INTERFACIAL CHEMISTRY IN SOLVENT
EXTRACTION SYSTEMS

Progress Report

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Progress Report

Our research this past year has continued to emphasize characterization 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 model for the aggregation of metal-extractant complexes. In addition, the macroscopic interfacial behavior of model extractant (surfactant) molecules was further investigated.

I. Association Microstructures in Model Extraction Systems

We previously investigated the role of water on reversed micellization and reversed micellar growth for both sodium di(2-ethylhexyl) phosphate (NaDEHP) and $\text{Ni}(\text{DEHP})_2$ in n-heptane. Two significant discoveries which are in marked contrast with the current literature views were evident: first, water can function as an anti-micellization agent and, secondly, reversed micellization is not a step-wise aggregation process. Furthermore, the $\text{Ni}(\text{DEHP})_2$ complex does not form reversed micelles if the amount of water present is insufficient. However, aggregates of the $\text{Ni}(\text{DEHP})_2$ complex can form and grow when the amount of water is $W_0 > 2$, where W_0 is the molar ratio of water to extractant. This past year we continued our investigation of the association microstructures in solvent extraction systems with the emphasis on the effects of mixing di(2-ethylhexyl)-phosphoric acid (HDEHP) with NaDEHP and of adding large amount of water to n-heptane solutions of NaDEHP.

The size of rodlike NaDEHP reversed micelles (initially as large as 170 nm) is strikingly reduced and the micellization ability of NaDEHP is considerably lowered when HDEHP is added to NaDEHP/n-heptane solutions. In fact, the NaDEHP reversed micelles can be eventually destroyed when [HDEHP] is sufficiently high. Furthermore, it appears that the decrease in the reversed micellar size by the presence of trace amount of water is not via hydrolysis of the extractant, but rather due to a decrease in interdipole interactions when the hydrophilic head group of the extractant or the sodium ions are hydrated by water molecules.

We have concluded that the large reversed micelles formed in NaDEHP/n-heptane solutions disappear when $[\text{HDEHP}]/[\text{NaDEHP}] > 1/4$. It should be noted that HDEHP/NaDEHP mixtures in benzene under uncontrolled conditions (ambient relative humidity) were reported by McDowell et al. (J. Inorg. Nucl. Chem., **26**, 2005, 1964) to form the acid-coordinated species $\text{NaDEHP} \cdot 3\text{HDEHP}$ when $[\text{HDEHP}]/[\text{NaDEHP}] > 3$, which is contrary to our findings for the apolar n-heptane system. Thus, it seems puzzling how sodium ions which do not have available d or f orbitals can form coordinated complexes with HDEHP in benzene and why such coordinated complexes are not observed in n-heptane. We have started an investigation of the aggregation behaviors of NaDEHP in benzene under controlled conditions in order to understand whether or not the $\text{NaDEHP} \cdot 3\text{HDEHP}$ complex exists in acidic organophosphorus (HDEHP) solvent extraction systems.

The aggregation behaviors of NaDEHP have been studied over a broad range of W_0 (up to $W_0=90$) by using NMR, VPO, rheology and light-scattering techniques. A new type of microemulsion -- one which consists of rodlike W/O microemulsion droplets -- was discovered. A general picture for the evolution of NaDEHP aggregates from rodlike reversed micelles to spherical W/O microemulsion droplets is proposed as shown in Fig. 1. As mentioned earlier, the size of swollen reversed micelles decreases tremendously with an increase in the amount of water

solubilized. NMR shows that both the line-width and chemical shift of the ^{31}P spectrum for NaDEHP, as well as those of the ^1H spectrum for the water in the NaDEHP aggregates, do not change with an increase in the water content when $W_0 > 20$, which suggests that large water pools form and that "free" water occurs in the W/O microemulsion droplets. Viscosity measurements, however, show that the size of the W/O microemulsion droplets still decreases with increasing W_0 above $W_0 = 20$ until $W_0 > 40$ where spherical microemulsion droplets begin to form (see Fig. 1). These results suggest that the aggregation behaviors of the extractant (surfactant) play an important role in determining the size and shape of the W/O microemulsion droplets.

Figure 1. Relative viscosity of apolar solutions of 58 w/w% NaDEHP in n-heptane as a function of added water at 20°C. W_0 is the molar ratio of water to NaDEHP.

