich phase without an added component (ref. 13).

This presentation focuses on the extraction of Group 1 and 2 cations from highly alkaline media. We learned from a paper by Goddard (ref. 27) that NaOH will salt out PEGs to form biphasic systems. We also knew that certain Group 1 and 2 cations (e.g., Sr^{2+} and Cs^+) present in highly alkaline waste storage facilities posed severe radiological and thermal hazards (ref. 28). The selective removal of these ions directly from the alkaline media is difficult with traditional systems, so we have attempted to assess the utility of using aqueous biphasic systems. Our first attempts, described here, involved the use of water soluble crown ethers, 18-crown-6 and 15-crown-5.

EXPERIMENTAL

The aqueous biphasic systems studied were always prepared by the addition of equal aliquots of a NaOH salt stock solution and PEG-2000 stock solution. The reference system was prepared with a 20% NaOH stock and 40% PEG-2000 stock solution. When a crown ether was used as an extractant it was diluted to a known molarity with 40% PEG-2000 to give the new PEG stock solution. When sodium nitrate was used, it was diluted to a known molarity with 20% sodium hydroxide to give the new salt stock solution. After addition of equal aliquots of each stock solution the systems were equilibrated prior to use by vortexing for 2 min. followed by 2 min. of centrifugation.

Tracer quantities of ^{133}Ba, ^{137}Cs, ^{85}Sr, ^{86}Rb, ^{45}Ca, and ^{22}Na were added to each system followed by 2 min. of vortexing and 2 min. of centrifugation. The phases were separated and equal, measured aliquots of each were removed for radiometric counting. All distribution ratios were measured at 25°C and are defined as D_M = (activity (cpm) in the PEG-rich phase)/(activity (cpm) in the salt-rich phase).

To determine the distribution ratios for the crown ethers, 1 mL of 1.0M 15-crown-5 or 18-crown-6 in 40% PEG-2000 was vortexed for 2 min. with an equal volume of 20% NaOH stock solution. Phases were disengaged by centrifuging for 2 min. and were then quantitatively separated. Both the PEG-rich and salt-rich phases were washed with four 1 mL aliquots of hexane and the washes collected into two 5 mL volumetric flasks. The hexane was evaporated by boiling and the residues diluted to 5 mL with $CHCl_3$. Aliquots were then removed for gas chromatographic analysis. The D values were calculated as the ratio of the integrated peaks (PEG-rich wash/salt-rich wash). The crown ether distribution ratios were also determined for the systems (1.0M $NaNO_3$ in 20% NaOH) + (1.0M crown ether in 40% PEG-2000). The values obtained without NO_3^- present (D_{15C5} = 0.70, D_{18C6} = 0.85) were lower than those observed with NO_3^- (D_{15C5} = 1.1, D_{18C6} = 1.0).

Radiometrically determined D values were determined using ^{22}Na for 15-crown-5 and ^{85}Sr for 18-crown-6. The crown ethers in $CHCl_3$ were contacted with a 1.0M $HClO_4$ solution and spiked with the respective nuclide. The solutions were vortexed and then centrifuged for 1 min. each. Phases were separated and a measured aliquot from each phase submitted for radiometric analysis. The metal ion distribution ratio was determined as above. Crown ether D values were then calculated as the ratio of the metal ion distribution ratios (without NO_3^- present D_{15C5} = 0.71, D_{18C6} = 0.71, with NO_3^- present D_{15C5} = 1.0, D_{18C6} = 1.8).

For the phase diagram, the binodial for each system was determined by turbity titrations according to the method of Albertsson (ref. 1). The concentrations of sodium hydroxide in the salt-rich phase and the PEG-rich phase were calculated by determining the distribution ratio of ^{22}Na radiometrically.

DISCUSSION

A phase diagram for the NaOH/PEG-2000 system is presented in Fig. 1. The curve represents the binodial, below which compositions result in a single phase and above which aqueous biphasic systems are observed. In this system PEG

preferentially distributes to the top phase and is thus represented as the ordinate. The straight line connecting two nodes (points A and C) on the binodial is a tie line. Preparing a system by adding the individual components in amounts anywhere along the tie line will result in a total system composition represented by point B on the tie line, and individual phase compositions represented by the nodes. The approximate phase ratio can be estimated as the ratio of the length along the tie line from the upper phase composition to the system composition over the system composition to the lower phase (AB/BC). Concentrations of solutes in each phase are independent of phase volume (ref. 1,2).
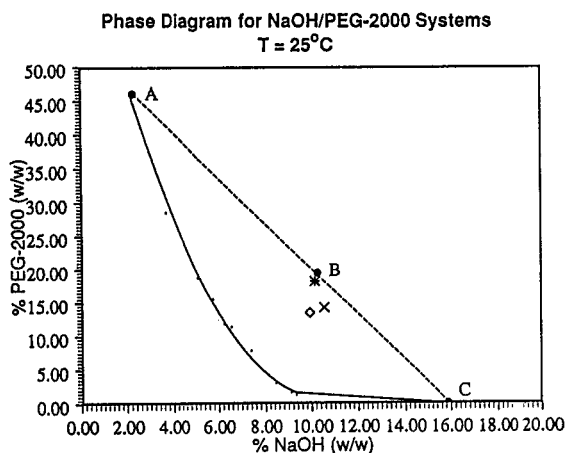

