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Extraction of Trivalent Metals and Separation of Binary Mixtures of Metals Using Winsor II Microemulsion Systems

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Abstract

We present experimental results for the extraction of a trivalent metal ion, chromium, into a water-in-oil microemulsion of Aerosol-OT. We show that it is possible to enhance the aqueous metal ion concentrations to a large extent by using suitable microemulsions as the extractant. The enhancement observed for trivalent metal ions is greater than for bivalent metal ions. The extraction process is successfully modeled by a simple electrostatic model. We also present experimental results on anion distributions in Winsor III systems and show that the microemulsion extraction process effectively separates the anions and cations in one step. Experimental results with a mixture of bivalent copper and trivalent iron solutions show that higher charge cations are preferentially extracted over the bivalent cation.

INTRODUCTION

Winsor II microemulsion systems are biphasic equilibrium systems in which a water-in-oil microemulsion exists over a lower, predominantly aqueous phase (*1*). The subject matter of this paper deals with a Winsor II microemulsion facilitated extraction study in two main areas. The first is a study of the extraction and concentration of trivalent metals. The second deals with a study of the separation of a binary mixture of a trivalent and a bivalent metal. In this context, the terms separation, extraction, and concentration refer to specific processes. *Extraction* refers to the removal of the solute into another phase. *Concentration* refers to obtaining a more concentrated form of the original aqueous solution. The term *separation* pertains to the physical separation of two or more species in solution.

The electrostatic theory for the extraction of metals using microemulsions implies that the extraction capacity of the system is directly dependent on the charge of the introduced metal ion (*2–4*). The *interfacial surfactant membrane* of a water-in-oil microemulsion droplet is formed by the cosurfactant and the anions of the surfactant. According to Hirasaki et al. (*2*), the cation of the surfactant can be thought to be electrostatically associated to the membrane. By introducing another cation into the system, one induces a competition between the two different cations at the interfacial membrane. This competition will favor the association of the higher charged cation preferentially to the interfacial surfactant membrane. Thus a trivalent metal introduced into the system will be more bound to the interface than an introduced bivalent metal. Moreover, if metal ions of different charges were to be simultaneously introduced into the system, then their extent of extraction will directly depend on their charge. This difference will give rise to separations between the ions introduced.

In the following pages the selective extraction of trivalent chromium (from aqueous chromium nitrate solutions) into a water-in-oil microemulsion system is demonstrated experimentally. The results are compared with those of the bivalent metal. A quantitative model based on electrostatic principles as pertaining to this aspect of the work is developed. Further, an experimental scheme was designed to demonstrate separation selectivity based on the charges of the solute species. The salts selected for this study were iron chloride and copper chloride, the iron being the trivalent and the copper being the bivalent metal. It was decided to use the same anion (Cl^-) in this phase of the work in order to eliminate interference effects due to the use of different anions in the same system. It will be seen that very good separations are possible based on the ionic charges of the species concerned.

BACKGROUND

Numerous publications deal extensively with electrical phenomena at interfaces, the various double layer models, and the theories associated with them (*2, 5–9*). Hirasaki et al. (*2*) used electrostatic models to interpret the association of sodium and calcium to surfactant micelles. Leodidis et al. (*9*) examined specific ion effects in reverse micelles using a phenomenological model. Ovejero-Escudero et al. (*3*) reported a preliminary experimental study on the extraction of bivalent metals in Winsor II microemulsion systems. The authors of the present work have done a detailed theoretical and experimental study on the extraction and concentration of bivalent metals in Winsor II microemulsion systems (*4*, *10*).

Bauer et al. (*11*, *12*) demonstrated the extraction of trivalent iron and aluminum by using two- and three-phase systems containing water-in-oil microemulsions. They used kerosene as the organic phase with commercial solvent extraction extractants like Kelex 100 and HDEHP. They performed the extraction experiments with different types of surfactants in the system and found that using a microemulsion particularly enhanced the rates of *metal-extractant* couples that are traditionally slow in classical solvent extraction systems.

Robbins et al. (*13*) demonstrated the separation of organic compounds from organic mixtures by using oil-in-water microemulsions. They effected separations based on the differences in the interfacial tensions of the different compounds. Ruckenstein et al. (*14–16*) selectively solubilized organics from binary mixtures into normal micelles (aqueous micellar solutions). They found that the selectivity was dependent on differences in molar solubilization ratios of the pure components. Baird et al. (*17*) selectively extracted a binary mixture of amines by using emulsion liquid membranes and found that reaction reversibilities were responsible for differences in extraction rates.

By using *micellar-enhanced ultrafiltration* (MEUF), Dunn et al. (*18*), demonstrated simultaneous extraction of dissolved organics and divalent metal cations from solution. They demonstrated that the removal of these species from the original mixture can proceed independent of each other because of the complete difference between the extraction mechanisms of the organics and the metals. Finally, traditional solvent extraction and separation of metal mixtures has been carried out in the past. For example, Zheng et al. (*19*) studied the selectivity between bivalent nickel and trivalent iron in mixtures by using standard extractant systems like LIX63–HDNNS. They found that the selectivity was dependent on the pH of the solution mixture.

EXPERIMENTAL DETAILS

Materials and Methods

The microemulsion system selected for the study was the system *water/Aerosol-OT/isooctane*. The solute species to be extracted was introduced into the system along with the water. The experiments were designed to yield Windsor II systems after the phase separation of the samples. Commercially available chemicals were used without further purification. The surfactant, Aerosol-OT [sodium bis(2-ethylhexyl) sulfosuccinate, (AOT)] was Fluka Purum grade ($\geq$98%). Isooctane (2,2,4-trimethylpentane), obtained from Fisher Scientific, was spectrophotometric grade. Copper chloride ($CuCl_2 \cdot 2H_2O$) and ferric chloride ($FeCl_3 \cdot 6H_2O$) were obtained from the Aldrich Chemical Company. Chromium nitrate [$Cr(NO_3)_3 \cdot 9H_2O$] was obtained from Fisher Scientific. The water used was deionized to a standard resistance of 18 MΩ.

UV/Vis spectroscopy was used to determine the inorganic salt concentrations. A Hewlett Packard 84512A Diode Array Spectrophotometer was used for rapid data acquisition over the entire spectral range of 190 to 820 nm at a resolution of 2 nm. IR spectroscopy was used to determine the water content of the microemulsion system. IR spectra were obtained with a Mattson Cygnus 100 Fourier Transform Spectrophotometer, using an attenuated total internal reflectance cell (ATR). The ATR element used was zinc selenide. Each spectrum was averaged for 200 scans at a resolution of 2 cm^{-1}.

Sample Preparation

Micelles of Aerosol-OT in isooctane were prepared, maintaining the Aerosol-OT to isooctane weight ratio at a constant value of 0.25 as was done in the bivalent study (*4*). In the trivalent study, aqueous chromium nitrate solutions of 0.1 and 0.15 *M* concentration were prepared. Identical volumes of these aqueous solutions were then added to different, fixed volumes of the Aerosol-OT/isooctane micelles to obtain two series of samples. The aqueous concentration of any one series was a constant, the only varying factor in the series being the AOT/H_2O mole ratio.

