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

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To cite this Article Neuman, Ronald D. , Zhou, Nai-Fu , Wu, Jinguang , Jones, Matthew A. , Gaonkar, Anilkumar G. , Park, S. J. and Agrawal, M. L.(1990) 'General Model for Aggregation of Metal-extractant Complexes in Acidic Organophosphorus Solvent Extraction Systems', Separation Science and Technology, 25: 13, 1655 — 1674

To link to this Article: DOI: 10.1080/01496399008050415

URL: http://dx.doi.org/10.1080/01496399008050415

SEPARATION SCIENCE AND TECHNOLOGY, 25(13-15), pp. 1655-1674 (1990)

GENERAL MODEL FOR AGGREGATION OF METAL-EXTRACTANT COMPLEXES IN ACIDIC ORGANOPHOSPHORUS SOLVENT EXTRACTION SYSTEMS

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ABSTRACT

The physicochemical nature of the metal-extractant aggregates formed in the organic phase of acidic organophosphorus solvent extraction systems was investigated to further understand hydrometallurgical extraction. The experimental techniques of fluorescence, FT-IR, and NMR spectroscopy, static and dynamic light-scattering, tensiometry, as well as classical physicochemical methods and extraction measurements, were employed to clarify the nature of the molecular aggregates associated with the extraction of Ca^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} by di(2-ethylhexyl)phosphoric acid (HDEHP) in n-alkane diluents. Significantly, there appears to be three regimes of aggregation behavior in solvent extraction systems consistent with the mechanism suggested earlier by Neuman and co-workers [Colloids Surfaces, 46, 45(1990)]. A simplified model is proposed herein for the aggregation of metal-

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extractant complexes in acidic organophosphorus solvent extraction systems: as the concentration of metal-extractant complexes increases, the initial metal-extractant complexes or nuclei grow in size via a stepwise polymerization mechanism to form linear aggregates that eventually undergo a structural reorganization to form cyclic aggregates or reversed micelles which, in turn, are capable of further growth. Furthermore, the role of reversed micelles and other association microstructures in solvent extraction is briefly addressed. Although the model seems to be fairly general and provides a unifying interpretation of the species formed in the organic phase of solvent extraction systems, complexities in practical extraction systems must be considered for a detailed understanding of the solvent extraction mechanism.

INTRODUCTION

Hydrometallurgical solvent extraction is an energy-efficient technology for the separation and concentration of metals, whether from terrestrial or oceanic sources or from industrial waste solutions. Examples of some metals produced by solvent extraction are Co, Ni, Zn, Cu, Cr, and Nb (1,2). Solvent extraction processes also find important application in spent nuclear fuel reprocessing and nuclear waste processing technologies (3).

Nevertheless, the complex chemistry which occurs in the solvent extraction of metal ions from an aqueous solution to a nonpolar organic diluent is still incompletely understood. In the past, the most common approach to investigating extraction behavior has been to perform equilibrium distribution studies and fit an extraction equation to the data in order to determine species stoichiometry. A generalization that can be drawn from these studies is that the stoichiometry (and perhaps the nature) of the metal-extractant complex changes. For example, early work on di(2-ethylhexyl)phosphoric acid (HDEHP) extraction of UO_2^{2+} (4) and Fe^{3+} (5) indicated that the initial extraction could be modeled by a simple cation exchange reaction, but additional extraction complexes were formed as the metal loading increased. Another example is the extraction of alkali and alkaline earth metals by HDEHP where aggregates apparently form as the amount of metal transferred increases (6-8). Also, in the extraction of divalent transition metals by organophosphorus acids, the stoichiometry of the extracted species changes as loading increases (9-12). This latter process has been described as aggregation (13) or, alternatively, polymerization (14). Clearly, detailed knowledge on the molecular aggregates is required, especially at high loading, in order to more fully understand the solvent extraction process.

In recent studies on the interfacial activity of hydrometallurgical (HDEHP) solvent extraction systems, it was suggested that the molecular aggregates correspond to reversed micellar structures (15-17). Although the formation of reversed micelles in organophosphorus extraction systems is not a generally accepted phenomenon, it is known that the sodium salt of HDEHP (NaDEHP) forms reversed micelles (18,19). In fact, it has been suggested that strontium (7) and nickel (20) are extracted into NaDEHP reversed micelles. Furthermore, under appropriate conditions, NaDEHP yields a water-in-oil (W/O) microemulsion (21). If indeed association microstructures also occur during the extraction process, a mechanism for their formation is required.

