INTERFACIAL CHEMISTRY IN SOLVENT
EXTRACTION SYSTEMS

Progress Report
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PROGRESS REPORT

Significant progress has been made in our research program investigating the interfacial chemistry in solvent extraction systems. Our research last year emphasized characterization in greater detail of the physicochemical nature of the microscopic interfaces, i.e., reversed micelles and other association microstructures, which form in both practical and simplified acidic organophosphorus extraction systems associated with nickel, cobalt and sodium in order to improve upon our recently proposed model for the aggregation of metal-extractant complexes. In addition, the macroscopic interfacial behavior of extractant molecules and their interactions with metal ions which occur in hydrometallurgical solvent extraction systems were further investigated. Some highlights of our recent accomplishments are summarized below.

Model Extraction Systems - Sodium

In order to fully understand the extraction of metals by di(2-ethylhexyl)phosphoric acid (HDEHP), knowledge of the aggregation behavior of sodium di(2-ethylhexyl)phosphate (NaDEHP) in apolar media is important since NaDEHP forms when the aqueous phase pH is adjusted with sodium hydroxide.

(a) On the Role of Water in the Formation of Reversed Micelles; An Anti-Micellization Agent

Micellization of NaDEHP in n-heptane has been studied under controlled environmental conditions by dynamic and static light scattering. The results clearly show that a trace amount of water has a very dramatic effect on reversed micellization. In contrast with results in the literature, water can function as an anti-micellization agent. The generality of and the evidence for supporting the current view that water is a prerequisite for the formation of reversed micelles are criticized.

(b) Reversed Micellization: Non-Universality of Step-Wise Aggregation

For a surfactant in apolar media, a sharp transition in physical properties, e.g., scattered intensity, with a critical micellar concentration (cmc) range as narrow as that in aqueous surfactant solutions was shown to occur for the first time. It thus appears that an equilibrium between monomeric surfactant and reversed micelles exists, and the concept of cmc which successfully characterizes surfactant behavior in aqueous solution can also be used for the NaDEHP/n-heptane system. Therefore, the current literature views that the formation of reversed micelles in organic solutions can take place only over a wide range of surfactant concentration and that reversed micellization is only a step-wise aggregation process appear to be, at least, not general phenomena in nonaqueous surfactant solutions.

(c) Thermodynamics of Reversed Micellization: Entropy-Controlled Aggregation Process

Thermodynamics of reversed micellization in apolar media was studied experimentally for the first time. The driving force for reversed micellization is an entropy increase, which is the same as that for aqueous systems, and the

enthalpy change opposes the formation of reversed micelles. It is suggested that the entropy increase comes primarily from an increase in the entropy of the solvent, analogous to that for aqueous systems. Presumably, interactions between the hydrogen atoms of the n-heptane and the oxygen atoms of the phosphate head group of the surfactant molecule lead to a "stiffness" of the alkyl chain, and the degrees of freedom of n-heptane are increased when reversed micelles form. The literature views that the entropy change in nonaqueous systems is unfavorable for the formation of reversed micelles and that the driving force behind the process of reversed micellization is essentially due to dipole-dipole interactions between the polar head groups of the amphiphilic molecules are criticized.

(d) Solution Behavior of Reversed Micelles and W/O Microemulsion

NaDEHP was shown to form large rodlike reversed micelles both in "dry" and "wet" n-heptane, in other words, association microstructures as large as 170 nm in length. This finding is in violent contrast with the literature view that the average aggregation number in nonaqueous systems is much smaller than that in aqueous systems, seldom exceeding an aggregation number of 10. Such reversed micelles are much larger than those in most aqueous micellar systems and, therefore, the existence of a sharp transition in physical properties or a very clear cmc can be well understood.

Water can be solubilized into the NaDEHP reversed micelles, but when it is, the micellar size is reduced tremendously. The probable cause is hydrolysis of the surfactant molecule when water is added to the apolar solvent. Swollen reversed micelles grow at high molar ratios (W_o) of water to surfactant, which may be interpreted using current theories for micellar evolution in aqueous solutions.

The phase diagram of the NaDEHP/n-heptane/water system shows the existence of a broad region where a W/O microemulsion with W_o as large as 90 can occur. The line width and chemical shift of P^{31} and H^1 NMR, FT-IR and viscosity measurements indicate that the shape of the W/O microemulsion droplets undergo a gradual change from rodlike to spherical microdroplets.

