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An Improved Model for the Extraction of Multivalent Metals in Winsor II Microemulsion Systems

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

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NOTE

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CHANDRA S. VIJAYALAKSHMI and ERDOGAN GULARI
DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN 48109

INTRODUCTION

Our earlier paper described a liquid–liquid extraction process for metal ions using a Winsor II microemulsion system (*1*). A Winsor II system is a biphasic system in which a water-in-oil microemulsion exists in equilibrium with a lower predominately aqueous phase (*2*). Complete details of the system, the experiments, and the modeling efforts have been given in our earlier work (*1*). Hence, to avoid redundancy, only the salient features are discussed here as a prelude to dealing with the extension of the model.

EXPERIMENTAL DETAILS

The extraction of bivalent copper ions was done using the water/Aerosol-OT/isooctane microemulsion system. 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 from deionized water and ACS reagent grade copper sulfate. Identical volumes of these three 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 ratio of any one series was a constant, the only varying factor in the series being the H_2O/isooctane weight ratio. The samples were maintained at room temperature and allowed to phase separate into Winsor II systems. The top phase was usually a vivid blue in color 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. The water and copper contents of the top phases were determined using FTIR and UV/VIS spectrophotometers. Large values of concentration enhancements compared to the original aqueous solutions were obtained in the top phases.

MODEL

Initial Formulation

The system we are modeling consists of a two-phase system of a W/O microemulsion in equilibrium with an aqueous phase in the presence of bivalent cations, specifically copper. The ions present in the solution are Na^+, Cu^{2+}, and SO_4^{2-}. Experimentally we observed that the copper tended to concentrate in the top microemulsion phase. Our approach was to model this phenomenon as a preferential substitution of the counterions of the surfactant by the bivalent cations. We assumed that the adsorption of counterions onto the surfactant surface of the reverse micelle can be modeled by the Stern double layer model (*3*, *4*). We also assumed that the surfactant molecules were dissociated and the negative heads of the ionized surfactant contributed to an electric field on the inside of the micelle, which tended to attract the positive counterions back to the interface. These counterions were considered bound to the anionic surface purely by electrostatic forces with no chemical bonding being involved.

The Stern adsorption isotherm proposed by Stern represents the relative amounts of cations attached to a charged surface (*5*, *6*). In the case of multiple ions in solution as in the case of our system, the Stern adsorption isotherm becomes

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

where τ_i is the surface coverage by the ith species, n_i is the bulk concentration of solute ions of the ith 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. In using the Stern equation for multiple adsorbents, we had neglected the effect of sulfate ions and had assumed that only the copper and sodium ions contribute toward surface coverage. The rationale behind this assumption was that the negatively charged bivalent sulfate ions would be strongly repelled by the negatively charged interfacial membrane. As a result, they would have a negligible surface coverage and, as such, exert little or no influence on the coverage of the positive cations. An estimate of the Stern potential ψ_δ to predict relative amounts of cations attracted to the charged surface was done by using the integrated planar Poisson-Boltzmann equation in one dimension for the case of multiple ions in solution (*7–10*):

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

where ψ_0 is the potential at the surface, σ is the surface charge, and ϵ is the dielectric constant. The effects of all three ions, i.e., Na^+, Cu^{2+}, and SO_4^{2-}, were taken into account in this equation. Since ψ_δ has an intermediate value between ψ_0 and 0, a working relationship of $\psi_\delta = 0.59\psi_0$ was used in the model.

The mass balance equations on sodium and copper were given by

$$n_i^0 V_0 = \tau_i N_{AOT} + n_i V_0 \tag{3}$$

where n_i^0 is the initial concentration of species i, V_0 is the initial aqueous volume, and N_{AOT} is the initial number of molecules of AOT. Once again, as in the case of the Stern equation, the effect of SO_4^{2-} ions was ignored here for the reasons mentioned earlier. Thus our model comprised five equations and five variables, and it was solved numerically by a combination nonlinear root solving technique. The values of copper/AOT in the top phase computed by this model were compared with the experimentally observed results. It was found that at lower initial aqueous concentrations the predictions of the theory matched the experimental results well. Deviations started occurring as the initial aqueous concentration increased, although the qualitative trends were still preserved.