In this paper, we propose a model, which includes the formation of linear aggregates and subsequent structural reorganization to reversed micelles, for the aggregation of metal-extractant complexes in acidic organophosphorus solvent extraction systems. This model is based on our recently proposed suggestion that the aggregation process in solvent extraction can be considered analogous to that for simple surfactants in nonpolar solvents (22). Although our earlier studies emphasized the extraction of calcium by HDEHP because of its simpler chemistry, the work reported herein was extended to more complex systems of immediate, practical relevance such as the extraction of Ni^{2+}, Co^{2+}, and Zn^{2+}. Evidence for this proposed model comes from the application of a variety of experimental techniques including physicochemical (metal distribution, vapor pressure osmometry and Karl Fischer titrimetry) and surface chemical (tensiometry) methodologies as well as spectroscopic (FT-IR, NMR and fluorescence) and scattering (static and dynamic light scattering) methods. This investigation, to our knowledge, is not only the first to perform quasi-elastic light scattering (QELS) or photon correlation spectroscopic (PCS) measurements but also fluorescence measurements on hydrometallurgical solvent extraction systems.

EXPERIMENTAL

A unique feature of this study is that rigorous surface-chemical techniques and procedures were employed. This is most important because the aggregation behavior of surfactants (and surface-active extractants such as HDEHP) can be greatly affected by impurities. The interfacial tension between the two bulk phases also is very sensitive to trace contaminants which, in turn, may significantly influence the kinetics of the extraction process. Thus, the excellent correlations found among the various experimental parameters, as will be discussed later in this communication, are due, in no small part, to the great care taken to generate reliable data of high quality.

Materials

HDEHP (96%, Morton Thiokol) was purified following the procedures of Partridge and Jensen (23) with the additional precaution that all solvents were distilled prior to use. The n-hexane diluent was purified as described earlier (24) while n-heptane (HPLC grade, Fisher) was doubly redistilled. Ultra-high purity grades of metal salts were used in this study. In the case of interfacial tension studies, the purified n-hexane was extracted with double-distilled water to remove any surface-active material remaining after purification, and the metal salt solutions also were extracted but with purified n-hexane to remove extraneous surface-active compounds. In the other measurements, n-hexane and n-heptane were employed and gave comparable results with n-heptane being preferred because of its lower volatility. NaOH (99.996%, Spex) and HCl (Ultrex, J. T. Baker) were used to adjust the solvent extraction systems to specific pH values.

Methods

The interfacial tensiometer employed and prerequisite procedures required to obtain accurate interfacial tension measurements on HDEHP/n-hexane/aqueous salt solutions are reported elsewhere (15). A Corona/Wescan Model 232A molecular weight apparatus was used for measurement of the vapor pressure lowering of the organic phase from which the average molecular weight (and aggregation number) was calculated; a solution of squalene in n-hexane was used for calibration. The organic phase water content was determined using a Coulometric Karl Fischer (K-F) Model 447 titrimeter as well as a Fisher L/I aquametry apparatus at high extractant concentrations. The equilibrium metal distribution coefficient, K_d, which is the ratio of the equilibrium concentration of a given metal in the organic phase to that in the aqueous phase, was measured in the case of calcium by the radiotracer technique described in our earlier studies (16). For cobalt, nickel, and zinc, however, the distribution experiments were performed at Oak Ridge National Laboratory using the radioisotopes ^{65}Zn, ^{60}Co, and ^{63}Ni. The Lewis-type mass transfer cell and radiotracer technique described elsewhere (16) were used to determine the metal ion transfer rate constant, k_{ao}, from the aqueous to organic phases. FT-IR and NMR spectra of the organic phase of HDEHP extraction systems were recorded using Nicolet Model 5SXC FT-IR and Bruker AM400 NMR spectrometers, respectively. A Spex Fluorolog-2 Model 212 spectrofluorometer equipped with double excitation and double emission spectrometers and a thermoelectrically cooled detector was employed to obtain fluorescence spectra of the fluorescent probe rhodamine B equilibrated in the organic phase of solvent extraction systems. Static and dynamic light-scattering measurements were also performed using the apparatus and procedures described in a recent publication (22). In addition, the aggregate size distribution was evaluated using the exponential sampling method of Ostrowsky et al. (25).