(e) Improvement of Laser-Light Scattering Technique Leading to the Significant Findings Made in Model Extraction Systems

It is often very difficult to obtain reliable light-scattering measurements on surfactant solutions, especially when extremely small particles occur in aqueous or apolar media or when the refractive index increment is very low. The effectiveness of a simple technique for preparation of high-quality optically clean samples for dynamic and static light-scattering measurements was demonstrated on three selected systems where the elimination of dust is very critical. The applications illustrated were measurements of the diffusion coefficient of perfluorinated surfactant micelles and organic ions in aqueous solutions and determination of the cmc of a surfactant in hydrocarbon solvent.

Model Extraction Systems - Nickel (II)

The phase diagram of the $\text{Ni}(\text{DEHP})_2/\text{n-heptane}/\text{water}$ system was obtained. Reversed micelles which are rodlike in shape are formed when $W_o < 11$. The concept of reversed micelles which are formed by metal-extractant complexes is introduced and compares with that of reversed micelles formed by surfactant monomers. There are two aspects of reversed micellization which, however, are different from normal surfactant reversed micelles. First, unlike the concentration dependence of normal surfactants, the $\text{Ni}(\text{DEHP})_2 \cdot 2\text{H}_2\text{O}$ complex itself does not form reversed micelles no matter how high the concentration. Secondly, nickel-HDEHP aggregates form and grow with increasing water content when $W_o > 2$; the monomeric complex, however, is not measurable when nickel-HDEHP aggregates occur in the apolar solvent.

The $\text{Ni}(\text{DEHP})_2 \cdot 2\text{H}_2\text{O}$ complex forms a viscous solution in the two-phase region due to the formation of large rodlike reversed micelles, which are similar to those found in the practical nickel extraction system. It was also found that dehydration can break down the resulting aggregates, a finding which may have application in reducing the viscosity of the organic phase of solvent extraction systems.

Cobalt-Di(2-Ethylhexyl)Phosphoric Acid Complexes and Co-Extractant Effect in Solvent Extraction Systems

Association microstructures formed by cobalt-HDEHP complexes and the effect of a co-extractant on the cobalt-HDEHP aggregates have been characterized by NMR, FT-IR, VIS absorption and photon correlation spectroscopic (PCS) techniques. The results obtained for the extraction of cobalt by HDEHP in apolar solvent (n-heptane or n-octane- d_{18}) demonstrate an anhydrous tetrahedral coordination structure for the cobalt ions in the association microstructure. The NMR results can be explained by the paramagnetic effect arising from the cobalt ions consistent with one-dimensional cylindrical aggregate growth.

However, the addition of a co-extractant (20% 2-octanol by volume) to the apolar solvent (80% n-heptane by volume) produced a marked effect on the physicochemical nature of the cobalt-HDEHP aggregates. In the presence of 2-octanol, a partially hydrated octahedral coordination structure was formed in equilibrium with the anhydrous tetrahedral structure for the cobalt-HDEHP aggregates in the organic phase. Furthermore, the cobalt-HDEHP aggregates in the presence of 2-octanol are capable of solubilizing water, and the particle size data obtained by PCS measurements suggests that the aggregates are swollen reversed micelles.

Liquid/Liquid Interface in Solvent Extraction Systems

Optical reflectivity measurements have been extended to solvent extraction systems in order to determine whether a thick interface is a common phenomenon in practical liquid/liquid extraction processes. The interfacial thicknesses in Lix 84 (Fe extraction) and Lix 622 (Cu extraction) systems were determined to be 290 and 330 Å, respectively. The interfacial thickness in the trilaurylamine/HCl system was also found to be relatively thick (> 100 Å).

The interfacial tension for the extraction system HDEHP/n-heptane/nickel nitrate solution was also measured. The interfacial tension of the liquid/liquid interface was essentially constant (3 mN/m) in the HDEHP concentration range where the interfacial region becomes of appreciable thickness. The possibility exists that the metal-extractant aggregates (or the cylindrical reversed micelles in this case) form in the liquid/liquid interfacial region and not in the bulk organic phase during the extraction process. Clearly, the generally accepted mechanisms for solvent extraction need to be re-examined in view of our interfacial thickness measurements.

DEGREES GRANTED

Three graduate students involved in this DOE-supported research have received advanced degrees during this time period:

1. Sang Joon Park, Ph.D. dissertation, "Solvent Extraction of Nickel from Nitrate Media by Di(2-Ethylhexyl)Phosphoric Acid under High Loading Conditions", March 1991.
2. Chin-Hsian Kuo, Ph.D. dissertation, "Viscoelasticity of Soluble and Insoluble Monolayers as Studied by Laser Light Scattering", March 1991.
3. Robert L. Himes, Ph.D. dissertation, "Fluorescence Recovery after Photobleaching, Fluorescence Microscopic and Surface Pressure-Specific Area Measurements of Insoluble Monolayers at the Air/Water Interface", March 1991.