Phase Diagram for NaOH/PEG-2000 Systems
T = 25°C

Fig. 1. The four system compositions represented by point B were prepared by equal additions of: • — 20% NaOH + 40% PEG-2000; X — 20% NaOH + (1.0M 15-crown-5 in 40% PEG-2000); ◊ — 20% NaOH + (1.0M 18-crown-6 in 40% PEG-2000); * — (1.0M NaNO₃ in 20% NaOH) + 40% PEG-2000.

D_M vs. [18-Crown-6]
20% NaOH + PEG-2000 System

Fig. 2.

We have shown that addition of large amounts of NaNO₃ or crown ether do not significantly change the position or nature of the binodial. Our experimental procedure of diluting NaNO₃ or crown ether to volume with the stock solutions does however, change the starting system compositions (point B, Fig. 1) which in turn alters the percent composition of each equilibrium phase. Further work will be necessary to determine the relationship between these system compositions and the observed partitioning behavior.

Phase separation times are highly dependent on system composition and temperature, however, dispersion numbers (ref. 29) are comparable to many oil/water systems in use today. The dispersion number is defined as $N_{Di} = (1/t_B)(\Delta Z/g)^{1/2}$ where N_{Di} is the dispersion number, t_B is the time needed for phase disengagement to result in a constant height interface, ΔZ is the total system height (cm), and g is the gravitational constant (981 cm/s²). N_{Di} values for the systems reported here include 1.77 x 10⁻⁵ (25°C), 2.02 x 10⁻⁴ (50°C) (20% NaOH + 40% PEG-2000 system), 2.83 x 10⁻⁵ (25°C), 3.2 x 10⁻⁴ (50°C) (1.0M NaNO₃ in 20% NaOH + 40% PEG-2000 system), and 3.66 x 10⁻⁴ (50°C) (20% NaOH + 1.0M 18-crown-6 in 40% PEG-2000 system). The last system does not disengage fully at 25°C after 1 h, however, as in all three systems, phase disengagement dramatically improves with increasing temperature.

Crown ethers were chosen as extractants because of their known size selectivity and utility in traditional solvent extraction of Group 1 and 2 cations. 18-Crown-6 and 15-crown-5 have high water solubilities and are readily available and thus were chosen for our initial investigations. Unfortunately, the crown ethers do not distribute quantitatively to the PEG-rich phase, a condition that must be met when extractant choice is optimized. The distribution ratio for 18-crown-6 is less than one, so while a significant amount of the ether is in the PEG-rich phase, most of it partitions to the salt-rich phase. 15-crown-5 partitioning is slightly lower. Increasing the amount of NaNO₃ present (from 0 to 1.0M) improves these D values to near one.
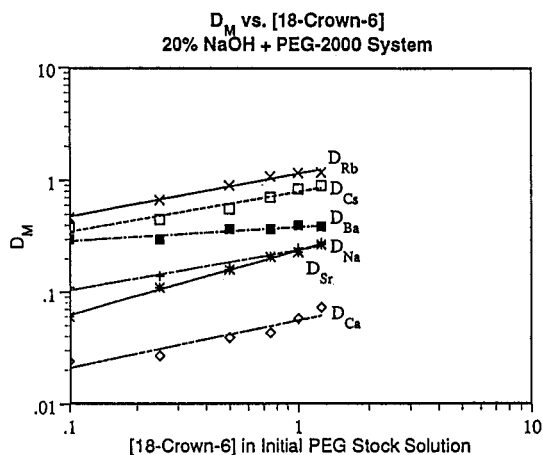
In the absence of an extractant, the distribution ratios for Group 1 and 2 cations between aqueous layers in the 20% NaOH + 40% PEG-2000 system are very low: D_{Na} - 0.098, D_{Rb} - 0.31, D_{Cs} - 0.33, D_{Ca} - 0.020, D_{Sr} - 0.022, D_{Ba} - 0.045. The addition of 18-crown-6 in a 1.25M concentration (in the initial 40% PEG-2000 stock solution) results in a distribution ratio just above one for Rb (Fig. 2). Cesium shows a similar extractant dependence with a slightly lower D_{Cs} value as compared to rubidium. Barium shows a flat extractant dependence while sodium is poorly extracted. The Group 2 metals Sr and Ca show lower distribution ratios compared to the Group 1 elements with D_{Sr} - 0.27 at 1.25M 18-crown-6 and D_{Ca} - 0.070 under similar conditions. The extractant dependence slopes range from 0.12 (Ba) to 0.38 (Rb), perhaps due to the low observed D_{CE} values.

