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Affinity Partitioning of Metal Ions in Aqueous Polyethylene Glycol/Salt Two-Phase Systems with PEG-Modified Chelators

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ABSTRACT

The systematic partitioning of metal ions in the presence of polyethylene glycol (PEG) chelate derivatives in PEG/salt two-phase systems is described. Results show that the partitioning is enhanced significantly, and this effect is apparently based on the characteristics of binding of the chelate and the nature of the metal ion in addition to the effect of the attached PEG molecule. Previous work with PEG–iminodiacetic acid has been extended with the chelating derivatives PEG–TED [tris(carboxymethyl)ethylene diamine], PEG–TREN-Cm [carboxymethylated-tris(2-aminoethyl)amine], and PEG–ASP (aspartic acid). Their effectiveness to selectively partition the metal ions is demonstrated and discussed. The partition experiments were performed using two-phase systems of PEG (8000 MW), sodium sulfate, the PEG-chelating derivatives, and different concentrations of copper, nickel, and cobalt as model metal ions. Partition coefficients (ratio of top to bottom metal concentrations) greater than 1 were obtained for the metal ions with all the chelating derivatives tested. Selective enhancement of partitioning was observed in all cases. Based on the experimental results and theoretical principles, the method shows potential as an alternative mode to remove efficiently and selectively metal ions from solutions using aqueous two-phase systems and PEG–chelate derivatives.

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INTRODUCTION

Although aqueous two-phase separation has been known for quite some time, as early as 1896 by Biejerink (1), it was not until the rediscovery of the phenomenon in 1956 by Albertsson when its regular application as a purification technique started (2). In the years that followed it was the pioneering work of Albertsson and collaborators that answered most of the questions relating to the newly rediscovered technique. Several studies have been carried out to determine the effect of the salt composition (3) and the molecular weight of proteins and their surface area in the partition coefficient (4, 5). Over the years, aqueous two-phase systems have become a common separation method in the biotechnology field, and the number of applications of the technique has expanded significantly.

One of the most popular aqueous two-phase systems has been the one formed by polyethylene glycol (PEG), dextran, and water; however, several other polymers, such as hydroxypropyl starch, pullulan, and polyvinyl alcohol, have been used successfully to replace dextran, a relatively high-cost polymer (6). Some cellulose derivatives like methyl cellulose and ethylhydroxyethyl cellulose have been utilized instead of PEG to form aqueous two-phase systems at low polymer concentrations in large-scale separations (7). A number of PEG/salt systems using sodium, magnesium, and ammonium sulfate, potassium phosphate, and sodium carbonate salts have also been reported (8).

A measure of the suitability of the separation of a particular molecule in a given two-phase system is its partition coefficient (*K*). This value is the ratio of concentrations in the top and bottom phases for the molecule. The success of aqueous two-phase systems in the bioseparations field lies in the fact that most biomolecules partition favorably into one phase, or its partition coefficient can be modified by changing some conditions in the system (9). Empirical evidence has shown that *K* is a function of the choice of phase polymers, their molecular weight, phase composition, system ionic composition, system pH, and temperature among others (10). Additionally, some physical characteristics of the molecule, like charge, hydrophobicity, size, and concentration, play an important role in the partition process (11).

Despite the fact that aqueous two-phase systems were introduced more than three decades ago, it has not been until recently that their use for the extraction of metal ions from aqueous solutions started. The first work in the area was by Zvarova et al. (12), who reported the partition coefficients of several metal ions using dyes at two different pH values. All the partition coefficients reported had a value lower than 1, ranging from 0.126 for sodium to 0.71 for indium. So far, dyes are among the most common type of chelators used in metal partitioning. In order for a particular dye to be effective in extracting metal ions, it needs to partition favorably to the top phase and have a relatively high association constant with the metal ions.

In the absence of any extractant or complexing agents, metal ions invariably tend to partition favorably to the salt phase in a polymer/salt aqueous two-phase system. However, a partition coefficient as high as 610 for technetium as the pertechnetate anion in PEG/sulfate and PEG/carbonate systems without the addition of chelating agent of any kind has been reported (13).

Most studies of metal ion partitioning in aqueous two-phase systems involve the addition of an organic extractant or an inorganic complexing agent that binds the metal ion and extracts it to the top phase. The most common inorganic anions used to increase the partition coefficient of metal ions in aqueous two-phase systems are thiocyanate, iodide, and bromide. All of these ions have been added to the system as the ammonium salt. Rogers et al. (13) provided an extensive list of references where these and other organic compounds, including dyes and crown ethers, have been employed to extract metal ions using aqueous two-phase systems.

