Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

# Equilibrium Extraction and Concentration of Multivalent Metal Ion Solutions by Using Winsor II Microemulsions

Chandra S. Vijayalakshmi[a]; Ananth V. Annapragada[a]; Erdogan Gulari[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN

**To cite this Article** Vijayalakshmi, Chandra S. , Annapragada, Ananth V. and Gulari, Erdogan(1990) 'Equilibrium Extraction and Concentration of Multivalent Metal Ion Solutions by Using Winsor II Microemulsions', Separation Science and Technology, 25: 6, 711 — 727

**To link to this Article: DOI:** 10.1080/01496399008050361

**URL:** http://dx.doi.org/10.1080/01496399008050361

PLEASE SCROLL DOWN FOR ARTICLE

SEPARATION SCIENCE AND TECHNOLOGY, 25(6), pp. 711-727, 1990

# Equilibrium Extraction and Concentration of Multivalent Metal Ion Solutions by Using Winsor II Microemulsions

---

CHANDRA S. VIJAYALAKSHMI, ANANTH V. ANNAPRAGADA
and ERDOGAN GULARI,

DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN 48109

## Abstract

Experimental results on the selective extraction and concentration of bivalent copper into the aqueous core of a water-in-oil microemulsion in equilibrium with an aqueous phase are presented. We have developed an electrostatic model which describes this phenomenon as a preferential substitution of the counterions of the surfactant by the introduced bivalent cations. We have assumed that the adsorption of counterions onto the charged surface of the reverse micelle can be modeled by the Stern double layer model. Comparisons of the theoretical predictions against the experimental results are encouraging. The positive features of the model and its limitations are discussed.

## INTRODUCTION

The possibility of using microemulsions for metal ion separation and enrichment purposes is based on the fact that the interfacial layer of a microemulsion droplet can be considered as a membrane formed by the co-surfactant and the anions of the surfactant. The cation of the surfactant (usually $Na^+$) can be thought of as electrostatically associated to the membrane (*1*). If one introduces another cation in the solution, it will be bound to the membrane in competition with the cation of the surfactant. If the introduced cation is of higher charge than 1, a physical process of this nature will tend to favor the binding of this multivalent metal over that of the monovalent sodium because of the larger electrostatic force associated with the higher charge.

In this paper a liquid–liquid extraction process for metal ions using a Winsor II system is considered. This is a system in which a water-in-oil microemulsion exists in equilibrium with a lower predominately aqueous phase (*2*). The equilibrium partitioning of an inorganic, hydrophilic solute between an aqueous solution of the solute and a W/O microemulsion is studied. Such a study has a bearing on a vital area of industrial research, namely concentration of effluent streams containing metal ion impurities. Ovejero-Escudero et al. (*3*) explored this possibility and provided initial feasibility data using Winsor II systems. The work of Li et al. on liquid surfactant membranes (*4–8*) and Scamehorn et al. on micellar-enhanced ultrafiltration (*9–12*) also deals with using surfactants and microemulsions to treat industrial streams. Electrical phenomena at interfaces, the various double layer models, the theories associated with them, and the corresponding references are dealt with extensively in a number of publications. We mention only some of them here (*13–16*). Hirasaki and Lawson (*1*) used electrostatic models to interpret the association of sodium and calcium to surfactant micelles. Very recently Leodidis and Hatton (*17*) examined specific ion effects in Winsor II systems through a phenomenological model and traced earlier modeling efforts in this area.

In this work the selective extraction of bivalent copper (from aqueous copper sulfate solutions) into a water-in-oil microemulsion system is demonstrated experimentally. It is also shown that a quantitative model of the electrostatic principles mentioned above is very successful in predicting the observed trends. While this work limits itself to the study of the extraction of a bivalent cation, it should be noted that the extraction of cations of even higher charge in similar systems should proceed with even higher extraction efficiencies.