Current Formulation

In a further attempt to improve the model and better explain the model discrepancy at higher concentrations, it was decided to reexamine the assumption regarding the neglect of anion effects. It was argued that the sulfate ions, while having a negligible coverage, could conceivably exert a cumulative effect on the overall behavior of the system. This hypothesis was tested by including the effect of sulfate ions in the surface coverage Eq. (1) and the mass balance Eq. (3). The system now comprises seven equations and seven variables. In the new system of equations the pro-

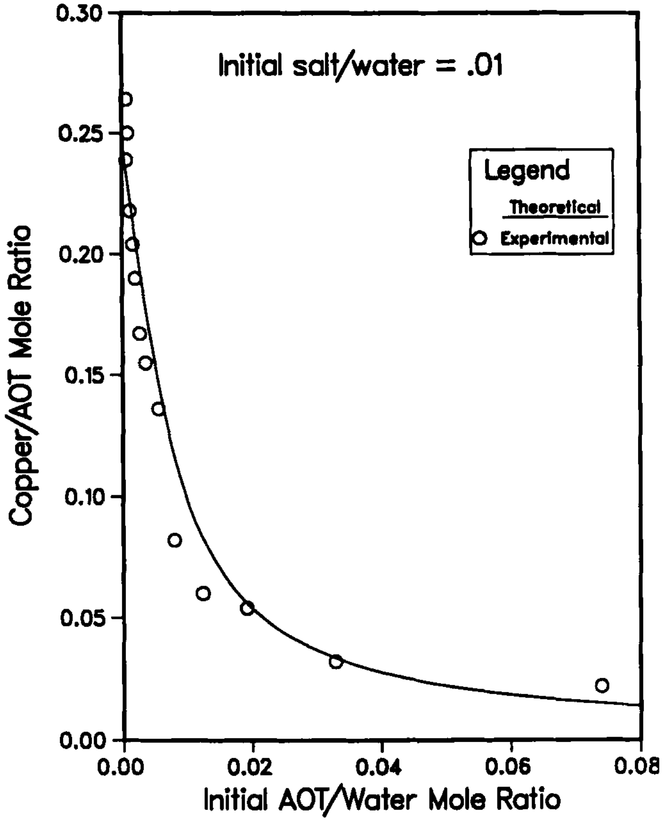

FIG. 1A. Comparison between theoretical predictions and experimental trends for the case of initial salt/water = 0.01: old model.

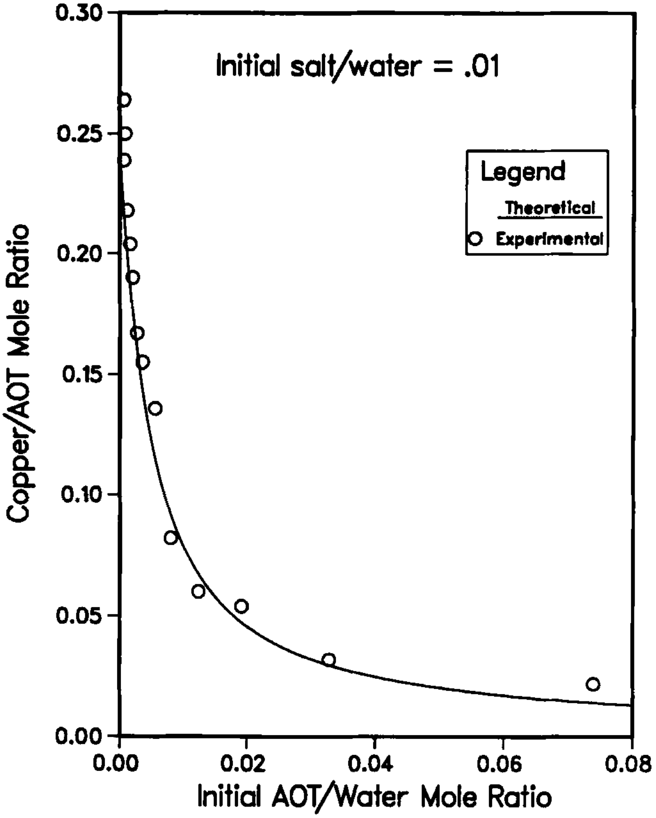

FIG. 1B. Comparison between theoretical predictions and experimental trends for the case of initial salt/water = 0.01: current model.