Distribution ratios can be greatly increased by the addition of $NaNO_3$. A system with 1.0M $NaNO_3$ (in the initial salt stock solution) gives a D_{Rb} value of 3.1 with the 1.25M 18-crown-6 PEG solution. D_{Ba} and D_{Cs} are both above one for this system while D_{Sr} and D_{Na} are still below one. Increasing the $NaNO_3$ concentration to 2.0M gives a D_{Ba} value of 7.4 while D_{Rb} increases to 4.2 (Fig. 3). D_{Cs} and D_{Sr} are above one, while sodium is the only metal not extracted. The use of 15-crown-5 in this basic system is much less effective with no distribution ratios above one and essentially flat extractant dependencies (Figs. 4,5).
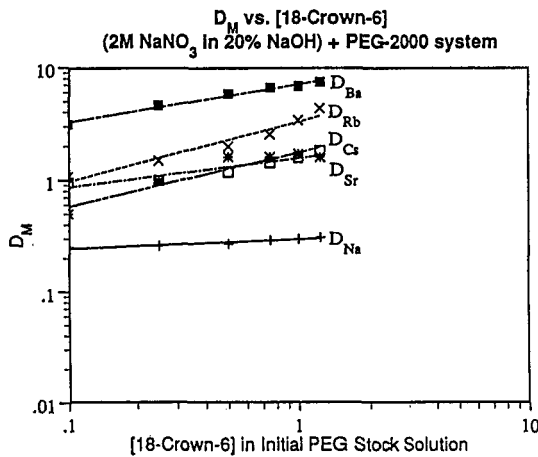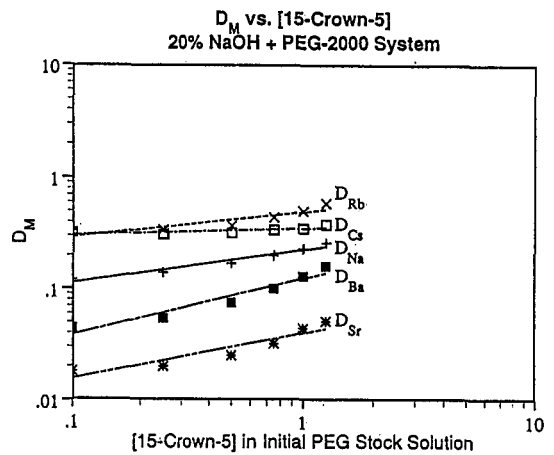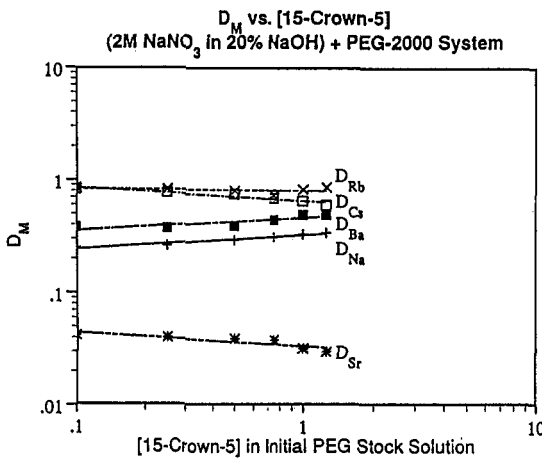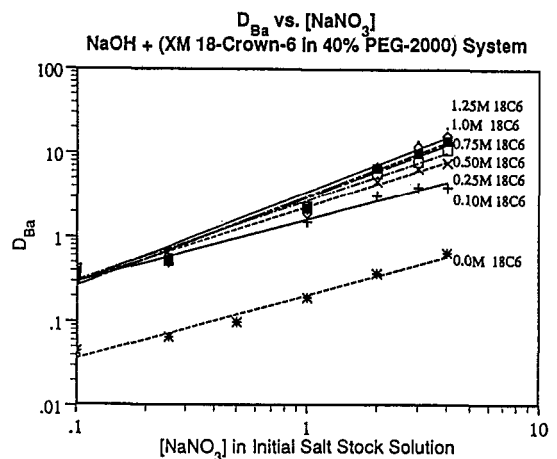

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

The highest distribution ratios are observed for Ba^{2+}. A closer look at the partitioning of this ion reveals a strong influence from NO_3^- concentration. The dependence of D_{Ba} on concentration of $NaNO_3$ in the initial salt stock solution is depicted in Fig. 6 for seven different concentrations of 18-crown-6 in the initial PEG stock solution.