## EXPERIMENTAL DETAILS

### Microemulsion System

The microemulsion system selected to extract the metal ions, i.e., concentrate the aqueous metal solutions, was the system water/Aerosol-OT/isooctane. The phase diagram of this system was examined (*18*) and a range of compositions which would form Winsor II systems was selected for the experiments. Since these experiments involved the use of aqueous $CuSO_4$ solutions instead of pure water, some deviation from this phase

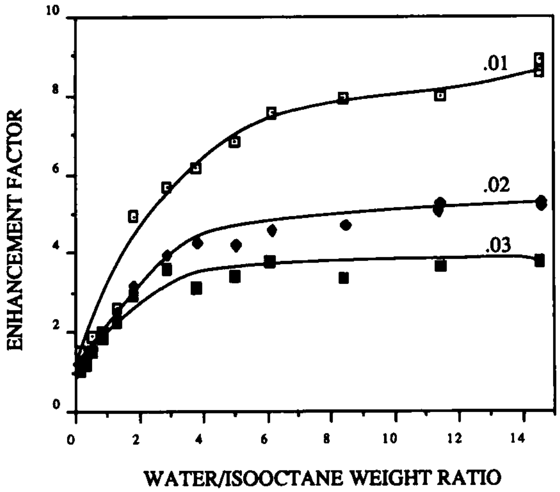


FIG. 1. Enhancement factor vs initial water/isooctane weight ratio for the three series of copper sulfate solutions.

behavior was to be expected. However, it was possible to obtain a reasonable number of sample compositions which formed Winsor II systems.

## Materials

Commercially available chemicals were used by us without further purification. The surfactant Aersol-OT [sodium bis(2-ethylhexyl) sulfosuccinate, (AOT)] was Fluka Purum grade (≥98%). Isooctane (2,2,4-trimethylpentane) obtained from Mallinckrodt was Spectrophotometric grade. Copper sulfate crystals ($CuSO_4 \cdot 5H_2O$) were obtained from Mallinckrodt. The water used was deionized to a standard resistance of 18 MΩ.

## Methods

UV/VIS spectroscopy was used to determine 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 Digilab FTS-20C Fourier Transform Spectrophotometer, using an attenuated total internal reflectance cell (ATR). Each spectrum was averaged for 200 scans at a resolution of 2 $cm^{-1}$. Radius measurements of swollen micelles were done by dynamic light scattering.

## 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. Aqueous copper sulfate solutions with $CuSO_4/H_2O$ weight ratios of 0.01, 0.02, and 0.03 were prepared. 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 $CuSO_4/H_2O$ weight ratios any one series was a constant, the only varying factor in the series being the $H_2O$/isooctane weight ratio. However, the $CuSO_4/H_2O$ weight ratio of each series was different. The samples were maintained at room temperature and allowed to phase separately.

Many of the samples phase separated into a Winsor II type of microemulsion. Some of the samples had a middle crystalline phase which over a period of time disappeared to leave behind a two-phase system. The top phase was usually a vivid blue as opposed to the much paler color of the lower aqueous phase, as would be expected if significant amounts of copper migrated into the top phase. This was later verified analytically.

## Analysis

The water and copper contents of the top phases were determined as mentioned earlier, using FTIR and UV/VIS spectrophotometers, respectively. This, in combination with previously obtained calibration data, yielded the copper/water ratio of the top phase microemulsion The enhancement factor, defined as given below, was determined for all the samples.

$$\eta = \frac{\left(\frac{\text{salt}}{\text{water}}\right)_{\text{T.P.}}}{\left(\frac{\text{salt}}{\text{water}}\right)_{\text{original}}} \tag{1}$$

where $\eta$ is the enhancement factor and subscripts "T.P." and "original" refer to the top phase and the initial aqueous solution, respectively. An alternative to $\eta$ would be to define a partition coefficient $\kappa$ given by

$$\kappa = \frac{\left(\dfrac{\text{salt}}{\text{water}}\right)_{\text{T.P.}}}{\left(\dfrac{\text{salt}}{\text{water}}\right)_{\text{B.P.}}}$$

where the subscript "B.P." refers to the bottom phase. In our work we have exclusively used the enhancement factor.

## Experimental Results

In Fig. 1 we have plotted the enhancement factors for the three series of copper sulfate samples against the water/isooctane weight ratio in the initial mixtures (i.e., based on amounts added to the sample before phase separation). It is observed that for low water/isooctane weight ratios (around 1), the enhancement factor increases as the water/isooctane weight ratio in the initial mixture is raised. At much higher water/isooctane weight ratios (around 5), a tapering toward a constant value of the enhancement factor is obtained. Partition coefficients for this system range from 1 to 12. It is also observed that as the initial $CuSO_4/H_2O$ weight ratio of the added aqueous solution decreases, there is a definite increase in the enhancement factors. Thus, for example, systems prepared with a $CuSO_4/H_2O = 0.01$ aqueous solution have greater enhancement factors than those with ratios of 0.02 and 0.03. As shown below, the enhancement factors will be even higher at still lower initial salt/water ratios. From a practical standpoint, this indicates that the extraction efficiency of this system increases upon going to lower and lower initial concentrations of copper. This makes the system rather attractive for the near-complete extraction of heavy metal traces in effluent streams.