In the separation study, equal volumes of equimolar solutions of iron chloride and copper chloride were mixed to form aqueous solutions containing a mixture of both the salts in equal concentrations. Three different aqueous solutions were prepared with the concentration of copper and iron in each being 0.05, 0.1, and 0.15 *M*, respectively. Identical volumes of these aqueous solutions were then added to different, fixed volumes of the Aerosol-OT/isooctane micelles to obtain three series of samples. The aqueous concentration of any one series was a constant with respect to both copper and iron. The only varying factor in the series was the water/isooctane ratio. Since the AOT/isooctane ratio was a constant in the system, the AOT/water ratio was dependent on the water/isooctane ratio. All the samples were then maintained at 25°C and allowed to phase separately.

Analysis

The efficacy of the experiments was determined, as in our bivalent study (*4*), by calculating the enhancement factors for the species of interest. The enhancement factor (η) is defined as

$$\eta = \frac{(\text{metal/water})_{T.P.}}{(\text{metal/water})_{\text{original}}} \tag{1}$$

where the subscripts *T.P.* and "original" refer to the top phase of a Winsor II microemulsion system and the initial aqueous solution, respectively.

RESULTS

Extraction and Concentration of Trivalent Metals

Contrary to expectations, the samples phase separated into three phase systems. The top phase of each sample was colorless and transparent. The middle phase was dark blue, and the bottom phase varied between colorless to pale blue. The visual appearance of the samples indicated that significant amounts of chromium had preferentially migrated into the middle phase. This was later verified analytically.

Spectroscopic Results

A combination of the results of UV/Vis and IR spectrometry of the three phases yielded information on the composition of the phases. This is illustrated in the following sections.

IR Results. Figure 1 shows the IR absorption spectra of the three phases of a typical sample in the range 2500 to 4000 wavenumbers. The sample shown here was part of the series prepared with an initial aqueous chromium concentration of 0.15 *M*. We see from Fig. 1(a) that the middle phase contains both water (3400) and isooctane (2900). Actually, the peaks in the 2900 wavenumber region correspond to the CH_3, CH_2, and CH symmetric and asymmetric stretches which could be attributed to both isooctane and AOT present in the samples. The samples have comparatively large amounts of isooctane, and in the concentration ranges where the work was done, the contribution to this peak from AOT is negligible. Further, it will be seen in the discussion of Fig. 2 that AOT can be uniquely identified by the sulfonate stretch around 1045 wavenumbers.

From Fig. 1(b) we find that the bottom phase has only water and no isooctane. The top phase, on the other hand, as seen from Fig. 1(c), has only isooctane and no water.

Figure 2 has the IR absorption spectra of the three phases of the same sample in the region 950 to 1100 wavenumbers. The peak around 1045 wavenumbers corresponds to the S=O band of AOT. It is apparent from the figure that most of the AOT is in the middle phase, with a small but definite amount in the bottom phase and negligible amounts in the top phase. The peak at 979 wavenumbers is unique to isooctane present in this system. This confirms what we found from Fig. 1, that the isooctane is found only in the middle and top phases.

UV Results. Figure 3 has the UV absorption spectra of the three phases of the sample in the region 100 to 900 nm. From Fig. 3(a) we see that the bottom phase has nitrate (302 nm) and chromium (twin peaks between 342 and 730 nm). Since the nitrate peak is not interferred with, we know that there is no organic in the bottom phase, or rather, if present it is in negligible amounts. This is confirmed by the IR findings of Figs. 1 and 2.

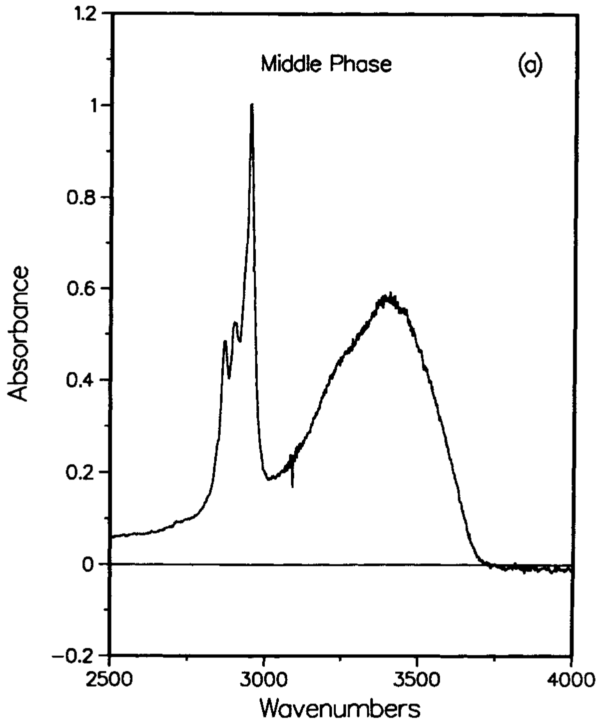
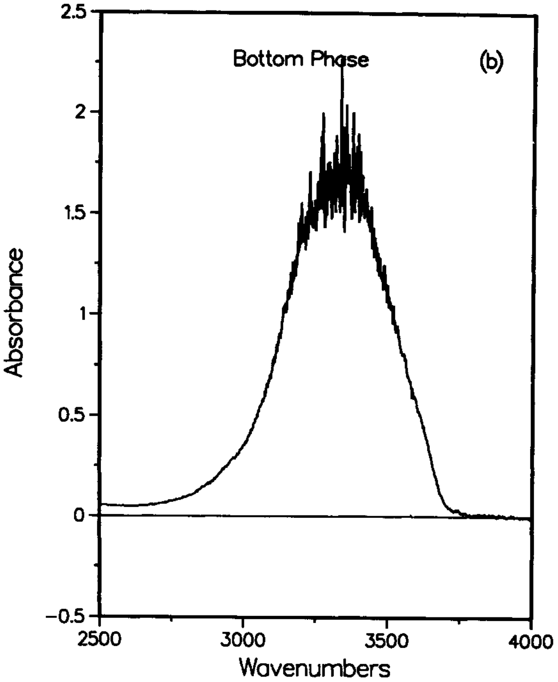
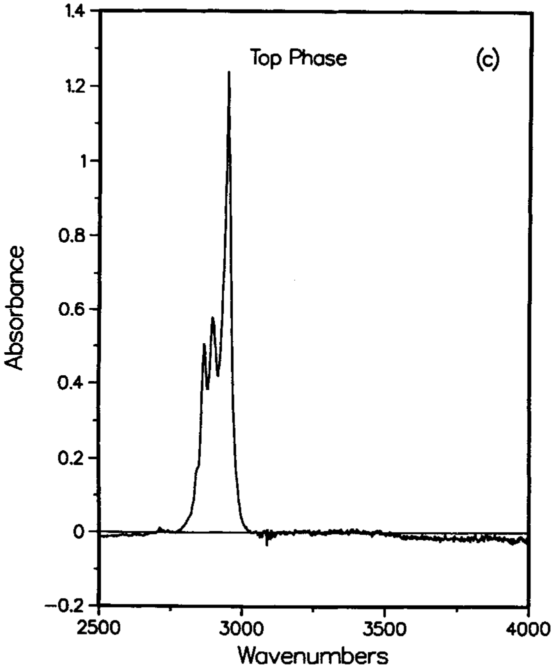


FIG. 1. IR absorption spectra of the three phases of a typical sample after phase separation. The spectra reveal the presence and absence of water and isooctane in the different phases. The peaks at 2900 and 3400 wavenumbers correspond to isooctane and water, respectively. (a) Middle phase, (b) bottom phase, (c) top phase.