RESULTS

The interfacial tension, equilibrium metal distribution coefficient, transfer rate constant, organic phase water content, and fluorescence intensity are plotted as a function of log [HDEHP] for the four organophosphorus extraction systems shown in Figs. 1-4. The concentration of HDEHP is expressed in terms of formality (F) because the stoichiometry of the extractant species varies in a complicated manner in the organic phase.

The scattered light intensity and the mean effective hydrodynamic radius, $\bar{r}$, for a typical nickel extraction system are shown in Fig. 5 as a function of log [HDEHP]. Figure 6 illustrates the effect of pH on the size distribution of metal-extractant aggregates for the extraction of nickel by HDEHP.

The relative intensity of the water absorption band from FT-IR spectra, which reflects the bulk water content in the organic phase, is plotted as a function of log [HDHEP] in Fig. 7 for two extractant systems. Figures 8-10 are representative FT-IR spectra of several model extraction systems examining metal-extractant (Ni-HDEHP and Co-HDEHP) aggregate behavior and the effect of NaDEHP on water solubilization.

DISCUSSION

The experimental findings, including the results of vapor pressure osmometric measurements, are summarized in Table 1. Significantly, there appears to be three regimes of extractant aggregation behavior. Analysis of these carefully conducted experiments reveals consistency with a model of surfactant aggregation in nonpolar solvents introduced originally by Eicke and his co-workers (26,27) and more recently by Verbeek et al. (28). It is possible therefore to explain the observed stoichiometries at low loading conditions and the "aggregation" or "polymerization" at high concentration of metal-extractant complexes by the model schematically illustrated in Fig. 11.

Simplified Model

According to the proposed model, the following physicochemical changes take place with increasing metal loading in the organic phase. In the case of acidic organophosphorus extractants, the initial metal-extractant complex which typically forms is the tetrameric species, for example, $CaR_2 \cdot 2HR$, where R represents the dissociated form of extractant (HR). These nuclei subsequently grow in size via a stepwise aggregation mechanism to form linear aggregates. But upon reaching a critical size, a structural reorganization occurs as the linear aggregates form cyclic aggregates or reversed micelles. Subsequent growth of the reversed micelles with accompanying solubilization of water can take place to form larger association microstructures. As will be communicated elsewhere, depending upon the extraction conditions, growth proceeds to form either spherical or cylindrical micellar aggregates.

It should be noted that linear aggregation becomes significant at a HDEHP concentration corresponding to that at which more-or-less abrupt changes occur in the interfacial tension, fluorescence intensity, scattered light intensity, and water proton chemical shift (^{1}H-NMR) curves. Evidence for a structural reorganization to reversed micelles is provided by the combined results of fluorescence, FT-IR, ^{1}H-NMR, water content, and PCS measurements. A detailed discussion of our results supporting the above model is presented next.

Table 1. Summary of experimental results

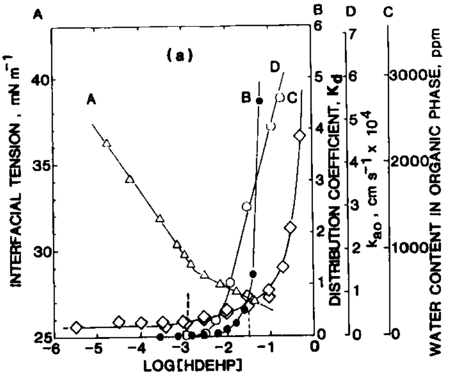
Region	I	II	III
	Nucleation	Linear Growth	Structural Reorganization and Growth
Experimental Information			
Distribution Coefficient, K_d :	negligible	smooth increase	abrupt increase
Transfer Rate Constant, k_{ao}:	negligible	smooth increase	abrupt increase
Interfacial Tension, γ :	decrease (break)	decrease	
Average Aggregation Number, $\bar{n}$:	slight increase	smooth increase	abrupt increase
Water Content in Organic Phase :	negligible	smooth increase	abrupt increase
Bulk Water by FTIR :	no information	no information	abrupt increase
Fluorescence Intensity :	negligible	smooth increase	abrupt increase
Particle Size by PCS :	no information	no information	measurable
Chemical Shift of Water Proton :	constant (break)	increase	constant

The interfacial tension, γ, versus logarithmic bulk HDEHP concentration curves shown in Figs. 1-4 are reminiscent of those for surfactants forming aggregates. The concentration at which the abrupt change occurs can be considered the critical HDEHP concentration, $[HDEHP]^{crit}$, at which the metal-extractant complexes begin to aggregate (15). In ref. 15 we suggested $[HDEHP]^{crit}$ corresponded to the formation of reversed micelles which consist of associated molecules whose hydrocarbon tails face the bulk organic phase and their polar head groups orient towards the center of the aggregate. These aggregates have a polar core which is capable of solubilizing water molecules. In this communication, however, we show that $[HDEHP]^{crit}$ is associated with the formation of linear aggregates rather than the cyclic aggregates which form at higher HDEHP concentrations.