From the definition of the enhancement factor in Eq. (1), we can see that the initial salt/water ratio appears in the denominator. One would therefore expect the enhancement factor to increase at lower initial concentrations. However, this is not the only effect seen here. This becomes obvious when the data are cast into a slightly different form. From the enhancement factor data and the compositions of the systems at each of the data points, we can determine the final copper/AOT mole ratio in each of the top phases. This is plotted in Fig. 2. From these data it is apparent that

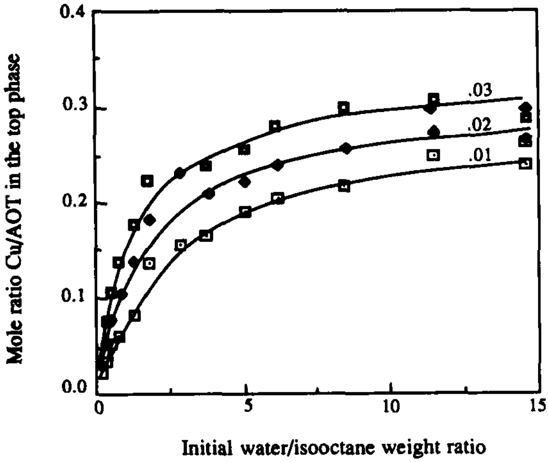


FIG. 2. Mole ratio Cu/AOT in the top phase vs initial water/isooctane weight ratio for the three series of copper sulfate solutions.

the copper/AOT ratio increases with increasing water/isooctane ratio and begins to saturate at higher values of water/isooctane. Data at higher water/isooctane ratios than those shown are difficult to obtain with our method of product analysis, but is does appear that a copper/AOT ratio of around 0.27–0.3 corresponds to the saturation limit for all three initial copper concentrations used. From the point of view of charge neutralization, one would expect this ratio to be close to 0.5. One possible explanation for this phenomenon is that not all of the surfactant is ionized in the swollen micelles; rather, some "active fraction" of the surfactant contributes to ion exchange. While it might be argued that the copper/AOT ratio of 0.3 indicates that 60% of the AOT is electrostatically associated with copper and that the rest is electrostatically associated wih sodium, this explanation would be inconsistent with the nature of the electrostatic association which typically is proportional to the exponent of some positive power of the charge of the cation, as shown in Eqs. (4) and (5). Such an active fraction has been postulated by a number of workers, but as stated by Evans et al. (*19*), recourse to such a postulation is not necessary for a complete explanation of the experimental data.

We have seen in this section that the AOT/isooctane micellar system is capable of extracting multivalent cations from aqueous solutions. We have attempted to quantitatively describe this phenomenon by a mathematical model based on electrostatic forces between the cations and the micellar surface. A complete description of this model, its features and its shortcomings, is the subject matter of the rest of the paper.

## THEORETICAL ANALYSIS

The system we are modeling consists of a two-phase system of a W/O microemulsion over an aqueous phase in the presence of bivalent cations, specifically copper. Experimentally, we observed that the bivalent cation seems to concentrate in the top microemulsion phase. Our approach has been to model this phenomenon as a preferential substitution of the counterions of the surfactant by the bivalent cations. We assume that the adsorption of counterions onto the surfactant surface of the reverse micelle can be modeled by the Stern double layer model (*1, 20*). 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 purely by electrostatic forces, with no chemical bonding involved.

The potential distribution arising in the vicinity of an electrically charged surface is governed by the generalized Poisson-Boltzmann equation (*14, 21-23*)

$$\nabla^2\psi = -\frac{4\pi e}{\varepsilon}\Sigma_i n_i Z_i \exp\left(\frac{-Z_i e\psi}{kT}\right) \tag{2}$$

subject to suitable boundary conditions for the problem in question. Solutions to this equation are, of course, dependent on the geometry of the specific system considered. In general, for a negatively charged surface the general solution in one dimension takes the form

$$-\psi_r = f(\psi_0, r) \tag{3}$$

where $\psi_0$ is the potential at the surface ($r = 0$) and $r$ is the distance from the surface. (For the special case of one-dimensional Cartesian coordinates, this solution is an exponential decay from $\psi_0$ and is known as the Gouy-

Chapman solution.) This behavior is often pictorially represented as in Fig. 3(a) (*15, 22*). The effect of such a potential distribution is to attract species of opposite charge to the surface and to repel species of similar charge. The corresponding concentration profiles are shown in Fig. 3(b).