PUBLICATIONS

1. "General Model for Aggregation of Metal-Extractant Complexes in Acidic Organophosphorus Extraction Systems," R.D. Neuman, N.F. Zhou, J. Wu, M.A. Jones, A.G. Gaonkar, S.J. Park and M.L. Agrawal, Sep. Sci. Tech., **25**, 1655 (1990).
2. "Comment on 'The Surface Tension of Water'", A.G. Gaonkar and R.D. Neuman, Colloids Surfaces, **61**, 353 (1991).
3. "Dihexadecyl Phosphate Monolayers at the Heptane/Water Interface: Model Interfacial System for Solvent Extraction Studies," N.F. Zhou and R.D. Neuman, Colloids Surfaces, in press.
4. "W/O Microemulsions Formed by Acidic Extractions and Effect of Lanthanides" Proc. Intern. Solvent Extraction Conf., ISEC 90, Kyoto, in press, J. Wu, F. Liu, Z.-J. Yu, N.F. Zhou and R.D. Neuman.
5. "Comparison of Aggregates Formed by Acidic Organophosphorus Extractants and Metals (Ni and Co) in Solvent Extraction Systems", Proc. Intern. Solvent Extraction Conf., ISEC 90, Kyoto, in press, N.F. Zhou, J. Wu, P.K. Sarathy, F. Liu, and R.D. Neuman.
6. "Model Interfacial System For Solvent Extraction Studies", Proc. Intern. Solvent Extraction Conf., ISEC 90, Kyoto, in press, N.F. Zhou and R.D. Neuman.
7. "Extraction of Nickel from Nitrate Media with Di(2-Ethylhexyl)Phosphoric Acid under High Loading Conditions", Proc. Intern. Solvent Extraction Conf., ISEC 90, Kyoto, in press, S.J. Park and R.D. Neuman.
8. "Characterization of Association Microstructures in Hydrometallurgical Nickel Extraction by Di(2-Ethylhexyl)Phosphoric Acid," R.D. Neuman and S.J. Park, J. Colloid Interface Sci., manuscript submitted, reviewed and revised.
9. "Physicochemical Properties of Aqueous Mixtures of Tetraalkylammonium Bromide and Perfluorinated Surfactants. 1. Rodlike to Giant Spherical Aggregate Transition", J. Phys. Chem., submitted, reviewed and being revised, Z.-J. Yu and R.D. Neuman.
10. "On Light-Scattering Measurements of Surfactant Solutions", Z.-J. Yu and R.D. Neuman, Langmuir, submitted.
11. "On the Role of Water in the Formation of Reversed Micelles: An Anti-Micellization Agent", Z.-J. Yu, N.F. Zhou and R.D. Neuman, Langmuir, submitted.
12. "Cobalt-HDEHP Aggregation and Co-Extractant Effect on Aggregates of Cobalt-HDEHP Complexes in Solvent Extraction", N.F. Zhou, Z.-J. Yu, J. Wu and R.D. Neuman, manuscript in preparation.

13. "Aggregates Formed by Acidic Extractants (Organophosphorus and Naphthenic Acids) in the Solvent Extraction of Rare Earths", N.F. Zhou, Z.-J. Yu, J. Wu and R.D. Neuman, manuscript in preparation.
14. "Association Microstructures in Solvent Extraction of Nickel by Di(2-Ethylhexyl)Phosphoric Acid: Effect on the Equilibrium Distribution and Kinetics", S.J. Park and R.D. Neuman, manuscript in preparation.
15. "Reversed Micelles Formed by Sodium Di(2-Ethylhexyl)Phosphate in n-Heptane" Z.-J. Yu, N.F. Zhou and R.D. Neuman, manuscript in preparation.
16. "Surface Viscoelasticity of Dodecyltrimethylammonium Bromide Solution: A Laser Light Scattering Study", C.H. Kuo and R.D. Neuman, manuscript in preparation.
17. "Physicochemical Properties of Aqueous Mixtures of Tetraalkylammonium Bromide and Perfluorinated Surfactants. 2. Effect of Tetrapropylammonium Bromide", Z.-J. Yu and R.D. Neuman, manuscript in preparation.
18. "Cloud Point in Perfluorinated Ionic Surfactant Solutions", Z.-J. Yu and R.D. Neuman, manuscript in preparation.
19. "Diffusion Properties of Organic Counterions Measured by Dynamic Light Scattering", Z.-J. Yu and R.D. Neuman, manuscript in preparation.
20. "Reversed Micelles Formed by Nickel-Di(2-Ethylhexyl)Phosphate Complex in n-Heptane", Z.-J. Yu, and R.D. Neuman, manuscript in preparation.

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