Vapor pressure osmometry, VPO, has been successfully employed in the past for studying the association of extractants, for example, hydroxyoximes (29) and dinonylnaphthalenesulfonic acid (HDNNS) (30, 31). Since interfacial tension measurements indicate aggregates form in solvent extraction systems employing organophosphorus acids, the VPO technique was used to study their association.

VPO investigations of the equilibrated organic phases reveal the conditions under which aggregates form in liquid/liquid extraction systems. In the absence of metal ions, the aggregation number within the concentration region of HDEHP from 10^{-4} to 10^{-1}F is two and is independent of the HDEHP concentration, thereby indicating that HDEHP forms dimers in n-hexane (17). This finding is in agreement with those in the literature (32,33). In the presence of Ca^{2+}, however, the aggregation number was found to increase after a certain [HDEHP]. The concentration of HDEHP at which the aggregation number begins to increase is lower than $[HDEHP]^{crit}$. This fact indicates the formation of metal-extractant complexes, which can be considered as the nucleation step of micellization since the stoichiometry has been determined from metal distribution equilibria studies to be $CaR_2 \cdot 2HR$. Only when log [HDEHP] increases to a value greater than about -1.5, there appears a significant increase in the average aggregation number which indicates an appreciable increase in the number and size of the aggregates.

The determination of the water content in the equilibrated organic phase is important for studying solubilization phenomena related to reversed micelles. Figures 1-4 show the water content in the organic phase of the system HDEHP/n-hexane/metal salt solutions. The water content remains constant (<100 ppm) at low concentrations of HDEHP (lower than 10^{-3}F) and begins to increase smoothly in the range about 10^{-3}-10^{-2}F. But beyond a concentration in the range 10^{-2}-10^{-1}F, there is an abrupt increase. It appears that the smooth increase corresponds to the formation and growth of linear aggregates of the metal-extractant complex and, on the other hand, the abrupt increase in the solubilization of water occurs when reversed micelles begin to form.



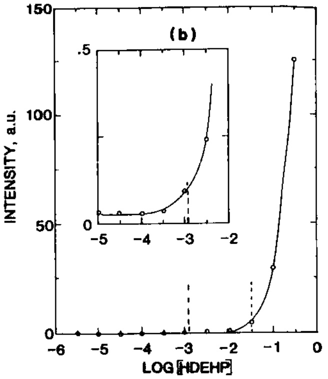
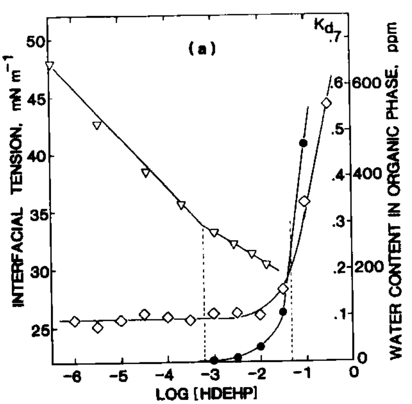


Fig. 1a. Interfacial tension (△), metal distribution coefficient (●), water content (◇), and transfer rate constant (○) versus log [HDEHP] curves for the system HDEHP/n-hexane/0.01 mol dm^{-3} $CaCl_2$ at pH 3.5 and 20°C.

Fig. 1b. Fluorescence intensity versus log [HDEHP] curves for the system HDEHP/n-hexane/0.01 mol dm^{-3} $CaCl_2$ at pH 3.5 and 20°C (Probe: Rhodamine B).