Since electrostatic forces are responsible for this concentration gradient, it is apparent that a negatively charged surface will tend to preferentially attract multivalent cations rather than monovalent cations. If concentration profiles for both are calculated, then the relative amounts of each type of cation attracted to the wall can be calculated by integrating each of these profiles from $r = 0$ to $r = \infty$.

In reality, however, the accumulation of cations close to the charged surface causes a distortion of the potential distribution, and the actual profile can be schematically represented as in Fig. 4 (, *13, 15, 16*). The thickness $\delta$ is called the Stern layer thickness (*20*). The behavior of $\psi$ in the range $0 \leqslant r \leqslant \delta$ is not completely understood, while in the range $\delta \leqslant r \leqslant \infty$ it is widely assumed to be governed by the Poisson-Boltzmann equation. Consequently, a simple expression for the concentration profiles of electrostatically attracted cations cannot be rrived at. Stern, however, has oposed an equation (the Stern adsorption isotherm) which has been accepted as representing the relative amounts of cations attracted to the surface. For ions of only the *i*th species adsorbed on the surface, the Sternisotherm is given by (*13, 15*)

$$\tau_i = \frac{\mu_0 n_i \exp\left(\dfrac{-\phi_i - Z_i e \psi_\delta}{kT}\right)}{\left(1 + \mu_0 n_i \exp\left(\dfrac{-\phi_i - Z_i e \psi_\delta}{kT}\right)\right)} \tag{4}$$

where $\tau_i$ is the surface coverage by the *i*th species, $n_i$ is the bulk concentration of solute ions of the *i*th species, $\mu_0$ is the molecular volume of the solvent, $\phi_i$ is the specific (nonelectrostatic) adsorption potential of one ion of the *i*th species, $k$ is the Boltzmann constant, $T$ is the temperature, $Z_i$ is the charge on the *i*th species, $e$ is the electronic charge, and $\psi_\delta$ is the electrostatic potential at the Stern plane.

In the case of multiple cations, the Stern adsorption isotherm becomes

$$\tau_i = \frac{\mu_0 n_i \exp\left(\dfrac{-\phi_i - Z_i e \psi_\delta}{kT}\right)}{\left(1 + \sum_i \mu_0 n_i \exp\left(\dfrac{-\phi_i - Z_i e \psi_\delta}{kT}\right)\right)} \tag{5}$$

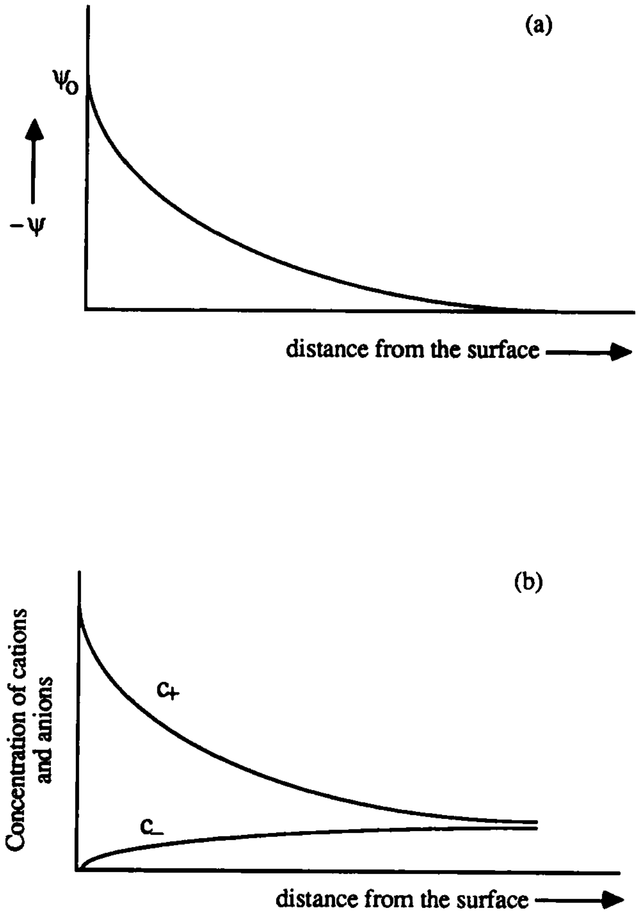


FIG. 3. The Guoy-Chapman model. (a) The potential distribution. (b) The concentration profiles for ions near a negatively charged surface indicated by $c_+$ and $c_-$.