Generally, with an increase in complexing agent there is an increase in the partition coefficient of the metal involved. Several studies have been carried out involving dyes, and for all of them there is a direct correlation between the amount of reagent added to the system and the metal extraction. In some cases an upper limit of separation is reached. It is not clear from the experiments if that limit is a feature of the system or is due to the gradual depletion of free metal ions by the complexing agent until all the available metal ions have been extracted into the top phase (13, 14).

In aqueous two-phase partitioning the selectivity of purification can be increased by introducing a ligand with affinity for the substance of interest in the system. This ligand should partition favorably to one of the phases in order for the process to be of use. In our approach, the modification of PEG with chelating ligands, which have affinity for metal ions, resulted in chelating–polymer derivatives that partition preferentially into the PEG phase of a PEG/salt aqueous two-phase system. Once the modified chelator binds the metal ion, the entire entity tends to concentrate into the PEG-forming phase, in principle as favorably as the unmodified polymer itself.

For affinity partitioning of proteins, an immense amount of work has been reported in the literature, where PEG has been modified with specific ligands including enzyme inhibitors, dyes, and lately chelating groups (15–20).

The metal-binding properties of these ligands are based on the chelating effect that some of their individual atoms display by acting as electron donors. Oxygen and nitrogen atoms in these molecules form coordination bonds with the metal ion in solution, producing a metal chelate. The IDA (iminodiacetic acid) ligand is tridentate and can form a double five-membered ring chelate with hexacoordinate metal ions, while TED (tris-carboxymethylated ethylene diamine) is pentadentate and capable of forming four five-membered rings (21). These ligands work better with transition metal ions that have several possible coordination sites and act as electron acceptors in the presence of this type of extractant.

We have taken the initiative of using PEG modified with chelating groups in an effort to enhance and increase the selectivity in the partitioning of metal ions (22). We previously reported the use of PEG–IDA as a ligand for the extraction of metals in aqueous two-phase systems (23). In this work we introduce the use of several other chelatants attached to PEG, namely tris(carboxymethyl)ethylene diamine (PEG–TED), carboxymethylated tris(2-aminoethyl)amine (PEG–TREN-Cm), and L-aspartic acid (PEG–ASP), to further study the affinity partitioning of metal ions in aqueous two-phase systems (22, 24).

EXPERIMENTAL

Materials

Polyethylene glycol (8000 MW) from Sigma Chemicals and anhydrous sodium sulfate from J.T. Baker Chemicals were used as received for the preparation of the systems.

Solutions of metals were prepared using salts, reagent grade, of $CuSO_4 \cdot 5H_2O$, $CoSO_4 \cdot 7H_2O$, and $NiSO_4 \cdot 6H_2O$ from Fisher Chemicals. The synthesis of the chelating–PEG derivatives has been described in detail elsewhere (24). Briefly, the chelating compounds IDA (iminodiacetic acid), TED [tris(carboxymethyl)ethylene diamine], Cm-TREN (carboxymethylated-tris(2-aminoethyl)amine and L-ASP (aspartic acid) were attached to polyethylene glycol (5000 MW) via the chlorinated derivative of the polymer by reaction with primary amines and after carboxymethylation of the resulting amino groups with bromoacetic acid ($BrCH_2COOH$). For the ligand L-ASP, no carboxymethylation was performed. Figure 1 shows the structure of the PEG derivatives used in this work.

Methods

All partition experiments in this work were performed in PEG/salt systems. Stock solutions of PEG were prepared by dissolving PEG (8000) in water to give a final concentration of 40% (w/w). PEG–chelator stock solutions were prepared by dissolving PEG–chelator in a solution of PEG (8000) to give a final concentration of the modified chelator of 2% (w/w)