A phase diagram study shows that there are two-phase regions for the NaDEHP/n-heptane/water and $\text{Ni}(\text{DEHP})_2/\text{n-heptane/water}$ systems. The current literature view is that cloud-point (two-phase boundary) systems always exhibit critical behaviors. Therefore, it is an important question whether the solution behaviors of these two systems as determined by light-scattering, VPO and other experimental techniques reflect the critical behaviors or other intrinsic solution behaviors. Critical behaviors can be accurately studied by light scattering, but only for those systems in which multiple scattering is not serious, for example, perfluorinated surfactant systems. Therefore, the solution properties of a cloud-point system, namely, sodium perfluorooctanoate/ H_2O /tetrapropylammonium bromide, were investigated by dynamic and static light-scattering techniques. Critical-type behavior is observed when the temperature approaches the minimum cloud point from the one-phase region. However, for

sodium perfluorooctanoate solutions of lower concentration than that corresponding to the minimum cloud-point temperature, the apparent hydrodynamic radius decreases as the temperature approaches the cloud point. It is thus shown that a cloud-point system may not always exhibit critical-type behavior as many authors believe in the literature, and that light scattering can be a powerful technique for the characterization of model solvent extraction systems.

II. Interfacial Structure and Dynamics in Model Extractant Systems

It is a common practice in studies of interfacial phenomena in solvent extraction systems to measure the interfacial activity or tension of the macroscopic liquid/liquid interface. The experimental data is then usually fit to a theoretical equation of state. This approach, however, assumes the liquid/liquid interface is homogeneous over the entire extractant concentration range. On the other hand, there are several reports in the general surfactant literature that a first-order phase change occurs (mainly from theoretical arguments) in the surface of dilute aqueous surfactant solutions. If so, then perhaps a similar transition occurs at liquid/liquid interfaces such as those of solvent extraction systems. Thus, we performed some preliminary experiments using the pulsed Nd:YAG/dye laser system (obtained with DOE URI grant funds) which have yielded results of far-reaching implications regarding the surface or interfacial structure of aqueous and apolar extractant (surfactant) solutions. In addition, we have continued to investigate the dynamics of interfacial systems using the advanced laser fluorescence (FRAP) apparatus available in our laboratory.

Surface Laser Light Scattering

In our previous DOE Progress Report for June 1, 1988-May 31, 1991, we reported surface laser light-scattering (SLLS) measurements on aqueous solutions of dodecyltrimethylammonium bromide (DTAB) -- a classical cationic soluble surfactant. At that time we stated that the dynamic interfacial elasticity (ϵ_d) obtained by SLLS measurements is in excellent agreement with the static interfacial elasticity (ϵ_s) determined from the surface pressure-concentration isotherm when the bulk DTAB concentration is below 6 mM. These results have not been published in the technical literature because the experimental ϵ_d values in a relatively narrow bulk concentration range deviated somewhat from the "best-fit" static elasticity curve, thereby suggesting that $\epsilon_d > \epsilon_s$ and, hence, some relaxation process is being detected by the high-frequency capillary wave experiments.

On the assumption that SLLS was detecting a heterogeneous surfactant monolayer, hexaethyleneglycol mono n-dodecyl ether ($C_{12}E_6$), a nonionic soluble monolayer, was chosen for further study since the "surface aggregates" of $C_{12}E_6$, if they exist, should be much larger than those of DTAB on the basis that nonionic surfactants form large micellar aggregates in the bulk aqueous phase. Indeed, when the interfacial elasticity was plotted against the bulk $C_{12}E_6$ concentration, it was clearly evident that $\epsilon_d > \epsilon_s$ over a ten-fold concentration range. However, this concentration range over which the nonagreement between ϵ_d and ϵ_s was observed does not correspond to that for a first-order phase transition, thereby raising many questions concerning the interfacial structure of extractant (surfactant) solutions.

Laser-Induced Fluorescence

The physical properties of adsorbed soluble monolayers of aqueous $C_{12}E_6$ solutions mixed with 2% pyrene were studied by time-resolved and static fluorescence spectroscopy at ambient room temperature in the bulk $C_{12}E_6$ concentration range from 10^{-8} to 10^{-5} M under controlled oxygen and humidity conditions. Three characteristic concentration regions were found. At concentrations $< 10^{-7}$ M and $> 10^{-5.7}$ M, the fluctuation of the measured fluorescence intensity (photon counting) is small and is consistent with that calculated from Poisson distribution statistics on the basis the adsorbed pyrene is homogeneously distributed in the interfacial phase. At the intermediate concentration region from 10^{-7} M $< C < 10^{-5.7}$ M, large fluctuations in the measured fluorescence intensity are observed, which are much larger than that expected from the Poisson distribution for a homogeneous monolayer. Time-resolved spectra also show a single-exponential decay of the pyrene fluorescence in the concentration regions of $< 10^{-7}$ M and $> 10^{-5.7}$ M and two-exponential decay in the concentration region 10^{-7} M $< C < 10^{-5.7}$ M. These results are consistent with our discovery of an unusually high interfacial elasticity measured by surface light-scattering. Therefore, it may be concluded that there is a phase transition in the dilute $C_{12}E_6$ monolayer. However, instead of being a first-order phase transition, it appears to be a cooperative transition which take place over a very large bulk concentration range. Further work is in progress to clarify the structure of adsorbed monolayers at the air/water interface prior to extending these measurements to solvent extraction systems.