When present in stoichiometric proportions, the UV peaks of nitrate and chromium are of comparative heights. In Fig. 3(a) the nitrate peak is disproportionately larger, indicating that most of the nitrate seems to have stayed behind in the bottom phase. This would indicate effective separations between the anion and cation of the same salt between the bottom two phases of the three-phase system.

Figure 3(b) of the middle phase shows the distinct presence of chromium. The nitrate peak appears here as a shoulder, indicating the presence of organics which interfere with it. As a complement to the bottom phase situation (Fig. 3a), the nitrate peak here is lower in height than the chromium peaks, indicating that more of the chromium than nitrate is present in this phase. Figure 3(c) of the top phase indicates the absence of both nitrate and chromium in that phase.


Bottom Phase
(b)
Absorbance
2.5
2
1.5
1
0.5
0
−0.5
2500
3000
3500
4000
Wavenumbers


Top Phase
(c)
Absorbance
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1.2
1
0.8
0.6
0.4
0.2
0
−0.2
2500
3000
3500
4000
Wavenumbers

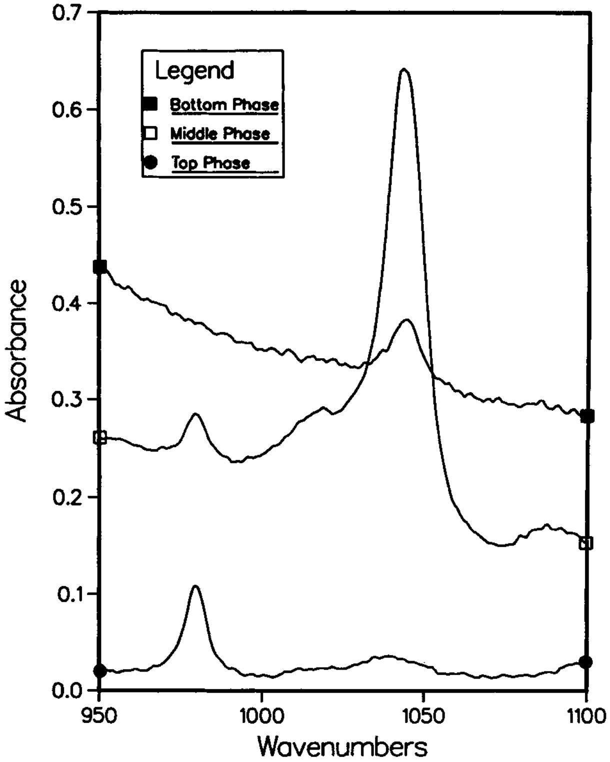


FIG. 2. IR absorption spectra of the three phases of a typical sample after phase separation. The spectra reveal the presence and absence of AOT and isooctane in the different phases. The peak at 979 wavenumber corresponds to isooctane and the peak around 1045 wavenumber corresponds to AOT.

Thus from IR and UV spectroscopy, the following information regarding the composition of the different phases is obtained.

Top phase: Isooctane, negligible Aerosol-OT, no water, no chromium, and no nitrate
Middle phase: Isooctane, Aerosol-OT, water, chromium, and some nitrate
Bottom phase: Water, nitrate, some Aerosol-OT, and some chromium

Winsor III System. From the literature (*1*, *3*, *20*) and our earlier bivalent experiments (*4*), the formation of two-phase systems was expected. Based on the fact that we have three-phase systems, it appears that the phase behavior is not only induced by the concentration but also by the charge of the metal ion. There is indirect evidence for this from the bivalent metal work of Ovejero-Escudero et al. (*3*).

Spectral data, described in detail in the previous two sections, seems to suggest that all of our three-phase systems are Winsor III systems. A Winsor III system is a three-phase system in which a microemulsion in the middle phase exists in equilibrium with an organic phase above it and an aqueous phase below it (*1*). Our IR and UV spectroscopic studies have shown us that the top phases of our samples essentially contain isooctane while the bottom phases contain aqueous solution. The middle phases, on the other hand, contain all the components needed to form a microemulsion, namely oil, surfactant, and aqueous solution.

Bound and free water are terms that describe the water found in a microemulsion based on the region in which it is present (*21–24*). Bound or interfacial water is the water present close to the interfacial surfactant membrane, up to a distance of 4–6 Å. Free or bulk water is water away from the interface. The asymmetric shape of the O—H stretch absorbance band shown in Fig. 1(a) is characteristic of water in water-in-oil microemulsions (*23*). The presence of a distinct shoulder at ~3250 cm^{-1} and a main peak of ~3450 cm^{-1} is semiquantitative evidence that a significant amount of the water in the middle phase is bound water. This can only be if water is the dispersed phase, as in a water-in-oil microemulsion. If water was the continuous phase, as in an oil-in-water microemulsion, then the free water peak would be much larger than the bound water peak. For example, in the bottom-phase spectrum in Fig. 1(b) where predominantly only water is present, for the same sample, analyzed with a sampling cell of the same pathlength, the free water peak is much higher. Further, comparison between the isooctane in the top phase (Fig. 1c), where only isooctane is present, and the middle phase (Fig. 1a), where other components are also present, indicates that the isooctane peaks are roughly of the same magnitude, with the isooctane in the top phase having the higher magnitude. This implies that the majority component in the middle phase is isooctane. Thus, based on the findings that in the middle phase the bound water peak is significant, the water is the minority component, and the isooctane is the majority component, we can reasonably assume that the middle phase is a water-in-oil microemulsion.

Quantitative Results

From the previous section we find that the two lower phases of our current three-phase systems correspond exactly to the two-phase systems of a Winsor II microemulsion. In essence, we can treat these three-phase systems as Winsor II systems with an oil phase on top. Since the oil phase