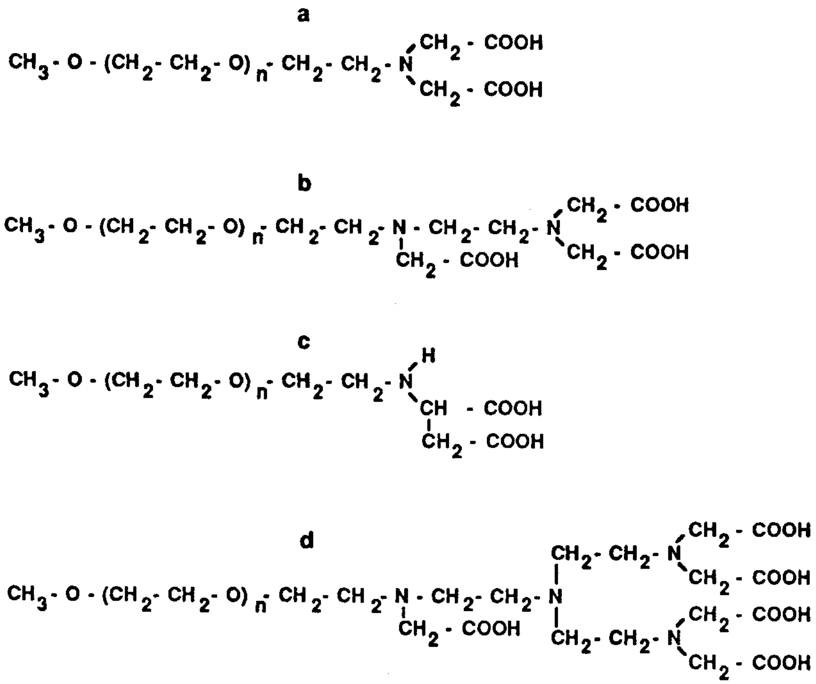

FIG. 1 Structure of the different PEG–ligands used in this work: (a) PEG–IDA, (b) PEG–TED, (c) PEG–ASP, (d) PEG–TREN-Cm.

and 38% (w/w) of PEG (8000). The salt solutions were prepared by dissolving anhydrous sodium sulfate in water to give a final concentration of 16% (w/w) in sodium sulfate.

Two-Phase Formation

Aqueous two-phase systems were prepared mixing 3.5 g of polymer stock solutions with 5.0 g of sodium sulfate stock solution. The phases were formed in plastic conical test tubes. One gram of metal solution (with a different concentration of metal for each case) was added to the freshly prepared two-phase system along with 0.5 g of deionized water to obtain systems of 10 g. The plastic test tubes were inverted 50 times, then centrifuged to speed up phase separation, and left for 20 minutes to reach equilibrium. The final concentrations of the systems prepared were 8% (w/w) in salt, 14% (w/w) in total polymer, and 0.7% in chelate–polymer and different metal concentrations. Metal dilutions of 3000, 2000, 1400, 1000, and 400 ppm, corresponding to metal concentrations of 0.326, 0.217, 0.152, 0.109, and 0.043 g/mL, respectively, were used in the experiments. After addition of all the components, the total weight of the system was 10 g and the total volume was 9.2 mL (4.9 mL in the bottom phase and 4.3 mL in the top phase). The pH of the systems was measured after addition of the metal solution and gave pH values of 6 for both phases at room temperature.

Partition Coefficient Determination

After phase separation, aliquots from top and bottom phases were withdrawn and analyzed for metal content, using flame emission spectrometry with appropriate standards in a Perkin-Elmer Atomic Absorption Spectrophotometer Model 2380.

The partition coefficient was measured as the ratio of the concentrations of metal found in the top and bottom phases.

The effectiveness of the partitioning effect with the PEG–chelators on the metal ions was estimated by measuring and comparing the partition coefficients of the tested metals in the presence and absence of the chelating-PEG derivatives (K and K_0, respectively). All the experiments were performed in duplicate.

RESULTS AND DISCUSSION

The control experiments without the chelating derivatives are summarized in Table 1. This table shows that in the absence of modified PEG, the tested metal ions (Cu^{2+}, Ni^{2+}, and Co^{2+}) remain preferentially in the salt (bottom) phase without much affinity for the PEG (top) phase. These results are in agreement with experimental data reported in the literature

TABLE 1
Partition of Metal Ions in Systems with Crude PEG

Metal concentration in the system (g/mL)	Cu^{2+} (K)	Ni^{2+} (K)	Co^{2+} (K)
0.043	0.1527	0.1527	0.1527
0.109	0.1885	0.1885	0.1189
0.152	0.1781	0.1781	0.1284
0.217	0.1885	0.1885	0.1189
0.326	0.1644	0.1644	0.0766

TABLE 2
Partition of Copper in Systems with Crude PEG and Chelatant-Modified PEG

Metal concentration in the system (g/mL)	PEG (*K*)	IDA (*K*)	TED (*K*)	TREN (*K*)	ASP (*K*)
0.043	0.1527	45.5	45.5	5.5	2.2
0.109	0.1885	9.95	2.796	0.846	1.234
0.152	0.1781	2.36	1.343	0.5820	1.0198
0.217	0.1885	1.23	0.846	0.4520	0.6929
0.326	0.1644	0.741	0.563	0.3533	0.4871

(12). Apparently this behavior is mainly due to the ionic strength provided by the higher concentration of salt in the lower phase, supplying an environment for the metal ions where ionic interactions are more significant with the water molecules than with the polymer. In the presence of chelating agents in the system and after binding, the metal ion could still remain in the lower (salt) phase unless the chelator prefers the upper (PEG) phase. The enhancing effect on metal partitioning when the modified chelator is added to the system is readily shown in Tables 2, 3, and 4. In all cases, once the modified chelator binds the metal ions, these tend to concentrate in the PEG (top) phase, obviously due to the preferential partitioning of the PEG attached to the chelator.