The sodium ion is least affected by addition of NO_3^- or crown ether. Distribution ratios have a very narrow range between 0.1 and 0.35 despite the wide ranging conditions. There is very little difference between 15-crown-5 with its better fit for Na^+ and the larger 18-crown-6. This is in keeping with our observation that the addition of 18-crown-6, 15-crown-5, and $NaNO_3$ does not drastically alter the binodial for the NaOH/PEG-2000 system.

For one system studied, ($NaNO_3$ in 20% NaOH) + (18-crown-6 in 40% PEG-2000), there is an excellent correlation between the log K values for crown ether complexation in H_2O (ref. 30) with the observed metal cation distribution ratios. A plot of both D_M and log K vs. effective ionic radius (ref. 31) reveals maxima at Ba^{2+} (Fig. 7). This would seem to indicate that the ion size/cavity size relationship can hold for crown ether extraction in aqueous biphasic systems. In the absence of $NaNO_3$ this relationship does not hold and instead a small general increase in D_M is observed with increasing r_{ion} (or decreasing hydrated radius).
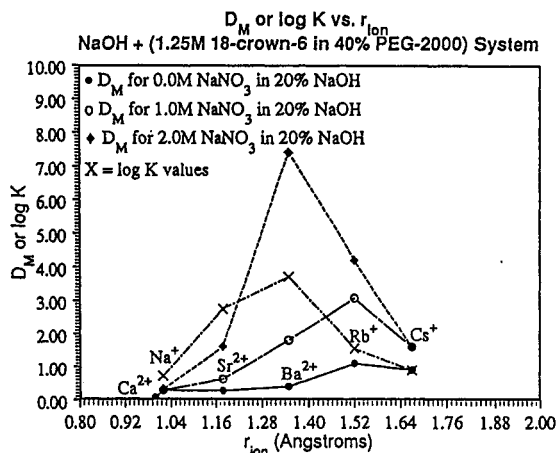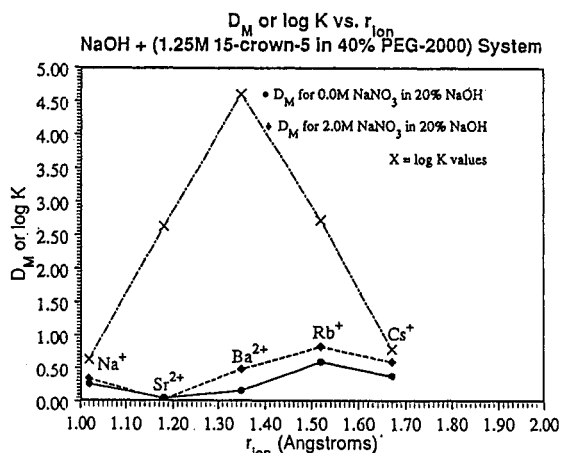

Fig. 7.

Fig. 8.

The log K values for 15-crown-5 complex stability constants (ref. 30) also show a maximum at Ba^{2+} when plotted against r_{ion}, however, the same correlation with D_M is not observed. In the presence or absence of $NaNO_3$ the D_M values generally increase slightly with increasing effective ionic radius (Fig. 8). The D_M values obtained for the systems with $NaNO_3$ are slightly higher than those without but there is no indication of the cavity size/ion size relationship observed for 18-crown-6.

CONCLUSIONS

This work, though preliminary in nature, has shown that crown ethers can be used to extract Group 1 and 2 cations from highly alkaline media utilizing PEG-based aqueous biphasic systems. The necessity to add large amounts of NO_3^- anion is not necessarily troubling since actual waste solutions with OH^- and NO_3^- levels of 3M and above are actually known (ref. 28). We have also shown that the biphasic systems can withstand the addition of large amounts of NO_3^- and crown ether without changing the fundamental nature of the biphase itself. This opens the door for further work investigating a wide variety of salts and extractants.

Three points regarding this work need to be kept in mind. First, the crown ether choice has not been optimized. It would be preferable to have an extractant that is quantitatively partitioned to the PEG-rich phase. Research is underway in our group to synthesize such macrocyclic ligands. Second, our experimental procedure of diluting the crown ether to volume with 40% PEG-2000 to prepare the PEG stock solution, lowers the total PEG-2000 present in the final system (see Fig. 1). Further research is needed to correlate total system composition with partitioning behavior. Third, the observed distribution ratios do not always follow the normal cavity size/ion size relationships commonly observed in crown ether extractions (e.g., the 15-crown-5 results). This underscores the need to fully investigate the partitioning chemistry and understand the fundamental parameters of this process. This forms the basis for our current research effort in this area.

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