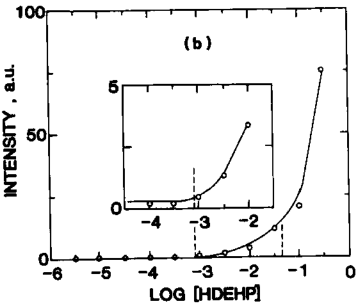
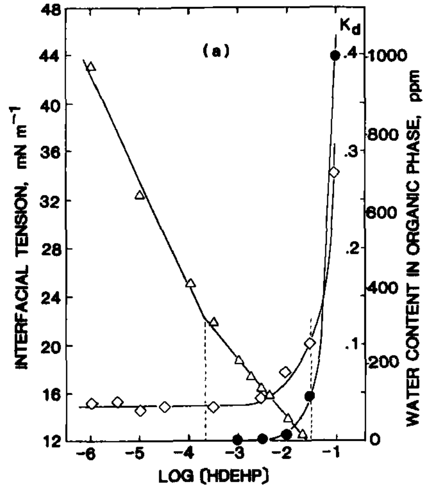


Fig. 2a. Interfacial tension (▽), metal distribution coefficient (●), and water content (◇) versus log [HDEHP] curves for the system HDEHP/n-hexane/0.1 mol dm^{-3} $ZnCl_2$ at pH 2.5 and 20°C.

Fig. 2b. Fluorescence intensity versus log [HDEHP] curves for the system HDEHP/n-hexane/0.1 mol dm^{-3} $ZnCl_2$ at pH 2.5 and 20°C (Probe: Rhodamine B).



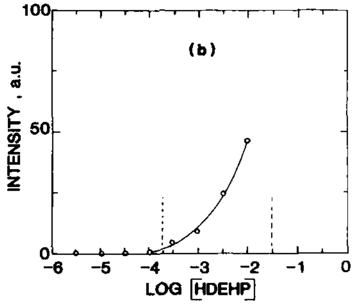
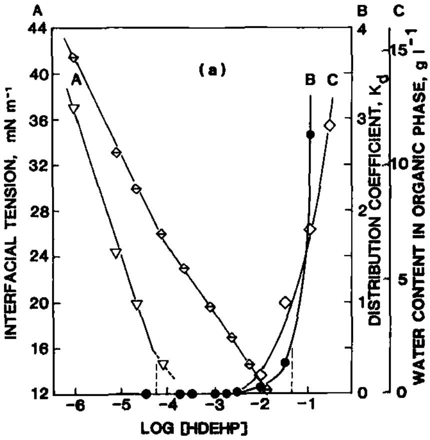


Fig. 3a. Interfacial tension (△), metal distribution coefficient (●), and water content (◇) versus log [HDEHP] curves for the system HDEHP/n-hexane/0.05 mol dm^{-3} $CoCl_2$ at pH 4.0 and 20°C.

Fig. 3b. Fluorescence intensity versus log [HDEHP] curves for the system HDEHP/n-hexane/0.05 mol dm^{-3} $CoCl_2$ at pH 4.0 and 20°C (Probe: Rhodamine B).



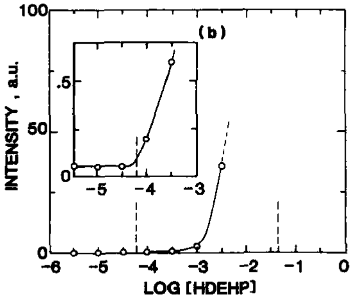


Fig. 4a. Interfacial tension at pH 4.0 (◈) and pH 5.0 (▽), metal distribution coefficient at pH 5.0 (●), and water content at pH 5.0 (◇) versus log [HDEHP] curves for the system HDEHP/n-hexane/0.05 mol dm^{-3} $NiCl_2$ at 20°C.

Fig. 4b. Fluorescence intensity versus log [HDEHP] curves for the system HDEHP/n-hexane/0.05 mol dm^{-3} $NiCl_2$ at pH 5.0 and 20°C (Probe: Rhodamine B).

Steady-state fluorescence intensity measurements have been utilized to determine the presence of reversed micelles in nonpolar solvents (34,35). Fluorescence experiments thus are also expected to provide information on the structural characteristics of extractant aggregates in organic diluents. However, fluorescence techniques, to our knowledge, have not been applied to investigations of the molecular aggregates known to exist in hydrometallurgical solvent extraction systems.