It can be seen that the results differ greatly with the type of chelator attached to the polymer, suggesting that the binding strength of the chelator for the metal ion is a relevant factor for effective partition and not only a function of the bound PEG molecule. This represents a significant finding since it is evident that the selectivity of extraction could be controlled by using specific chelators with more or less affinity for the target

TABLE 3
Partition of Nickel in Systems with Crude PEG and Chelatant-Modified PEG

Metal concentration in the system (g/mL)	PEG (*K*)	IDA (*K*)	TED (*K*)	TREN (*K*)	ASP (*K*)
0.043	0.1527	22	45	1.666	1.0232
0.109	0.1885	1.0185	1.5	0.562	0.4520
0.152	0.1781	0.7764	0.8937	0.423	0.2631
0.217	0.1885	0.6723	0.627	0.3525	0.3084
0.326	0.1644	0.452	0.417	0.266	0.2661

TABLE 4
Partition of Cobalt in Systems with Crude PEG and Chelatant-Modified PEG

Metal concentration in the system (g/mL)	PEG (K)	IDA (K)	TED (K)	TREN (K)	ASP (K)
0.043	0.1527	2.75	5.5	1.023	0.3548
0.109	0.1189	0.562	0.8461	0.4520	0.1885
0.152	0.1284	0.423	0.582	0.2894	0.2321
0.217	0.1189	0.3084	0.3525	0.1885	0.1885
0.326	0.0766	0.2391	0.2661	0.1885	0.1645

metal ions. The resulting partition coefficients in the presence of the chelating polymer derivatives are given in Tables 5, 6, and 7, where ΔK represents the ratio of the partition coefficients (K/K_0). These coefficients reflect the improvement in the extraction of metals into the polymer phase when the PEG derivatives are included in the system compared with systems that lack such derivatives. At lower concentration of metal ions the effect of the modified PEG was particularly significant. For copper the partition coefficient experienced an increase of 300-fold when PEG–IDA and PEG–TED were used, 40-fold with PEG–TREN-Cm, and almost 15-fold with PEG–ASP. The partition coefficient for nickel increased almost 150-fold with PEG–IDA, 300-fold with PEG–TED, 10-fold with PEG–TREN-Cm, and only 6-fold with PEG–ASP. Despite the fact that the partition coefficients for cobalt increased in the presence of the PEG derivatives, the values were lower than for nickel and copper. The higher value was for PEG–TED with a 40-fold increase while the partition observed for PEG–ASP was only about 2-fold. The partition behavior was

TABLE 5
Comparison of Partition Coefficients of Copper in Systems with Crude PEG and Chelatant-Modified PEG

Metal concentration in the system (g/mL)	IDA (ln ΔK)	TED (ln ΔK)	TREN (ln ΔK)	ASP (ln ΔK)
0.043	5.697	5.696	3.584	2.667
0.109	3.966	2.697	1.501	1.878
0.152	2.584	2.02	1.184	1.745
0.217	1.875	1.501	0.875	1.301
0.326	1.505	1.231	0.765	1.086

TABLE 6
Comparison of Partition Coefficients of Nickel in Systems with Crude PEG and Chelatant-Modified PEG

Metal concentration in the system (g/mL)	IDA ($\ln \Delta K$)	TED ($\ln \Delta K$)	TREN ($\ln \Delta K$)	ASP ($\ln \Delta K$)
0.043	4.97	5.685	2.389	1.902
0.109	1.686	2.074	1.092	0.8745
0.152	1.472	1.613	0.865	0.390
0.217	1.272	1.202	0.626	0.492
0.326	1.0114	0.931	0.481	0.481

more effective at lower concentrations of metal ions in the system, and the metals invariably were driven to the PEG phase. This behavior suggests that the partition phenomena observed in the systems is strongly influenced not only by the nature of the attached polymer (PEG) to the chelator but also is a strong function of the strength and binding affinity between the chelating derivatives and the metal ions. For instance, in all the partition experiments the concentration of PEG–chelator was only 0.7% (on a weight basis), a condition where the binding is obviously more effective at lower concentrations of the corresponding metal. This suggests that by increasing the concentration of PEG–chelate derivatives, more metal ions will be bound and thus will partition more efficiently into the desired phase according to the dissociation constant and affinity for particular metal ions.