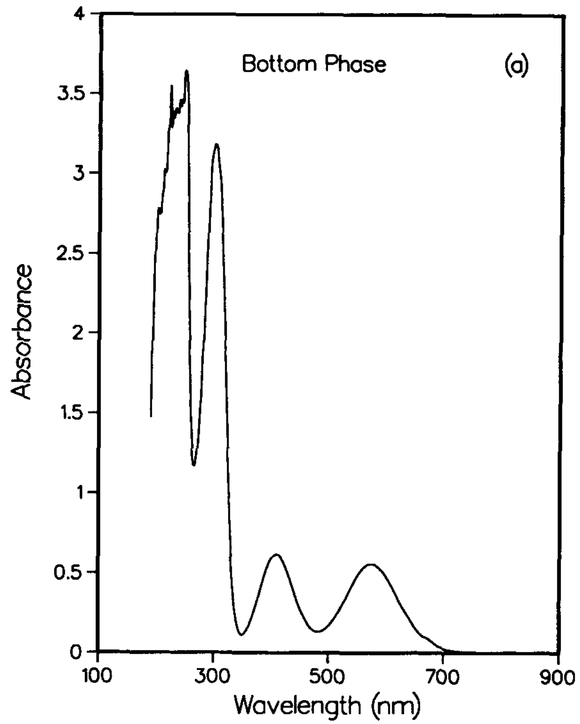
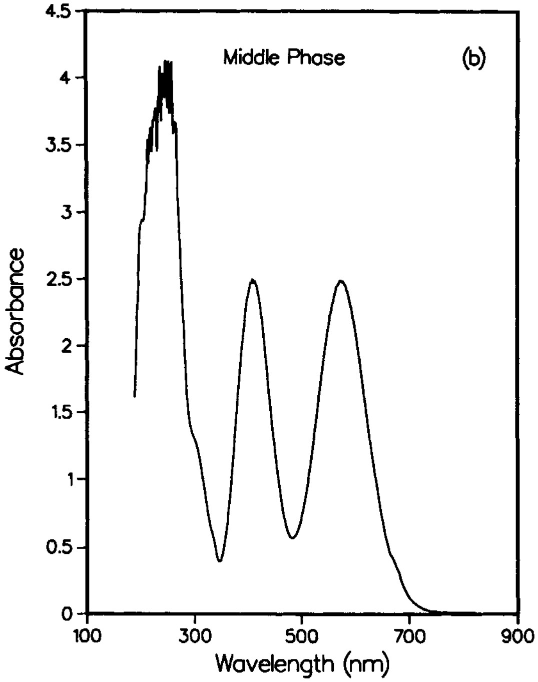
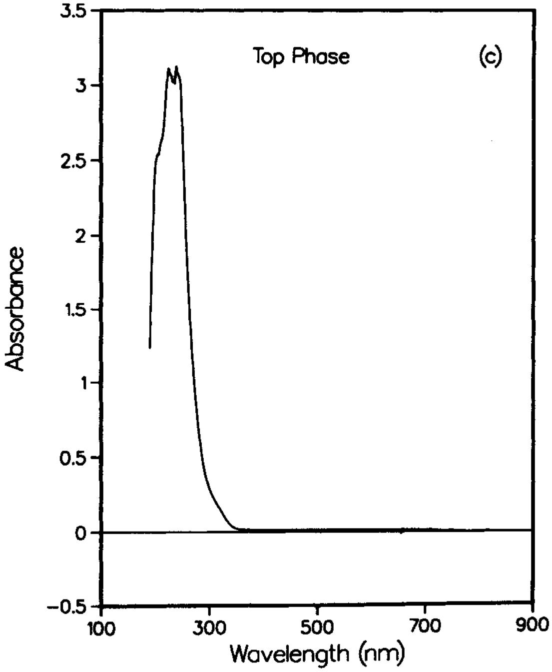


FIG. 3. UV absorption spectra of the three phases of a typical sample after phase separation. The spectra reveal the presence and absence of chromium and nitrate in the different phases. The peak at 302 nm corresponds to nitrate. The twin peaks between 348 and 730 nm correspond to chromium. (a) Bottom phase, (b) middle phase, (c) top phase.

has no chromium (Fig. 3c), it has no bearing on the surface coverage and enhancement factor calculations. The enhancement factor was appropriately redefined with respect to the middle phase and determined for all the samples.

In Fig. 4 we have plotted the enhancement factors for the two series of chromium nitrate samples against the AOT/water mole ratios in the initial mixtures (i.e., based on amounts added to the sample before phase separation). As the AOT/water mole ratio in the initial mixture is lowered, the enhancement factor increases. This gradual increase in the enhancement factor values continues until an AOT/water mole ratio of 0.015 is reached. At still lower AOT/water mole ratios, an abrupt increase in the values of the enhancement factor is seen. Unlike the corresponding bivalent cases (*4*), it is observed that there is no significant difference in the values


Middle Phase
(b)
Absorbance
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
100
300
500
700
900
Wavelength (nm)


Top Phase
(c)
Absorbance
3.5
3
2.5
2
1.5
1
0.5
0
−0.5
100
300
500
700
900
Wavelength (nm)

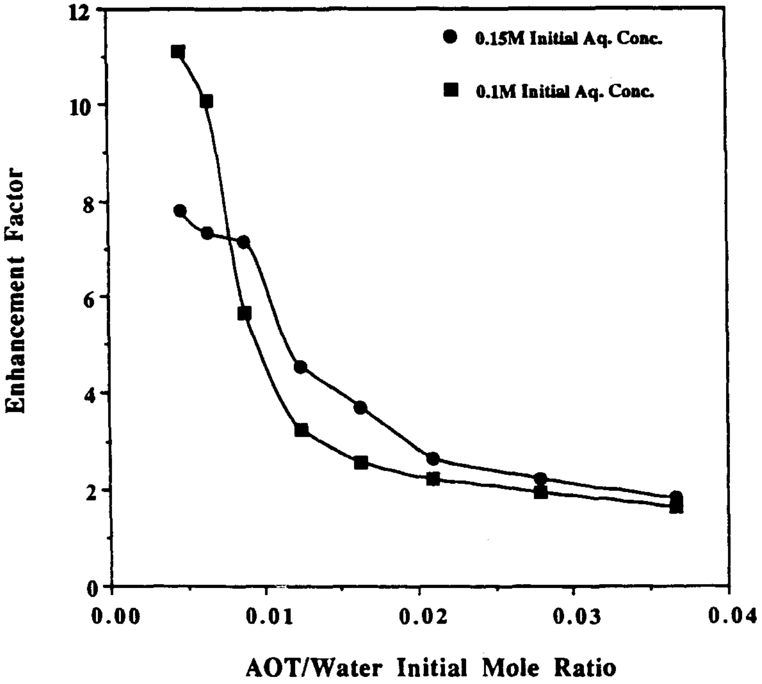


FIG. 4. Enhancement factor vs initial AOT/water mole ratio for the two series of chromium solutions of different initial concentrations.

of the enhancement factors obtained in the two cases. This lack of difference could be the direct result of the system reaching saturation for the case of trivalent chromium. However, in the trivalent case there is a difference in the behavior of the two curves at low AOT/water mole ratios, i.e., in the case of the initial concentration being 0.15 *M*, the enhancement factor tends toward a value of 8, while in the case of the initial concentration being 0.1 *M*, the enhancement factor tends toward a value of 12. This could be explained as being due to the tendency of the system to taper toward lower saturation at higher initial concentrations. A similar phenomenon was observed in the case of the bivalent metals (*4*) where it was found that for lower initial aqueous concentrations, higher enhancement factors were obtained. However, in the case of trivalent metals, this effect is exhibited at low AOT/water ratios and not all along the curve, as was the case in the bivalent metals.

One feature to be noted is that on the high end we get high enhancement factors of between 8 and 12. These are a factor of 2 or more higher than the corresponding cases in the bivalent experiments [(*4*), curves 0.02 and 0.03]. This supports the hypothesis that the higher the charge of the introduced metal ion, the greater is its attraction to the interfacial surfactant membrane, resulting in greater extraction capabilities by the microemulsion system.

Theoretical Analysis

Having shown the excellent extraction capabilities of the AOT/isooctane system for trivalent metals, we now turn our attention toward quantitatively describing this phenomenon by a mathematical model based on electrostatic forces between the cations and the micellar surface. This system can be considered as a Winsor II system in equilibrium with an oil phase on top. Since the top phase has no chromium in it, we can essentially model the distribution of introduced trivalent chromium in a two-phase system of a water-in-oil microemulsion over an aqueous phase. Since an extensive treatment of the model, the system philosophy, and origin and need for certain equations have been previously introduced (*4*, *10*), we give here only the salient points.