Fluorescence Recovery After Photobleaching

We have been employing laser fluorescence techniques to study surface or lateral diffusion (mobility) in interfacial systems. Our objective has been to use the fluorescence recovery after photobleaching (FRAP) technique to analyze the effect of anions on the water structure in the interfacial region to determine whether a structure-breaking action of chaotropic anions on water is observed which may be helpful in interpreting the extraction rates observed in solvent extraction systems.

We have recently completed a detailed study on surface diffusion in a classical "insoluble" monolayer, i.e., myristic acid. It appears that we have made another significant discovery, namely, a plot of the lateral diffusion coefficient versus reciprocal free area per molecule ($A_f = A - A_c$) displays three distinct regimes. To the best of our knowledge, this diffusional behavior has never been reported before. The present results, therefore, suggest an interpretation where the fluctuations responsible for the creation of a hole equal to or larger than the molecular cross-sectional area (A_c) in the monomolecular film do not operate on a single characteristic scale but have multiple scales of length.

These findings, however, have not been published nor have our measurements of lateral diffusion at a liquid/liquid interface. The reason is that a follow-up study has raised the question whether "residual" microscopic convective currents were responsible for the observed diffusivity behavior. The Ph.D. candidate who is continuing the study of interfacial diffusional processes is presently upgrading the FRAP apparatus by constructing a thermostatted cabinet around the diffusion cell to eliminate any "forced" or convective flows in the interfacial region due to microscopic temperature gradients.

III. General Model of Micellar Growth

In order to fully understand the extraction of metals by HDEHP, knowledge of the aggregation behaviors of NaDEHP is important since NaDEHP forms when the aqueous phase pH is adjusted with sodium hydroxide. NaDEHP is capable of forming aggregates in both the organic phase and the aqueous phase. It should be noted that the aggregation behaviors (e.g., effect of inorganic ions) of reversed micelles and W/O microemulsion droplets have some similarity to their aqueous counterparts. Therefore, we have made an examination of micellar evolution in the aqueous phase and have proposed a general model for micellar growth.

We have proposed a new concept of inorganic co-ion adsorption onto ionic surfactant micelles to account for the observed phenomena of decreases in micellar size with increasing inorganic salt concentration and with roughly the order of the lyotropic series for inorganic co-ions. These phenomena, however, cannot be interpreted by the current literature views. Thus, a thermodynamic model for micellar growth was deduced in which the role of inorganic co-ion adsorption on the micellar size and size distribution was considered. The charge density and the electrical energy of the micelles can be obtained by the method of Yu et al. (J. Phys. Chem., 94, 3675 (1990)). We therefore introduced an electrical energy term into the "ladder" model of Missel et al. (J. Phys. Chem., 84, 1044 (1980)) for micellar evolution, i.e., we employed the electrochemical potential of the surface-active ions instead of the chemical potential as used in the original "ladder" model for the chemical equilibrium conditions. We then deduced the micellar size distribution as $[C_{n_0+n}] = [C](1-a)/[n_0(1-a)+a]a^n$, where $a = k^{\circ}_1 \exp[-(1+\beta_c-\alpha_c-\gamma_c)Ze\phi_c/RT] \cdot [C][D]^{\alpha_c}[E]^{\beta_c}[F]^{\gamma_c}$ can be obtained either from thermodynamic calculations or from the measured weight-average molecular weight of the micelles $M_w = M[a^2(n_0^2-2n_0+1) + a(2n_0-2n_0^2+1) + n_0^2]/(1-a)/[n_0(1-a)+a]$. Work is in progress to directly test the concept of co-ion adsorption and to evaluate the necessary parameters needed in our proposed model for micellar growth.

IV. National Laboratory, Industry and Research Institute Interactions

Herein, we briefly discuss our activities to keep abreast of research developments which can significantly benefit our solvent extraction research program. In addition, we document a spin-off of our DOE-supported research which may benefit the U.S. pharmaceutical industry.

(1) In August 1992 I was invited to give a seminar entitled "Microscopic Interfaces in Organophosphorus-Metal Extractant Systems" to the Division of Chemistry, Oak Ridge National Laboratory. Dr. Bruce A. Moyer and I both agreed that it would be highly desirable if our laboratories could cooperate in the future. I believe that our laboratory has much to offer in the way of characterization studies, and as such, I offered to make our laboratory facilities available for specialized measurements on extractant systems of interest to ORNL separation activities.

It should prove very useful to extend the computer modeling approach of Dr. Moyer to the organophosphorus solvent extraction system in view of the detailed knowledge which we have acquired on aggregation phenomena in both aqueous and apolar media. In fall 1992, I taught ChE620, Graduate Thermodynamics, and assigned a research paper to analysis the hydrometallurgical solvent extraction of nickel by HDEHP under high loading conditions. Simply put, I wanted to apply thermodynamics solution theories to a "practical world

problem". Next year, I would like to require a computer analysis of the problem using Dr. Moyer's SXLSQA program.