The difference in binding strength as well as the difference in affinity characteristics of the chelating agents used in this work, cannot be ex-

TABLE 7
Comparison of Partition Coefficients of Nickel in Systems with Crude PEG and Chelatant-Modified PEG

Metal concentration in the system (g/mL)	IDA ($\ln \Delta K$)	TED ($\ln \Delta K$)	TREN ($\ln \Delta K$)	ASP ($\ln \Delta K$)
0.043	2.89	3.58	1.902	0.843
0.109	1.55	1.88	0.875	0.460
0.152	1.19	1.511	0.812	0.592
0.217	0.953	1.086	0.460	0.460
0.326	1.138	1.082	0.90	0.764

plained entirely in terms of the dentatity of the chelatants. IDA for instance, is a tridentate agent, TED is pentadentate, TREN-Cm is heptadentate, while L-ASP is tridentate. However, the binding strength difference between the metal ion and the chelatants IDA and L-ASP is very significant according to the experimental results despite the same dentatity of both chelatants. This difference can be justified in terms of the distribution in the molecule of the atoms responsible for coordination with metal ions. In this particular case the nitrogen atom in L-ASP is farther separated from its carboxylic moieties with respect to the spatial arrangement of the same atoms in IDA. Thus, based entirely on the dentatity number of the chelatants, the metal binding stability of the metal–chelate should follow the order TREN-Cm > TED > IDA > L-ASP (25). Still, there are some other factors to consider, such as the nature and number of coordination sites on the metal, the symmetry of the molecule, and the stretching effect associated with the strain energies of the chelating ligand and free metal ions (26).

Our results agree with the observations described by Hancock and Martell (26) who postulated that an increase of chelate ring size leads to an increase in complex stability. However, they also noted that an increase in chelate ring size leads to a greater reduction in complex stability with larger metal ions (e.g., Cu^{2+} (0.55 Å), Ni^{2+} (0.671 Å) and Co^{2+} (0.73 Å)), a well-known fact of coordination chemistry (27). Accordingly, the effect of chelate ring size is of significant relevance in controlling complex stability and selectivity, this apparently due mainly to steric aspects.

In Figs. 1–3 we have plotted the values of the ratio of partition coefficients [$\ln(K/K_0)$] with respect to the concentration of metals in the copper, nickel, and cobalt system, respectively. These figures show a similar behavior for all the chelating derivatives. In Fig. 1 the K/K_0 values for copper with all the ligands is presented, and a larger increase in the partition coefficient can be observed at lower concentrations of metal in the system. The same tendency can be seen in general for the four PEG derivatives as the concentration of the metal ion declines. The effect with PEG–IDA and PEG–TED on partitioning is, however, more significant. As the concentration of copper approaches a low value, the affinity of IDA and TED for the metal apparently exhibits a similar behavior. But, in general, for all other concentrations, PEG–IDA seems to have higher stability than PEG–TED. The observed behavior may be explained in terms of the match in size between the metal ion and the chelating cavity in the ligand. It can also be seen that the stability of copper for IDA is higher than for TED, TREN-Cm, and L-ASP. This effect is probably due to the nature of copper which has four planar coordination sites and probably fits more effectively in the IDA chelating cavity. The cavities in TED and TREN-

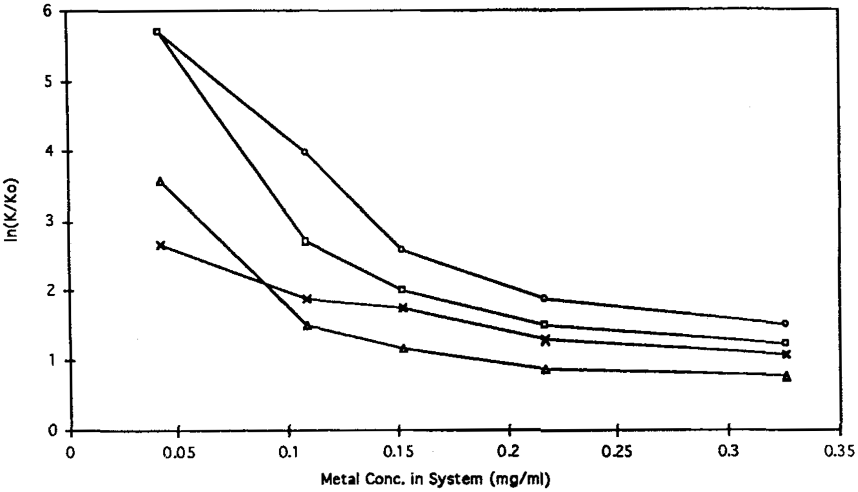

FIG. 2 Effect of PEG–chelator on partition coefficient of copper in PEG/Na_2SO_4 aqueous two-phase systems: PEG–IDA (○), PEG–TED (□), PEG–TREN-Cm (△), PEG–ASP (×).