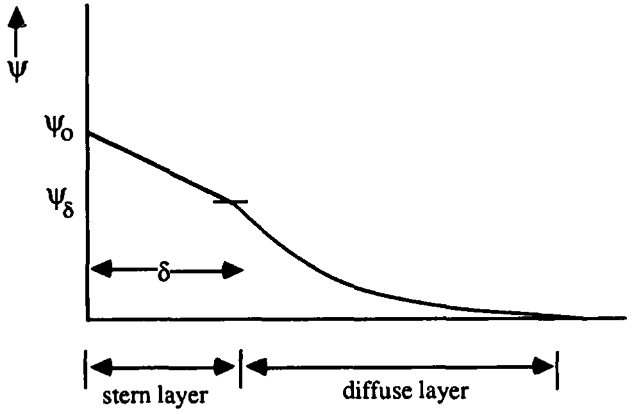


FIG. 4. Stern double layer model.

In using the Stern adsorption equation for multiple adsorbents we have neglected the effect of sulfate ions and have assumed that only the copper and sodium ions contribute toward surface coverage. This is consistent with the picture of a negatively charged surface repelling the negative sulfate ions away from the surface. Assuming total dissociation of the surfactant 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. Hence, the nonelectrostatic adsorption potential $\phi_i$ was neglected. Such an assumption has also been successfully employed by Hirasaki and Lawson (*1*). Since the right-hand side of the Stern equation does not contain the entire potential distribution $\psi$ but rather contains the variable $\psi_\delta$, one only needs an estimate of the Stern potential $\psi_\delta$ to predict the relative amounts of cations attracted to the charged surface. Hence, a reasonable estimate for $\psi_\delta$ in the case of spherical microemulsion particles is required. No analytical solution satisfying the surface boundary conditions is possible in the case of the spherical Poisson-Boltzmann equation (*14, 23*). As shown in the Appendix, for the conditions of this study the analytical solution of the planar Poisson-Boltzmann equation in one dimension can be shown to admit of a solution that is identical for numerical purposes to the numerical solution of the generalized spherical Poisson-Boltzmann equation. Therefore the analytical solution was used in our work. The determination of $\psi_\delta$ from this is done as follows.

The planar Poisson-Boltzmann equation in one dimension for the case of multiple ions in solution is written as

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi e}{\varepsilon} \quad \Sigma_i n_i Z_i \exp\left(\frac{-Z_i e\psi}{kT}\right) \tag{6}$$

subject to the boundary conditions

$$\frac{d\psi}{dx}\bigg|_{x=0} = -\frac{4\pi\sigma}{\varepsilon}$$

$$\psi(x)\,|_{x=0} = \psi_0$$

and

$$\psi(x)\,|_{x\to\infty} \to 0$$

On integrating Eq. (6) once and substituting the boundary conditions to eliminate the constant of integration, we get

$$\left(\frac{4\pi\sigma}{\varepsilon}\right)^2 = \frac{8\pi kT}{\varepsilon} \quad \Sigma_i\left(n_i \exp\left(\frac{-Z_i e\psi_0}{kT}\right) - n_i\right) \tag{7}$$

where $\psi_0$ is the potential at the surface, $\sigma$ is the surface charge, and $\varepsilon$ is the dielectric constant. In this work $\varepsilon$ was taken to be a constant and equal to that of water. It would appear that $\psi_\delta$ would be some value between $\psi_0$ and 0. For this work a working relationship of $\psi_\delta = 0.59\psi_0$ was used. Varying this factor between 0.59 and 1.0 did not alter the form of the solution, although 0.59 was found to be optimal for purposes of comparison with the experiments.

The mass balance equations on sodium and copper are given by

$$n_i^0 V_0 = \tau_i N_{\text{AOT}} + n_i V_0 \tag{8}$$

where $n_i^0$ is the initial concentration of Species $i$, $V_0$ is the initial aqueous volume, and $N_{\text{AOT}}$ is the initial number of molecules of AOT. The mass balance equations have been written to be consistent with the assumption of total surfactant dissociation.