(2) In October 1992, I presented a talk entitled "Interfacial Dynamics in Organic Thin Films" at the Workshop on Advanced Laser Technology for Chemical Measurements which was held in Santa Fe, NM. This workshop was supported by the Offices of Health and Environment Sciences and Basic Energy Sciences.

(3) In addition, we have developed a novel approach to the examination of very small molecular aggregates by dynamic light scattering. For example, we recently published a paper entitled "Light Scattering Measurements of Surfactant Solutions". In January 1993, I was invited by Pfizer Inc to present a talk on applying our light-scattering techniques to polypeptide association and aggregation. Thus, our DOE-sponsored research may have a direct spin-off in the pharmaceutical industry related to the characterization and development of new drugs from biotechnology research.

(4) It should also be noted that I spent several months last year on a research visit at the Institute for Surface Chemistry in Stockholm, Sweden, to collaborate with Dr. Per M. Claesson on the direct measurement of surface forces. The surface force technique which directly measures the interaction forces between solid surfaces immersed in liquids has many fundamental and technical applications. In addition, three lectures on "Mass Transfer Processes at Liquid/Vapor and Liquid/Liquid Interfaces", "Critical Surface-Chemical Methodologies in Monomolecular Film Studies", and "Surface Viscoelasticity of Soluble and Insoluble Monolayers: Past, Present and Future" were given at the Institute for Surface Chemistry in February 1992.

The surface force technique offers a novel approach to the study of solvent extraction systems. For example, the surface force apparatus can be used to (i) characterize the interparticle interactions between aggregates of metal-extractant complexes which are of fundamental importance in governing the macroscopic properties of hydrometallurgical solvent extraction systems and to (ii) study the diffusional processes which occur in the permeation of metal-extractant species through supported liquid membranes (SLM). In particular, the measured interaction force vs. distance profiles can be compared with the theoretical profiles calculated upon consideration of the polydispersity and hard-(or soft-)sphere nature of the reversed micelles which occur in hydrometallurgical solvent extraction systems. In addition, the diffusivity of reversed micelles, containing solubilized fluorescent probes, can be measured *in-situ* by the FRAP technique as a function of the separation distance in order to study the hindered diffusion of molecular aggregates which occurs in SLMs.

We have recently prepared two research proposals to acquire a state-of-the-art surface force apparatus:

- DOE URI Program, "Novel *In-Situ* Laser Spectroscopic Studies of Hindered Diffusion in Separation Processes", \$158,400, August 1, 1993-July 31, 1995.
- NSF, "Engineering Research Equipment: Surface Force/Laser Spectroscopy System," \$86,200, September 1, 1993-August 31, 1994.

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3. "The Role of Water in the Formation of Reversed Micelles: an Anti-Micellization Agent," Langmuir, 8, 1885, 1992 (with Z.-J. Yu and N.-F. Zhou).
4. "Light-Scattering Measurements of Surfactant Solutions," Langmuir, 8, 2074, 1992 (with Z.-J. Yu).
5. "Model Interfacial System for Solvent Extraction Studies," in Process Metallurgy. Solvent Extraction 1990 (T. Sekine, Ed.), Part A, p.75. Elsevier, New York, 1992 (with N.-F. Zhou).
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7. "W/O Microemulsions Formed by Acidic Extractants and Effect of Lanthanides," in Process Metallurgy. Solvent Extraction 1990 (T. Sekine, Ed.), Part A, p.195. Elsevier, New York, 1992 (with J. Wu, F. Liu, Z.-J. Yu, and N.-F. Zhou).
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12. "Dynamic Light-Scattering Measurement in Perfluorinated Surfactant Solutions," Colloids Surfaces, submitted (with Z.-J. Yu).
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14. "Aqueous Mixtures of Perfluorinated Surfactants and Organic Salts. 2. Rodlike Micellar Growth," Journal Colloid Interface Sci., manuscript being revised (with Z.-J. Yu).
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16. "Reversed Micelles Formed by Nickel-Di(2-Ethylhexyl)Phosphate Complexes in n-Heptane," manuscript in preparation (with Z.-J. Yu).
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18. "Aggregates Formed by Acidic Extractants (Organophosphorus and Naphthenic Acid) and Effect of Lanthanides," Separation Sci. Technol., manuscript in preparation (with N.-F. Zhou, Z.-J. Yu and J. Wu).
19. "Association Microstructures in Solvent Extraction of Nickel by Di(2-Ethylhexyl)Phosphoric Acid: Effect on Equilibrium Distribution and Kinetics," Hydrometallurgy, manuscript in preparation (with S. J. Park).