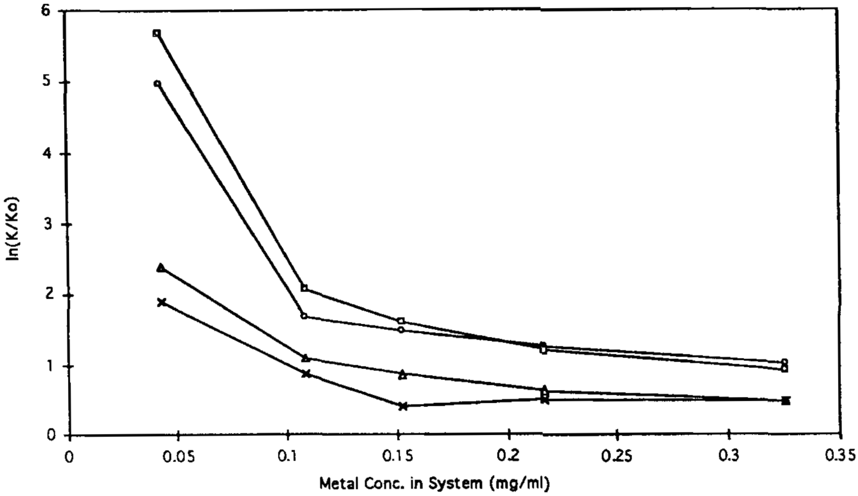

FIG. 3 Effect of PEG–chelator on partition coefficient of nickel in PEG/Na_2SO_4 aqueous two-phase systems: PEG–IDA (○), PEG–TED (□), PEG–TREN-Cm (△), PEG–ASP (×).

Cm ligands would have to stretch more to reaccommodate and bind the four coordination sites of the metal. This effect apparently results in lower stability and ability to partition the metal into the PEG phase. On the other hand, L-ASP is tridentate, the same as IDA. However, in this case one of the atoms (N) involved in the coordination effect with the metal is sterically less accessible in PEG–L-ASP than in the PEG–IDA ligand, thus reflecting a lower stability and affinity for copper.

On the other hand, when dealing with hexacoordinated metals such as nickel and cobalt, TED and TREN-Cm seem to work better than IDA and L-ASP, respectively, as shown in Figs. 2 and 3. This might be a result of the number of coordination sites that TED occupies on the metal ions. TED occupies 5 out of 6 coordination sites in nickel and cobalt unlike IDA and L-ASP, which bind via three coordination sites, although L-ASP has a weaker interaction than IDA with the metals for the reasons presented above. TREN-Cm, however, does not seem to bind very tightly to the metal, and this can be explained only on the basis of steric hindrance. Although PEG–TREN-Cm performs better than PEG–ASP, it appears that the behavior observed in Figs. 1, 2, and 3 for these two chelatants might be a consequence of the strain energy. Thus, the lower the steric strain in the complex on coordination of the ligand to the metal ion, the more sterically efficient is the ligand (26).

In Figs. 4 to 8 the values of ln (K/K_0) are plotted with respect to the total concentration of metal in the system for each individual chelating

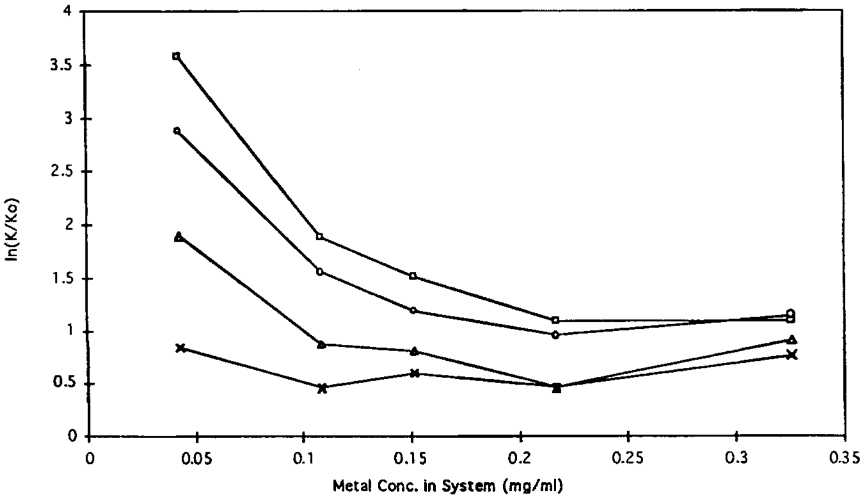

FIG. 4 Effect of PEG–chelator on partition coefficient of cobalt in PEG/Na_2SO_4 aqueous two-phase systems: PEG–IDA (○), PEG–TED (□), PEG–TREN-Cm (△), PEG–ASP (×).