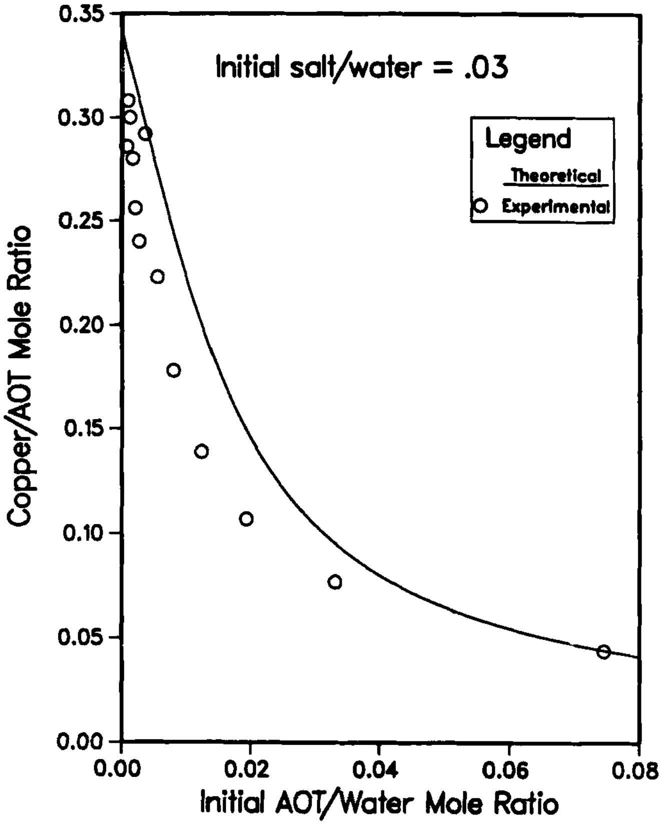

FIG. 2A. Comparison between theoretical predictions and experimental trends for the case of initial salt/water = 0.03: old model.

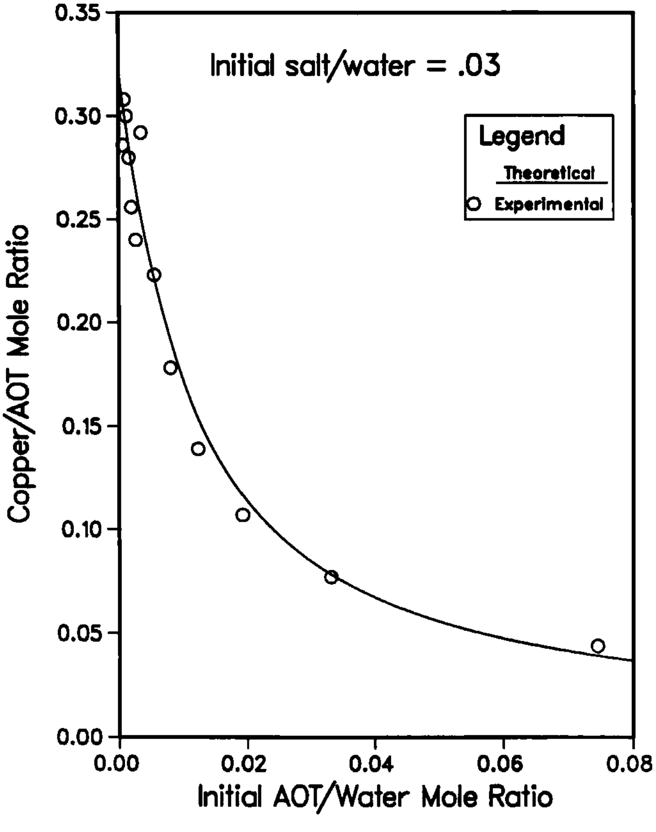

FIG. 2B. Comparison between theoretical predictions and experimental trends for the case of initial salt/water = 0.03: current model.

portionality constant between ψ_δ and ψ_0 in our working relationship was changed from 0.59 to 0.65. The effect of the sulfate inclusion was rather dramatic. The resultant comparisons between the theoretical predictions and the experimental results are shown in Figs. 1 and 2. It will be seen that there is excellent agreement between theory and experiment at all concentrations.

CONCLUSIONS

We have presented an improved model of metal extraction by microemulsions that correctly includes all the ionic species in the Stern adsorption equation, the Poisson-Boltzmann equation, and the mass balance equation. The new formulation significantly improves the agreement between theory and experiment. It is therefore not correct to neglect an ionic effect simply due to the low coverage of the ion since other effects also exist.

NOMENCLATURE

e	the electronic charge
k	the Boltzmann constant
n_i^0	the initial concentration of Species i
n_i	the bulk concentration of solute ions of the ith species
N_{AOT}	the initial number of molecules of AOT
T	the absolute temperature
V_0	the initial aqueous volume
z_i	the charge on the ith species
ϵ	the dielectric constant
μ_0	the molecular volume of the solvent
σ	the surface charge
τ_i	the surface coverage by the ith species
ϕ_i	the specific (nonelectrostatic) adsorption potential of one ion of the ith species
ψ_δ	the electrostatic potential at the Stern plane
ψ_0	the potential at the surface

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