Equations (5), (7), and (8) give 5 equations and 5 variables which were solved numerically by a combination nonlinear root-solving technique. The values of copper/AOT in the top phase computed by this model are shown in Fig. 5 compared with the experimentally observed results. It is seen from the figure that at low initial aqueous concentrations the predictions of the theory match the experimental results well. Deviations start

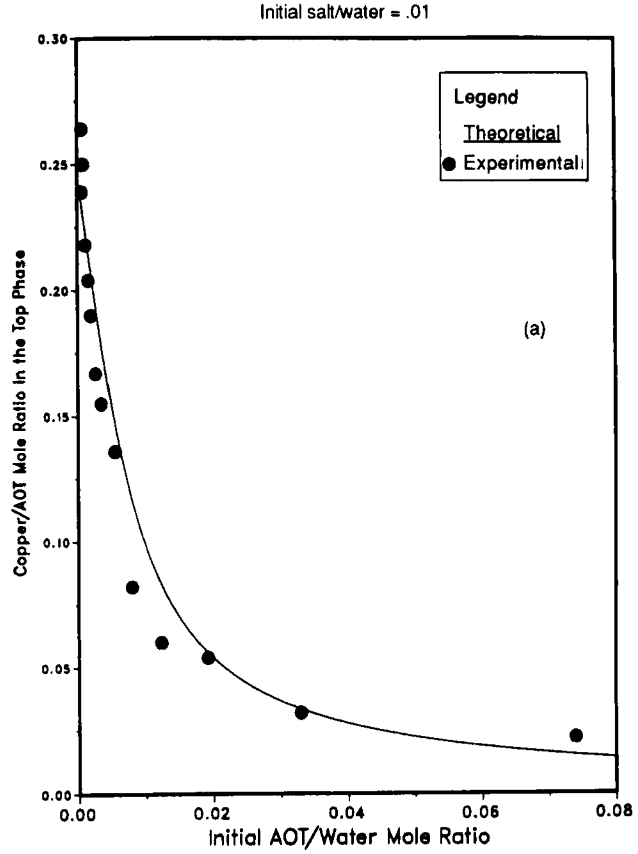
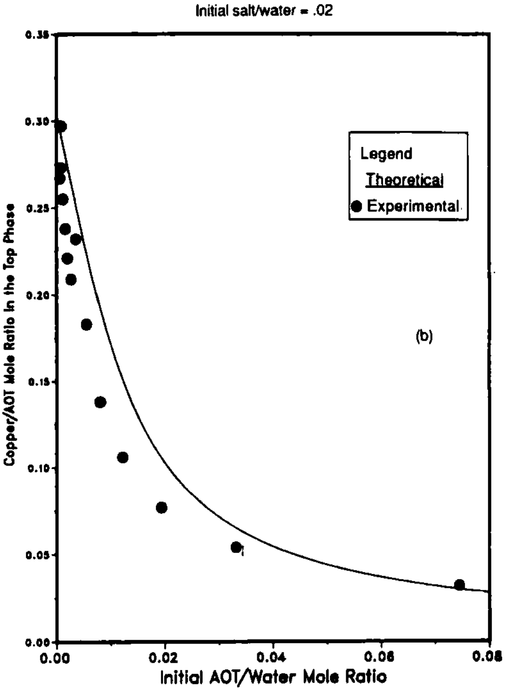
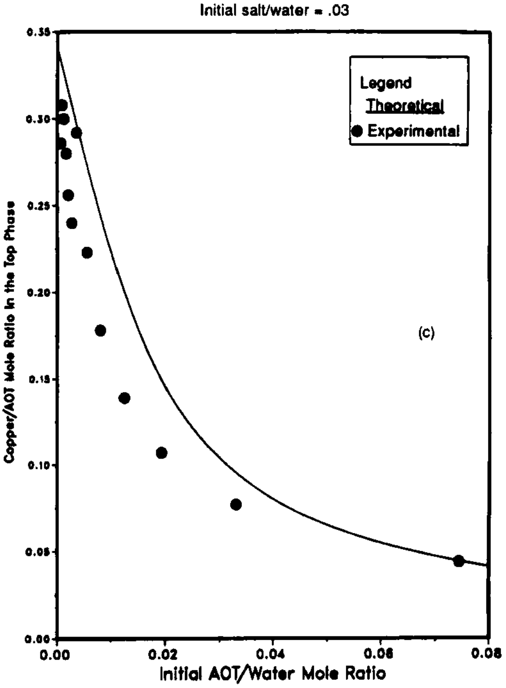


FIG. 5. Comparison of theoretical predictions vs experimental trends for the three series of copper sulfate solutions: (a) initial salt/water = 0.01, (b) initial salt/water = 0.02, (c) initial salt/water = 0.03.