Accordingly, in order to draw meaningful information from solvent extraction experiments, it is instructive to carry out fluorescence measurements on a well studied or characterized simple surfactant system, for example, AOT in iso-octane where AOT is di(2-ethylhexyl) sodium sulfosuccinate. The fluorescence intensity of rhodamine B thus was measured as a function of AOT concentration using iso-octane as the solvent. Rhodamine B is slightly soluble in nonpolar solvents (n-hexane, iso-octane) and almost nonfluorescent, but it becomes fluorescent when adsorbed on aggregates (34). In the region below 10^{-5}M AOT, the fluorescence intensity is very low and remains constant which indicates that molecular aggregates are not present in the AOT solution. In the region about 10^{-5}-10^{-2}M AOT, the fluorescence intensity slowly increases and is interpreted as evidence of aggregate formation. In the region above 10^{-2}M AOT, the fluorescence intensity sharply increases, indicating the occurrence of reversed micelles. In this region rhodamine B appears to solubilize in the core of reversed micelles, and hence there is an abrupt increase in fluorescence intensity. The fluorescence measurements are entirely consistent with the model for aggregation behavior of surfactants in apolar solvents.

The fluorescence intensity of rhodamine B was next measured for equilibrated organic phases of hydrometallurgical solvent extraction systems. Figures 1-4 show the fluorescence results obtained when calcium, zinc, cobalt, and nickel were extracted with HDEHP in n-hexane. There appears to be three regions of fluorescence behavior: Region I, essentially nonfluorescent at low [HDEHP]; Region II, smooth increase in fluorescence at intermediate [HDEHP]; and Region III, abrupt increase in fluorescence at high [HDEHP]. For cobalt and nickel extraction, however, the abrupt fluorescence intensity increase in Region III could not be observed due to absorbance by the highly colored organic phase in both cases. Importantly, the general fluorescence behavior provides strong evidence for the proposed model for aggregation of metal-extractant complexes.

It can be thought that the increase in fluorescence intensity arises because the cationic rhodamine B interacts electrostatically with the anionic HDEHP. This, however, is not the case because similar behavior was observed when an anionic (PSA) probe was employed. Therefore, the smooth increase in fluorescence intensity is due to adsorption of the probe by the aggregates formed during the extraction process, and the abrupt increase in fluorescence intensity is due to probe solubilization in the core of reversed micelles.

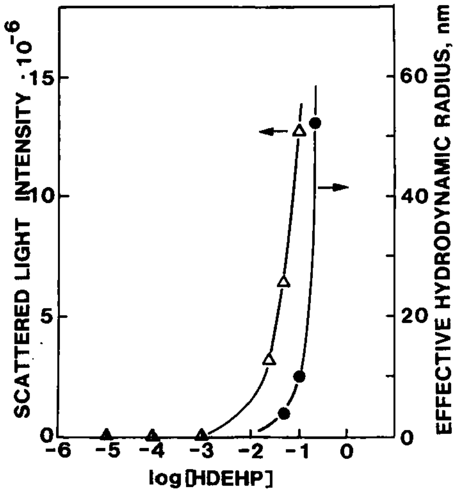


Fig. 5. Scattered light intensity (Δ) and effective hydrodynamic radius (●) versus log [HDEHP] curves for the system HDEHP/ n-heptane/0.35 mol dm^{-3} $NiCl_2$ at pH 5.7 and 20°C.

In addition to steady-state fluorescence intensity measurements, fluorescence depolarization was measured at 0.1F HDEHP for the calcium extraction system and was found to be 0.05 which approaches that of rhodamine B in bulk water. This further supports the hypothesis of reversed micelle formation in hydrometallurgical solvent extraction systems.

Static light scattering measurements were performed to examine aggregate formation in solvent extraction systems. Once again, there appeared to be three regions of scattered light-intensity behavior as shown in Fig. 5. At low [HDEHP], the intensity was esentially constant; at intermediate [HDEHP], the intensity increased; and at even higher [HDEHP] in Region III there was a very large increase in the scattered light intensity. This behavior is entirely consistent with the proposed aggregation model.