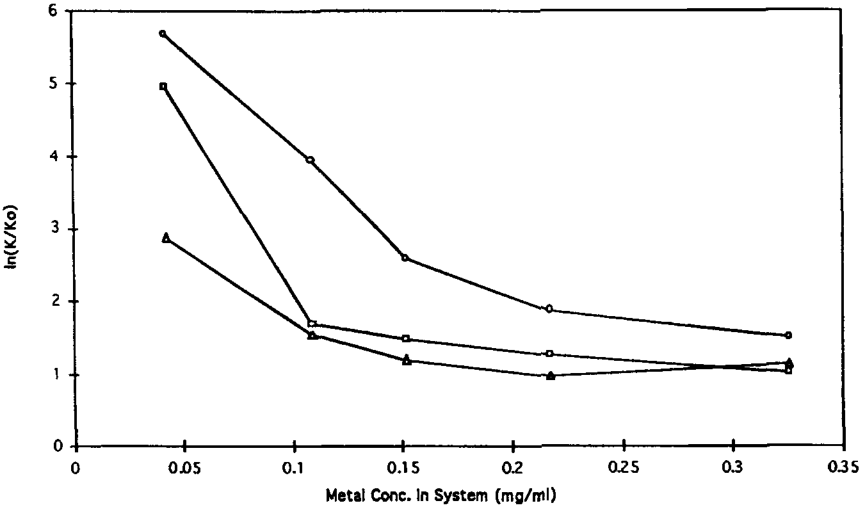

FIG. 5 Effect of PEG-IDA on partition coefficient of metals in PEG/Na_2SO_4 aqueous two-phase systems: Cu^{2+} (○), Ni^{2+} (□), Co^{2+} (△).

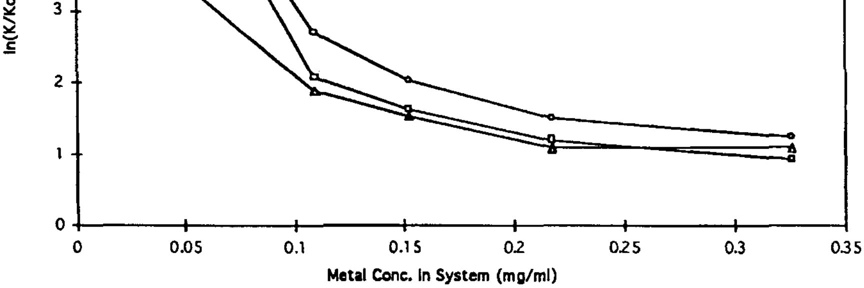

FIG. 6 Effect of PEG-TED on partition coefficient of metals in PEG/Na_2SO_4 aqueous two-phase systems: Cu^{2+} (○), Ni^{2+} (□), Co^{2+} (△).

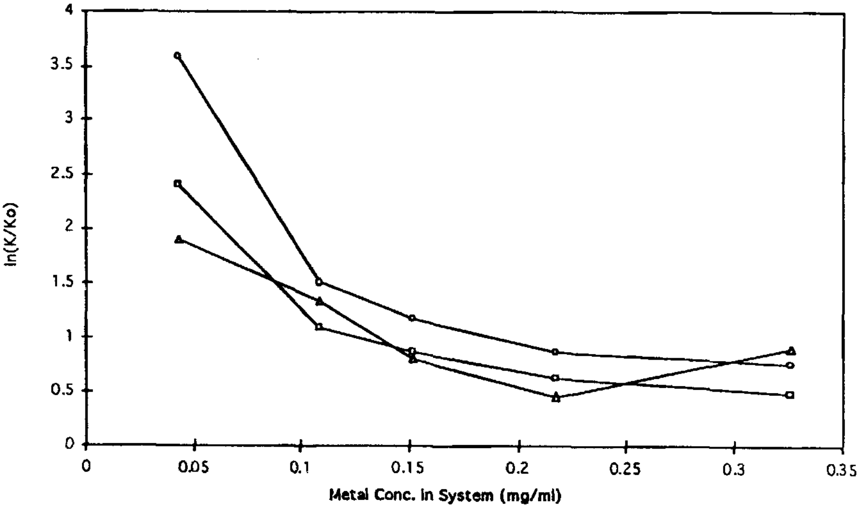

FIG. 7 Effect of PEG–TREN-Cm on partition coefficient of metals in PEG/Na_2SO_4 aqueous two-phase systems: Cu^{2+} (○), Ni^{2+} (□), Co^{2+} (△).