Ions present in the system are chromium, nitrate, and sodium ions. These ions must be introduced in the model in order to predict the results of the experiment. The system we are modeling consists of a two-phase system of a water-in-oil microemulsion over an aqueous phase in the presence of trivalent cations, specifically chromium. Experimentally, we observe that the trivalent cation seems to concentrate in the top microemulsion phase (actually the middle phase of the three-phase system). Our approach has been to model this phenomenon as a preferential substitution of the counterions of the surfactant by the trivalent cations. We assume that the adsorption of counterions on to the surfactant surface of the reverse micelle can be modeled by the Stern double layer model (*2*, *25*). We also assume that the surfactant molecules are dissociated, and the negative heads of the ionized surfactant contribute to an electric field on the inside of the micelle which tends to attract the positive counterions back to the interface. These counterions are considered bound to the anionic surface by electrostatic forces with no chemical bonding being involved.

For the case of multiple ions present in solution near an electrically charged surface, the Stern adsorption isotherm is given by the following equation (*5*, *7*):

$$\tau_i = \frac{\mu_0 n_i \exp\left((-\phi_i - z_i e\psi_\delta)/kT\right)}{\left(1 + \Sigma_i \mu_0 n_i \exp\left((-\phi_i - z_i e\psi_\delta)/kT\right)\right.} \tag{2}$$

where τ_i is the surface coverage by the *i*th species, n_i is the bulk concentration of solute ions of the *i*th species, μ_0 is the molecular volume of the solvent, ϕ_i is the specific (nonelectrostatic) adsorption potential of one ion of the ith species, k is the Boltzmann constant, T is the temperature, z_i is the charge on the ith species, e is the electronic charge, and ψ_δ is the electrostatic potential at the Stern plane.

As a direct result of our experience with modeling bivalent metals, we have not neglected the effect of nitrate ions in using the Stern adsorption isotherm. Thus, we have three surface coverage equations corresponding to the chromium, sodium, and nitrate ions present in solution. We assume that the specific adsorption potential is negligible for the system and that there is total dissociation of the surfactant. The latter assumption suggests the absence of a significant degree of chemical bonding between the cations of the surfactant and the surfactant tails when in reverse micellar form. Such an assumption has also been successfully employed by Hirasaki et al. (*2*), Leodidis et al. (*9*), and Ovejero-Escudero et al. (*3*).

Since the right-hand side of the Stern equation does not contain the entire potential distribution ψ (rather it contains the variable ψ_δ), one only needs an estimate of the Stern potential ψ_δ to predict the relative amounts of cations attracted to the charged surface. Hence, a reasonable estimate for ψ_δ in the case of spherical microemulsion particles is required. The potential distribution arising in the vicinity of an electrically charged surface is governed by the generalized Poisson–Boltzmann equation (*6*, *26–28*). However, no analytical solution satisfying the surface boundary conditions is possible in the case of the spherical Poisson–Boltzmann equation (*6*, *28*), which is what needs to be used in this case. As explained in the bivalent work (*4*), the planar assumption was made and the planar analytical solution was used in our work. The determination of ψ_δ from this is done as follows.

The planar Poisson–Boltzmann equation in one dimension for the case of multiple ions in solution, when integrated with the appropriate boundary conditions, yields (*4*)

$$\left(\frac{4\pi\sigma}{\epsilon}\right)^2 = \frac{8\pi kT}{\epsilon}\sum_i \left(n_i \exp\left(\frac{-z_i e\psi_0}{kT}\right) - n_i\right) \tag{3}$$

where ψ_0 is the potential at the surface, σ is the surface charge, and ϵ is the dielectric constant. In this work ϵ was taken to be a constant and equal to that of water.

It appears that ψ_δ would be some value between ψ_0 and 0. For this work, a working relationship of $\psi_\delta = 0.65\psi_0$ was used. The 0.65 factor, though a logical choice, and one that was extremely successful in the bivalent modeling (*10*), is by necessity an adjustable parameter. If we use the same factor in the trivalent case successfully, then a strong case can be made for its selection, since that would indicate an internal consistency in the extraction system as a whole.

The mass balance equations on sodium, chromium, and nitrate are given by

$$n_i^0 V_0 = \tau_i (\mathrm{AOT})_m + n_i V_0 \tag{4}$$

where n_i^0 is the initial concentration of species i, V_0 is the initial aqueous volume, and $(\mathrm{AOT})_m$ is the number of molecules of AOT in the middle phase. The mass balance equations have been written to be consistent with the assumption of total surfactant dissociation. Moreover, it has been assumed that the concentration of the solute species in the core (excluding the surfactant membrane) and the bottom phase are equal at equilibrium.

Comparison between Theoretical Predictions and Experimental Results. Equations (2), (4), and (5) give seven equations and seven variables which were solved numerically by a combination nonlinear root-solving technique. The values of chromium/AOT mole ratio in the middle phase for the case of 0.1 *M* initial aqueous concentration computed by this model are shown in Fig. 5 compared with the experimentally observed results.

It is seen from the figure that in the range of the experimental data points, the theoretical predictions match the experimental data rather well. At higher coverages no data are available due to experimental limitations, since the samples either did not phase separately or the volumes were too small to be analyzed accurately. Figure 6 has the same details as Fig. 5 plotted for the case of an initial aqueous concentration of 0.15 *M*. From Fig. 6 we see that at lower coverages the theoretical predictions match the experimental data points reasonably well. However, the experimental maximum tends toward a value of 0.6 while the theoretical curve predicts saturation at a coverage of 1.0. In retrospect, we notice that even in Fig. 5 the beginnings of deviation exist at low AOT/water initial ratios.

Separation of Anions

While the main thrust of this work has been with cations, it is apparent that a study of the anion distribution will be beneficial to the overall characterization of the system. The nitrate ion is negatively charged. By electrostatics, it will be repelled by the negatively charged, interfacial surfactant membrane. As a consequence of this, while the cations preferentially move over to the middle phase of a Winsor III system (or the top phase of a Winsor II system), the anions would preferentially stay back in

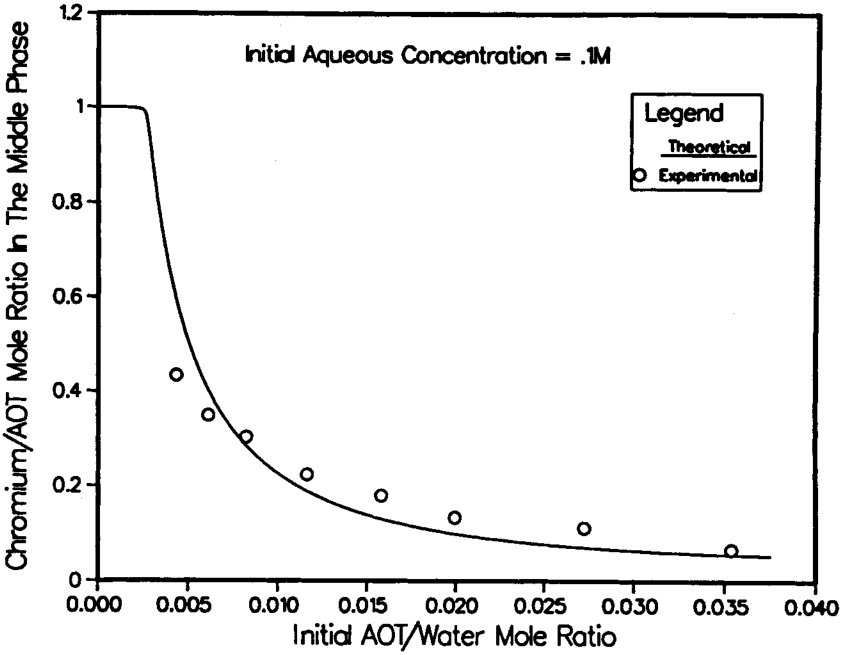


FIG. 5. Comparison of theoretical predictions vs experimental trends for chromium solution of 0.1 *M* initial concentration.

the bottom phase. Thus, by the unique nature of the microemulsion system itself, an effective physical separation between the anions and cations of the same salt can be effected. This was also one of the primary considerations in selecting Winsor microemulsion systems as our model extraction systems. As discussed under spectroscopic results, the nitrate can also be spectroscopically studied and was therefore selected as the anion in the chromium salt used in this study.