Photon correlation spectroscopy, PCS, was employed to further characterize the aggregates existing in the organic phase of solvent extraction systems. PCS is a light-scattering technique in which the intensity fluctuations of scattered light are measured to obtain information on the Brownian motion of particles in solution, namely, the diffusion coefficient, which can be related to the particle size

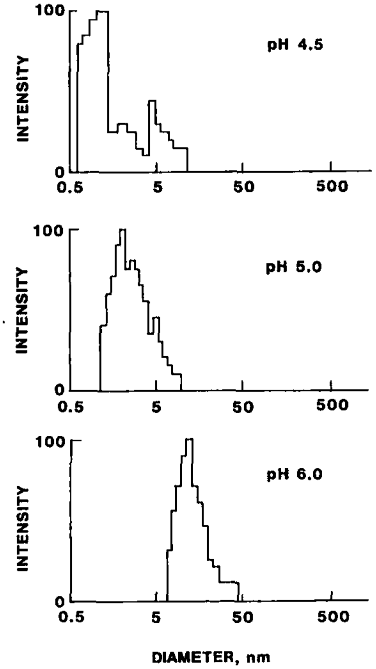


Fig. 6. Effect of pH on size distribution of metal-extractant aggregates formed in the system HDEHP/n-hexane/0.05 mol dm^{-3} $NiCl_2$ at [HDEHP] = 0.1 F and 20°C. pH 4.5, $\bar{r}$ = 1.2 nm; pH 5.0, $\bar{r}$ = 1.5 nm; pH 6.0, $\bar{r}$ = 5.9 nm.

and size distribution for simple assumed shapes. As such, PCS measurements were performed on the equilibrated organic phase of HDEHP solvent extraction systems of cobalt, nickel, zinc and calcium. The measurement of very small micellar aggregates, however, is not a trivial matter. Nevertheless, we have shown that, with appropriate precautions and care, PCS can be applied to provide reliable size information on the metal-extractant aggregates in solvent extraction systems (22).

Figures 5 and 6 show the size and size distribution of the aggregates which can form in nickel extraction systems under various conditions. The fact that very large particles, apparently as large as about 100 nm, can occur in Region III is shown in Fig. 5. In addition, Fig. 6, being representative of our results, shows the effect of the aqueous phase pH. At a lower pH, say 4.5, $\bar{r}$ is only 1.2 nm and the distribution appears bimodal; but at higher pH, the size distribution shifts to larger particle sizes and the bimodal nature more or less disappears. This is very evident for the nickel extraction system at pH 6 where the histogram reveals a narrow size distribution and aggregates having a mean size as large as 12 nm which lies in the microemulsion-size regime.

Proton magnetic resonance spectroscopy can provide additional information on the aggregation process taking place in liquid/liquid extraction systems (36). ^{1}H-NMR spectra of the equilibrated organic phase for a variety of extraction systems have been obtained and will be reported elsewhere (manuscript in preparation). In the case of cobalt and nickel, the ^{1}H-NMR spectra were more difficult to interpret because of interference arising from their paramagnetism. Nevertheless, it should be noted that the chemical shift of water protons, δ, relative to tetramethylsilane, remained at a constant value (4.7 ppm) equal to that of bulk water for the extraction system HDEHP/n-octane-d_{18}/Co(II) solution at high HDEHP concentrations. In addition, we earlier found δ to approach that of bulk water in the system HDHEP/benzene-d_6/$CaCl_2$ solution (36). These findings provide strong evidence supporting the proposition that reversed micellization can occur in the organic phase of hydrometallurgical solvent extraction systems employing the extractant HDEHP.

Additional evidence that bulk water can exist in solvent extraction systems under appropriate conditions was provided by FT-IR spectroscopy. Figure 7 shows the relative intensity of the water absorption band as a function of log [HDEHP], where the relative intensity (I_{3400}/I_{1460}) is the intensity ratio of the OH stretching band (~3400 cm^{-1}) of bulk water to the bending mode of the CH_2 groups which is used as an internal standard (37). From Fig. 7, an appreciable amount of solubilized water in Region III exists as bulk water in the nickel system.

On the other hand, much less water is solubilized in the cobalt system. Therefore, the aggregation of Co-HDEHP and Ni-HDEHP complexes appears somewhat different. Practical solvent extraction systems obviously are very complicated such that the simplified model must be "fine tuned" to given situations, e.g., metal ions, co-extractants, etc., as discussed in the next section.