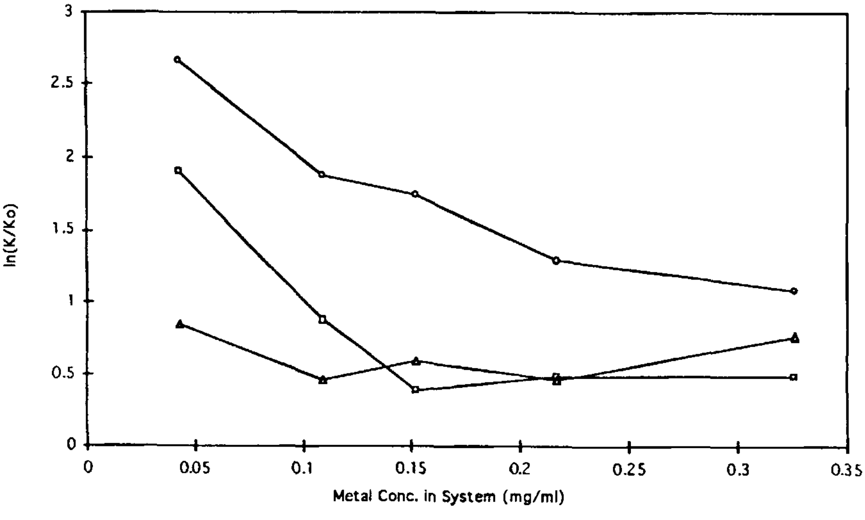

FIG. 8 Effect of PEG–ASP on partition coefficient of metals in PEG/Na_2SO_4 aqueous two-phase systems: Cu^{2+} (○), Ni^{2+} (□), Co^{2+} (△).

derivative. Copper exhibited the highest affinity and thus the highest enhancing effect on partitioning into the PEG phase, regardless of the PEG–ligand used. Nickel performed similarly in the presence of PEG–TED. In this case the same chelatant agent might require less effort to accommodate a tetracoordinated structure of the ion than hexacoordinated one. As explained earlier, copper has the lower ionic radii among the metals in question, with nickel the next in size and cobalt the largest of the three. The results seem to be in good agreement with the theory that an increase of chelate ring size leads to a greater degree of complex destabilization for larger metal ions than for smaller ones (26).

CONCLUSIONS

The metal extraction approach as well as the experimental results presented here show excellent potential as an alternative technique to selectively remove metal ions from aqueous solutions. The results presented with the different PEG–chelate derivatives complement previous studies performed with PEG–IDA (23).

The feasibility of the approach was tested and demonstrated with several PEG–chelate derivatives (PEG–IDA, PEG–TED, PEG–TREN-Cm, and PEG–ASP) and with several metal ions (copper, cobalt, and nickel). The effectiveness of the PEG–chelates and their influence on metal partitioning show evidence that the technique has potential as an alternative route for the efficient and selective separation of metal ions from solution, and for replacing the traditional organic solvents used in metal extractions aqueous two-phase systems along with the proposed or similar PEG–chelate derivatives.

The enhanced separation of several metal ions with the different PEG–chelators has been demonstrated and discussed. The apparent selectivity of the chelate derivatives in these aqueous two-phase systems appears to follow fundamental principles of coordination chemistry.

The method obviously requires improvement. Additional research is needed to determine the specificity of the ligands toward given metal ions and evaluation of the extraction when several transition metal ions are present in solution. Based to some extent on the principles of hard and soft acids and bases (HSAB) developed by Pearson (28), we can make this technique selective by designing chelatants (bases in the HSAB approach) with different degrees of hardness and softness. Polymers (e.g., other PEGs) that by themselves partition favorably into a given phase of a polymer/salt or polymer/polymer two-phase systems need to be evaluated. Modifications of these polymers with other groups that enhance their own partitioning is also an alternative to consider.

The polymer–chelatants are usually stable under a wide range of solvent conditions and temperatures. As a result, they could be recycled a very large number of times with negligible loss of performance, making this approach more viable and suitable for large-scale separations.

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