Figure 7 is the plot of the enhancement factor of nitrate with respect to the bottom phase plotted against the initial parameters of the system. Since nitrate separates into the bottom phase selectively, the enhancement factor was modified with respect to the bottom phase.

Figure 8 is a comparison between the bottom phase nitrate concentrations computed by the model and the experimental data points, both of which are plotted against the initial AOT/water mole ratio. It is seen from the plot that the theoretical curve passes very close to the experimental data points in the region in which data are available. Though not perfect, the match between theory and experiment is reasonably good.

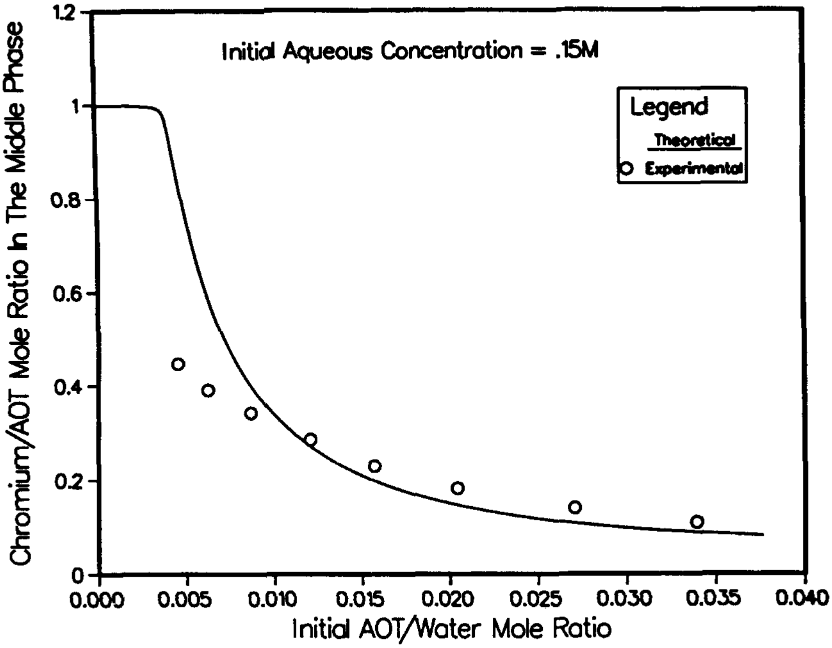


FIG. 6. Comparison of theoretical predictions vs experimental trends for chromium solution of 0.15 *M* initial concentration.

Separation of a Binary Mixture of Metals

In this phase of the study, most of the samples phase separated into two-phase systems. A few samples formed either three-phase systems or took a long time to phase separately and were not used in the analysis. Visually the samples could be described as follows: The top phases were transparent and strongly yellow. The bottom phases varied between a vivid blue and a vivid green. It is known that solutions containing Fe^{3+} ions are bright yellow while those containing Cu^{2+} ions are bright blue. Further, a mixture of the primary colors yellow and blue produces green. Thus, based on the visual appearance of the samples, one could immediately predict that the top phases had a predominance of iron while the bottom phases had mainly copper or copper and iron. This was borne out later by actual spectroscopic analysis.

Figure 9 is a plot of the enhancement factors of both copper and iron plotted against the initial water/isooctane weight ratios of the samples, i.e., against the values before phase separation. The copper and iron enhancements have been plotted on the same graph in order to facilitate easy

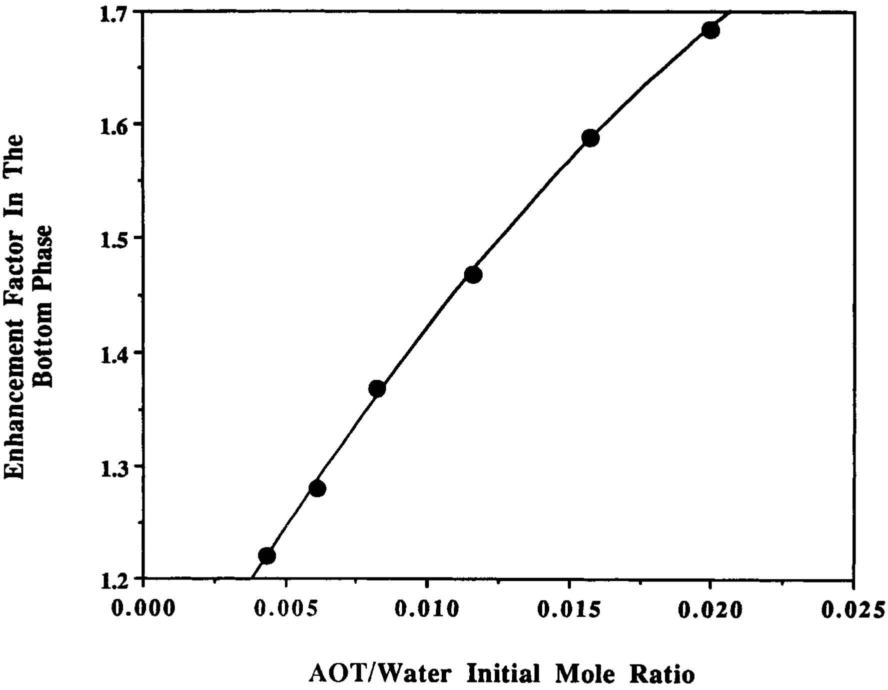


FIG. 7. Enhancement factor vs initial AOT/water mole ratio for the case of an initial nitrate concentration of 0.3 *M*.

comparisons. The upper plot pertains to the copper results and the lower to the iron results. The three curves in each of the plots correspond to the results of the three series which had three different starting aqueous concentrations.

For the case of copper, high enhancement factors of up to 18 were obtained, the values increasing with water/isooctane ratios. Further, higher enhancements are obtained at lower initial aqueous concentrations. The fact that the copper enhancement factors obtained here are marginally higher than those in our earlier copper study (*4*, *10*) is probably due to different anions being used in the two studies. There bivalent sulfate ions were used, while here monovalent chloride ions are being used.