Initial salt/water = .02
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Copper/AOT Mole Ratio in the Top Phase
0.00
0.02
0.04
0.06
0.08
Initial AOT/Water Mole Ratio
Legend
Theoretical
● Experimental
(b)


Initial salt/water = .03
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Copper/AOT Mole Ratio in the Top Phase
0.00
0.02
0.04
0.06
0.08
Initial AOT/Water Mole Ratio
Legend
Theoretical
● Experimental
(c)

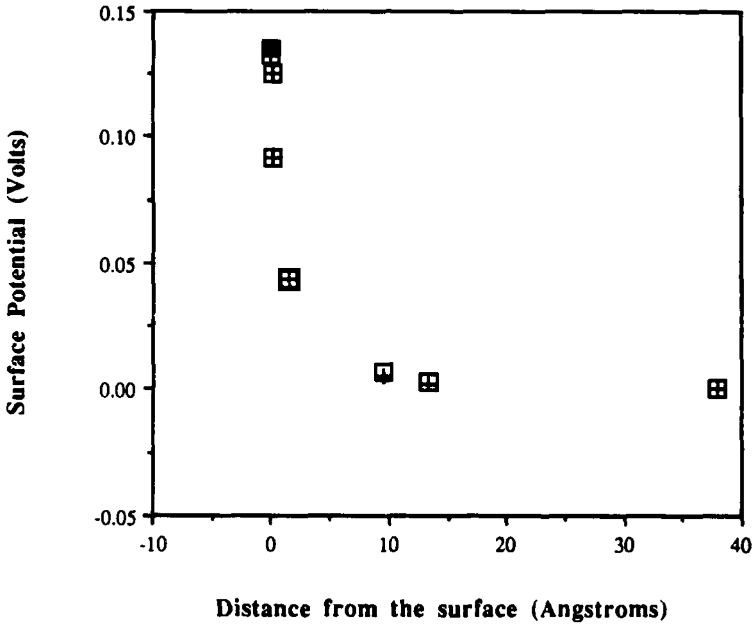


FIG. 6. A comparison of the numerical spherical solution (□) obtained by finite element method (FEM) and the planar analytical solution (+) of Poisson-Boltzmann equation for the case of initial salt/water = 0.02.

occurring as the initial concentration increases, although the qualitative trends are still preserved. This work was done using somewhat higher concentrations of initial salt solutions than most related work (*5*, *8*, *9*) because the analytical technique we used, UV/VIS spectroscopy, required it. One would expect that the agreement between theory and experiment would be even closer at concentrations lower than those we investigated.

The deviations for higher initial metal concentrations probably reflect a breakdown of the working relationship $\psi_\delta = 0.59\psi_0$. We fully recognize that this is only a working relationship. A more complete analysis of the potential within the Stern layer is definitely in order. A phenomenological model of such behavior has been very recently proposed by Leodidis and Hatton (*17*). Their approach leads to a complete solution for the potential and concentration distributions within the micelle, including layers close to the micellar wall. However, their approach is computationally far more intensive than the simpler one used by us.

From a physical point of view, cations of a charge higher than 2 are expected to be even more attracted to the micellar surface. Our model has the capability to take this into account and is capable of predicting the selective extractabilities of mixtures of cations of different charges.

In the past a full solution of the Poisson-Boltzmann equation for the non-Z-Z electrolyte case has rarely been discussed. 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) with relative ease. Therefore, all the ions involved in our system, i.e., $Cu^{2+}$, $SO_4^{2-}$, 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-Boltzman equation can only be solved numerically. This is further complicated by a lack of knowledge regarding the potential distribution close to the charged surface, i.e., within the Stern layer. Our approach 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.

## CONCLUSIONS

Experimental results for the extraction of a bivalent metal, copper, 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 more pronounced in the case of dilute metal solutions.

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. Some shortcomings still exist in the model when quantified; specifically, the Stern potential $\psi_\delta$ is assumed to be proportional to the wall potential $\psi_0$. A better independent estimate of the Stern potential would eliminate the only adjustable parameter in this model and make it truly predictive.

## APPENDIX

*Ka* is a measure of sphericity for spherical particles of radius *a*, where *K* is the inverse Debye screening length. For *Ka* greater than 10, the planar double layer model would be a good approximation to the spherical double layer (*22*). In our case, estimates of *Ka* indicated that it was greater than 30. As a further check, the spherical Poisson-Boltzmann equation was discretized and solved by the finite element method. This was compared to the analytical solution of the planar Poisson-Boltzmann equation. Figure 6 is an example of the superposition of the numerical spherical solution and the planar analytical solution under the same conditions. The two sets of solutions for the experimental range of concentrations were found to be numerically identical.