Now, looking at the bottom half of Fig. 9 that deals with the iron results, it is seen that in all cases the enhancement factors are higher than in the case of copper. In fact, at higher water/isooctane weight ratios, the values are about 15–20 times higher than the corresponding copper cases. (Note that the *y*-axis scale is much larger in the iron case). Large values of water/

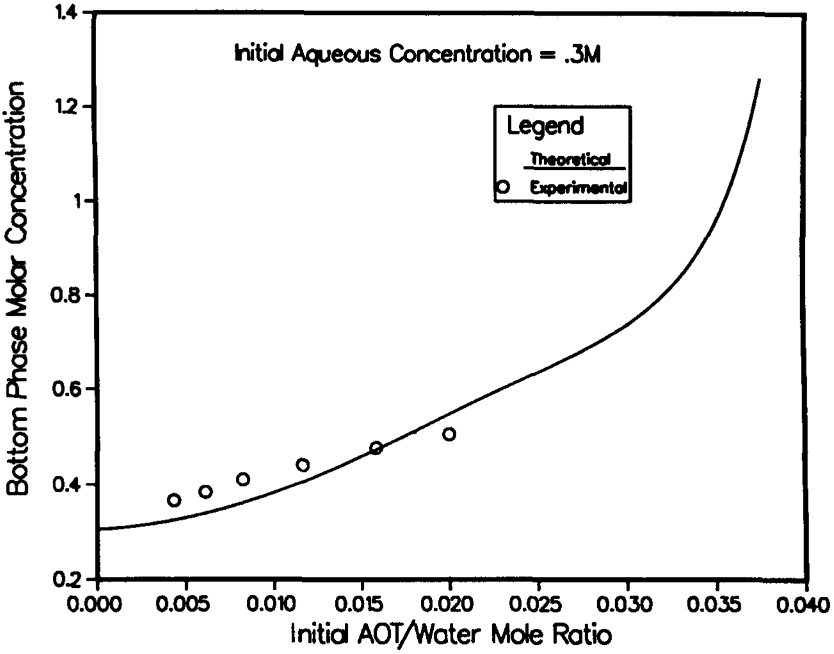


FIG. 8. Comparison between theoretical predictions and experimental trends for the case of an initial nitrate concentration of 0.3 *M*. The *y*-axis represents the molar concentration of nitrate in the bottom phases.

isooctane ratios seem to be conducive to obtaining large separations between the bivalent and trivalent ions.

DISCUSSION

It is seen from Fig. 5 that in the case of the trivalent study at low initial aqueous concentrations, the predictions of the theory match the experimental results well. Deviations start occurring as the initial aqueous concentration increases (Fig. 6), although the qualtitative trends are still preserved. From a perusal of related literature dealing with bivalent metals, we do know that our trivalent work has been done by using somewhat higher concentrations of initial salt solutions than most related work (*29–31*). This was because we used UV/Vis spectroscopy to determine metal concentrations due to certain inherent advantages possessed by that method of analysis. This technique is generally more sensitive at higher concentrations. The conventional method of metal determination is by using atomic absorption spectroscopy, which is more sensitive at lower concen-

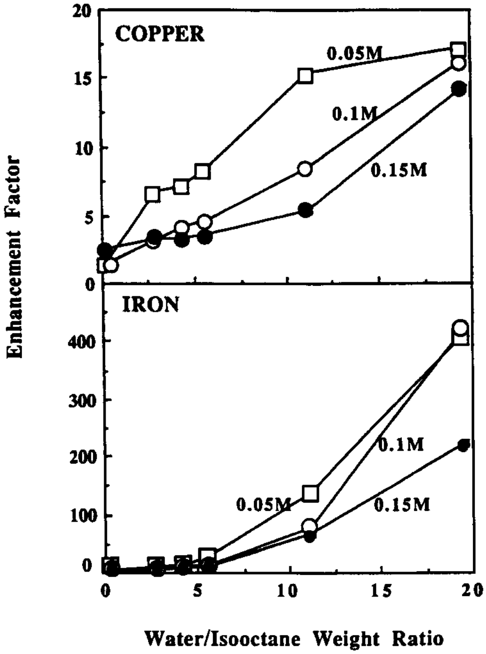


FIG. 9. Enhancement factor vs initial water/isooctane weight ratio for the three series of copper and iron solutions.

trations. One would expect that at even lower concentrations than those that we have investigated, the agreement between theory and experiment would be even closer. Also, these small deviations at higher concentrations occur only at low AOT/water initial mole ratios.

We notice, again from Figs. 5 and 6, that the model tends toward an idealized surface coverage of 1.0. This is correct since τ, the surface coverage, can be ≤ 1.0. Consider the following:

$$\tau = \frac{\text{numerator}}{1 + \text{numerator} + \cdots} \qquad (5)$$

from Eq. (2). Therefore, for large values of the numerator, the surface coverage approaches 1.0. The fact that the theoretical curve is flat for a while at a surface coverage of 1.0 means that the coverage saturates at a finite value of AOT/water.

The deviation of the model from the experimental results can possibly be explained when one considers that the Stern isotherm on which the model is based lacks a specific term for ion–ion interaction. The interactive force between ions can generally be represented by the *inverse square law*

$$F \propto \frac{q_1 q_2}{r^2} \tag{6}$$

where F is the force between the two charged particles, q_1 and q_2 are the charges on the ions, and r is the distance between the centers of the charges. At lower coverages, the distance between the ions will be greater and therefore, based on Eq. (6), the repulsive force between them will be less than at higher coverages. In the absence of such a term, the model indicates saturated coverages at low AOT/water ratios. This is not realized experimentally, possibly due to ion–ion repulsions.

The fact that this ion–ion interaction did not play a significant role in the bivalent study (*4*, *10*) can be explained when we consider that there $F \propto (2*2) = 4$ while here $F \propto (3*3) = 9$. Thus, in the case of trivalent ions the interactive force is more than twice the value for bivalent metals and hence could be causing the deviations. From the fact that the predictions match at low coverages, we see that whatever modifications are made to the model must essentially come into play only at higher coverages.

From a physical point of view, we had expected cations of charge higher than 2 to be even more attracted to the micellar surface. Our model successfully predicts this trend.

Our method of calculation eliminates the need for a full solution of the Poisson–Boltzmann equation and is therefore capable of dealing with generalized systems (non Z-Z electrolytes) with relative ease. Therefore, all the ions involved in the system, i.e., Cr^{3+}, NO_3^-, and Na^+, are taken into account.

One of the problems often encountered when modeling micellar systems with electrostatic theory is the fact that the spherical Poisson–Boltzmann equation can only be numerically solved. This is further complicated by lack of knowledge regarding the potential distribution close to the charged surface, i.e., within the Stern layer. Our approach, as in the bivalent case, has circumvented this problem by directly using the Stern adsorption isotherm to describe the affinity of charged species to the surface. An explicit solution for the potential and concentration profiles within the micelle is therefore not required in this model. Thus, while preserving the electrostatic nature of this separation, we have significantly simplified the problem in order to deal with concentration enhancements in extraction processes. Our simple but effective model eliminates to a large extent the need for the use of several empirical relations and adjustable parameters.

We see from Fig. 7, dealing with the anion results, that the enhancement factors steadily increase with increasing AOT/water initial mole ratios. This can be explained as follows.

Increasing values of the AOT/water initial ratios (x-axis) can be achieved by decreasing the volume of water added to the system at constant volume of micelles (since in our system AOT/isooctane is a constant). Now, though the amount of water added to the system decreases, the absolute amount of water taken up by the micelles is a constant since the volume of the micelles is a constant. Therefore, the fraction of water remaining in the bottom phase becomes smaller and smaller as we go to higher and higher AOT/water ratios. Hence, the final concentration of nitrate in the bottom phase is essentially equal to the ratio of the initial concentration of the nitrate to the fraction of water retained in the bottom phase. The surfactant takes up water to the exclusion of the nitrate ions which, being negatively charged, are repelled from the negatively charged surfactant wall and stay in the bottom phase. Thus, as the fraction of water retained in the bottom phase decreases, the final concentration of nitrate in the bottom phase goes up and we get increasing values of enhancement factors in the bottom phase for any given initial nitrate concentration.

In the case of cation (chromium), enhancement factors as high as 12 were obtained in the top phase. In the case of anion (nitrate), enhancement factors only as high as 1.7 have been obtained in the bottom phase. This can be explained when we consider that only a relatively small amount of the original water is taken into the micelles. This is what makes the system very attractive for the extraction of cations; namely, that we are able to take up a large amount of metal with relatively small amounts of water, leading to high metal concentrations in the extracted phase. As a direct consequence of this, in many of the cases, almost all of the initial nitrate and most of the initial water are in the bottom phase, leading to bottom-phase nitrate concentrations which are only marginally higher than that of the initial solution. The advantage of this system is that in one stroke we achieve extraction and concentration of the cation into the microemulsion while simultaneously achieving an effective separation of the cation from the anion.

The sharp increase in the theoretical bottom-phase nitrate concentration at high AOT/water ratios in Fig. 8 is consistent with the previous explanation regarding water uptake. The absolute water uptake is an increasing function of the absolute amount of AOT in the system. Thus, at high AOT/water initial ratios, the fractional water uptake into the microemulsion will be very high. Since the nitrate essentially remains in the bottom phase, the bottom-phase nitrate concentration at high AOT/water ratios is expected to be very high, as seen in the theoretical prediction.

As far as the separation study is concerned, the fact that the numbers in the copper case in Fig. 9 are far less than the numbers in the iron case indicates a consistency between the predictions of the electrostatic theory and the experimental results. According to the theory, all other conditions remaining the same, the extraction capability of the system will be predominantly dependent on the valency of the metal being extracted. Thus, the trivalent ions, by virtue of their higher charge, would experience a greater attraction to the interfacial surfactant membrane than would the corresponding bivalent copper ions. Hence, though the iron and copper will both tend to displace the monovalent counterion (Na^+) of the surfactant, the bivalent copper itself will be displaced at the surfactant wall by the trivalent iron.

This method of extraction is thus ideal when a mixture of metal ions of different charges are present in solution. In practically a single step, effective separation of bivalent and trivalent ions can be achieved while simultaneously concentrating each of the ions of different charges. For example, in this study, starting out with equimolar solutions of copper and iron, we have obtained in the final top phases an iron concentration that is about *20 times* higher than that of copper, in the more favorable cases. At the same time, the final bottom phases have a preponderance of copper over iron. To sum up: Considering only simple extraction and concentration, the process can successfully yield final concentrations that are much higher than initial values in the case of ions of all charges. When looked at from the more complex aspect of separation, the system is successful due to the differences in the extent of extraction between ions of different charges.

Now we come to the question of why there is a vast difference between the values of the enhancement factors obtained in the case of chromium and iron. Both metals are trivalent, and the microemulsion system should have values in the same range for both cases according to the electrostatic theory. In reality, however, the iron values are up to an order of magnitude higher than the chromium values. In the mixture separation experiments, a brown precipitate was noticed in some of the samples after long periods of time. This was not the case in the independent chromium experiments. This gave rise to the question of the stability of the iron samples. Iron is known to form polynuclear hydroxide complexes in aqueous solutions (*32*), and iron solutions are sensitive to fluctuations in pH. Seemingly stable solutions can precipitate out over a period of time when in contact with microemulsions or after phase separation. Moreover, iron can also form chemical complexes with the anions of the surfactant. In previous modeling work, the assumption of purely electrostatic interactions between the metal ion and surfactant membranes has been successfully used (*2*, *10*). Such an assumption presupposes the absence of strong chemical interactions between the introduced metals and the anions of the surfactant, and worked well in the case of chromium. In the light of the high enhancement factors obtained in the case of iron, it seems reasonable to assume that iron may be undergoing complexation with the anions. If this were true, then it is possible that specific interactions are present in the iron samples, playing a major role in the concentration and separation process.

In such cases, modeling based on a purely electrostatic assumption will be invalid and the model will have to be modified. It appears that in the long run, specific interactions, if responsible for the high enhancements in the case of iron, are beneficial in the extraction, concentration, and separation process. They can be exploited to separate different ions of the same charge present in a mixture. Further, the recovery of the extracted metal from the microemulsion may also be facilitated if the metal precipitates out or forms complexes that separate from the oil.

CONCLUSIONS

Experimental results for the extraction of a trivalent metal, chromium, into swollen reverse micelles of AOT in isooctane have been presented. We have effectively shown that it is possible to enhance aqueous metal ion concentrations to a large extent by using suitable microemulsion systems. This enhancement is greater in the case of trivalent metals than in the case of bivalent metals.

The phenomenon is modeled well by a process which assumes that the cations are completely dissociated from the rest of the surfactant in the reverse micelles and are loosely held in the core of the reverse micelles by electrostatic forces. The nature of this force suggests that the extraction of metal cations with even higher positive charge will probably be even more efficient. The model, while being predictive at low concentrations, shows small deviations at higher concentrations of initial aqueous solutions. These deviations are confined to low initial AOT/water mole ratios. The high concentrations at which deviations occurs are usually not encountered in actual practice as in effluent treatment or in mining technology. Hence, if this extraction technique were to be adapted to practical situations in the future, the deviations will not affect the potential use of the model. The model needs to be modified for the case of systems where specific interactions appear to play a major role.

Experimental studies have been conducted on anion distributions in Winsor III systems. We have experimental evidence pointing to the rejection of the anions by the micellar phase. This leads to good separations between the anions and the cations. We find that the concentration of the anion in the bottom phase is enhanced over that of the initial concentration, and we have quantified this. Finally, the trends in the bottom phase anion concentration match the theoretical predictions well. The predictions in the regions where data are not available are consistent with a picture of anion rejection from the mnicroemulsion phase. As explained in the text, ion–ion interactions could possibly account for the discrepancy between theory and experiment.

We have successfully demonstrated the effective separation of a binary mixture of a bivalent and a trivalent metal. The work is unique in that it is the first of its kind in experimentally attempting to demonstrate microemulsion facilitated separation of metal ions in a mixture based on ionic charges. We have shown that in addition to good separations between the bivalent and trivalent ions, each of these charged species present in the mixture can themselves be independently extracted and concentrated over and above their starting concentrations. We have also touched upon some of the issues involved in the choice of the metal ion in the extraction process.

NOMENCLATURE

AOT_m	number of molecules of AOT in the middle phase
e	electronic charge
F	interionic force
k	Boltzmann constant
original	initial solution
n_i^0	initial concentration of species i
n_i	bulk concentration of solute ions of the ith species
N_{AOT}	initial number of molecules of AOT
q_1	charge on the first ion
q_2	charge on the second ion
T	absolute temperature
$T.P.$	top phase
V_0	initial aqueous volume
z_i	charge on the ith species
ϵ	dielectric constant
η	enhancement factor
κ	partition coefficient
μ_0	molecular volume of the solvent
σ	surface charge
τ_i	surface coverage by the ith species
ϕ_i	specific (nonelectrostatic) adsorption potential of one ion of the ith species
ψ_δ	electrostatic potential at the Stern plane
ψ_0	potential at the surface

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