## NOMENCLATURE

| | |
|---|---|
| $e$ | the electronic charge |
| $k$ | the Boltzmann constant |
| $\eta_i^0$ | the initial concentration of Species *i* |
| $\eta_i$ | the bulk concentration of solute ions of the *i*th species |
| $N_{\mathrm{AOT}}$ | the initial number of molecules of AOT |
| $T$ | the absolute temperature |
| $V_0$ | the initial aqueous volume |
| $Z_i$ | the charge on the *i*th species |
| $\varepsilon$ | the dielectric constant |
| $\eta$ | the enhancement factor |
| $\kappa$ | the partition coefficient |
| $\mu_0$ | the molecular volume of the solvent |
| $\sigma$ | the surface charge |
| $\tau_i$ | the surface coverage by the *i*th species |
| $\phi_i$ | the specific (nonelectrostatic) adsorption potential of one ion of the *i*th species |
| $\psi_\delta$ | the electrostatic potential at the Stern plane |
| $\psi_0$ | the potential at the surface |

## Acknowledgments

Financial support of this project by the National Science Foundation Grant CBT 87-01718 is gratefully acknowledged. The authors would also like to acknowledge Michael Call and Georgios Georgiou of the University of Michigan for assistance provided with the numerical computations.

## REFERENCES

1. G. J. Hirasaki and J. B. Lawson, *SPE Reservoir Eng.* March 1986.
2. P. A. Winsor, *Trans. Faraday Soc.*, *44*, 376 (1948).
3. F. J. Ovejero-Escudero, H. Angelino, and G. Casamatta, *J. Dispersion. Sci. Technol.*, *8*(1), 89 (1987).
4. N. N. Li, U.S. Patent 3,410,794 (1968).
5. N. N. Li, J. W. Frankenfeld, T. Kitagawa, and Y. Nishikawa, *Environ. Sci. Technol.*, *11*(6), 602 (1977).
6. N. N. Li and R. P. Cahn, *Sep. Sci.*, *9*(6), 505 (1974).
7. D. T. Wasan, Z. M. Gu, and N. N. Li, *Faraday Discuss. Chem. Soc.*, *77*, 67 (1984).
8. D. T. Wasan, Z. M. Gu, and N. N. Li, *Sep. Sci. Technol.*, *20*(7&8), 599 (1985).
9. J. F. Scamehorn, R. T. Ellington, S. D. Christian, B. W. Penney, R. O. Dunn, and S. N. Bhat, *AIChE Symp. Ser.*, *82*(250), 48 (1986).
10. R. O. Dunn, J. F. Scamehorn, and S. D. Christian, *Sep. Sci. Technol.*, *20*(4), 257 (1985).
11. R. O. Dunn, J. F. Scamehorn, and S. D. Christian, *Ibid.*, *22*(2&3), 763 (1987).
12. R. O. Dunn, J. F. Scamehorn, and S. D. Christian, *Colloids Surfaces*, *35*, 49 (1989).
13. B. V. Derjaguin, N. V. Churaev, and V. M. Muller, *Surface Forces*, Consultants Bureau, New York, 1987.
14. R. J. Hunter, *Foundations of Colloid Science*, Vol. 1, Oxford Science Publications, 1987.
15. M. J. Jaycock and G. D. Parfitt (eds.), *Chemistry of Interfaces*, Ellis Horwood Ltd., 1981.
16. A. Kitahara and A. Watanabe (eds.), *Electrical Phenomena at Interfaces* (Surfactant Science Series, 15), Dekker, New York, 1984.
17. E. B. Leodidis and T. A. Hatton, *Langmuir*, *5*(3), 741 (1989).
18. H. Kunieda and K. Shinoda, *J. Colloid Interface Sci.*, *70*(3), 577 (1979).
19. D. F. Evans and B. W. Ninham, *J. Phys. Chem.*, *87*, 5032 (1983).
20. O. Stern, *Z. Elektrochem.*, *30*, 508 (1924).
21. F. Booth, *J. Chem. Phy.*, *19*(7), 821 (1951).
22. S. Usui, in *Electrical Phenomena at Interfaces* (Surfactant Science Series, 15), A. Kitahara and A. Watanabe, eds.), Dekker, New York, 1984.
23. L. R. White, *J. Chem. Soc., Faraday Trans. II*, *73*, 577 (1977).

*Received by editor August 11, 1989*