Complexity of Solvent Extraction Systems

Our simplified model for aggregation of metal-extractant complexes in solvent extraction systems, it will be recalled, is shown in Fig. 11. On the other hand, it can be called a general model because it is applicable to the aggregation of metal-extractant complexes which consist not only of monovalent alkali metal ions but also of divalent metal ions. For example, the aggregation of Ni-HDEHP complexes in the organic phase during extraction is very well explained by the proposed model. In addition, the model also applies to other organophosphorus extractants, namely, phosphonic and phosphinic acid esters (a comparison of HDEHP, PC 88A, and CYANEX 272

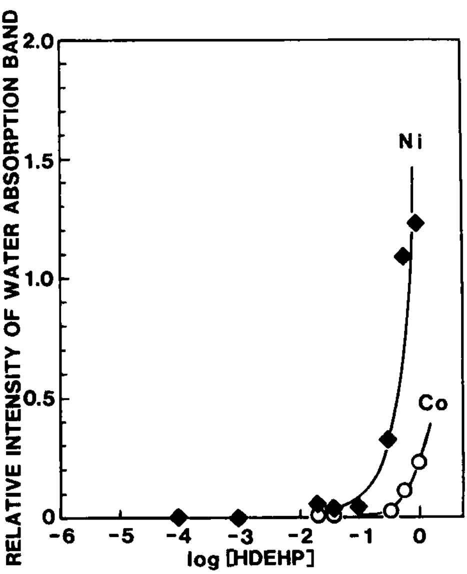


Fig. 7. Relative intensity of water absorption band versus log [HDEHP] curves for the systems HDEHP/n-heptane/0.35 mol dm^{-3} $NiCl_2$ at pH 5.7 and 20°C (◆) and HDEHP/n-heptane/0.35 mol dm^{-3} $CoCl_2$ at pH 5.0 and 20°C (○).

will be communicated elsewhere). However, for certain systems, reversed micelles form under more restrictive conditions. For example, although Ni-HDEHP complexes readily form reversed micelles, Co-HDHEP complexes alone do not[a] on the basis of the FT-IR results but require the presence of a co-extractant such as the sodium (or alkali metal) salt of HDEHP or 2-octanol for the existence of bulk water in the micellar aggregates.

This complexity is demonstrated by the results shown in Figs. 8-10. HDEHP was reacted with $NiCO_3$ or $CoCO_3$ to form sodium-free Ni-HDEHP or Co-HDEHP aggregates in n-heptane. FT-IR spectra were

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[a] The authors thank one of the reviewers for bringing to our attention a recent small-angle neutron-scattering study of cobalt-organophosphorus extractant aggregation. Thiyagarajan et al. (38) showed that Co(II)-HDEHP aggregates, formed in the organic phase under stoichiometric (1:2) conditions without the presence of sodium, exist as long thin rod-like polymeric structures of constant cross-sectional radius (1 nm) and variable lengths.

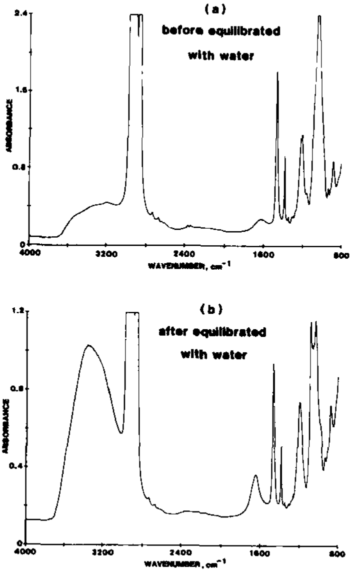

Fig. 8. FT-IR spectra of the model system sodium-free Ni-HDEHP aggregates in n-heptane (a) before and (b) after equilibration with water. 70-80% of the HDEHP estimated to react with nickel ions.

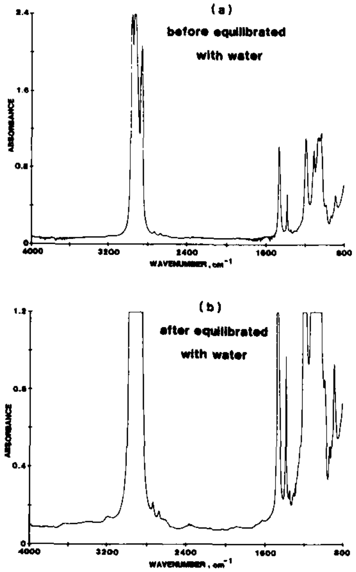

Fig. 9. FT-IR spectra of the model system sodium-free Co-HDEHP aggregates in n-heptane (a) before and (b) after equilibration with water. 100% of the HDEHP estimated to react with cobalt ions.

obtained before and after equilibration of the organic solution with water. Figure 8a shows that the Ni-HDEHP aggregates contained bulk water in contrast to the Co-HDEHP aggregates (see Fig. 9a). It should be noted that water results as a by-product of the metal salt formation in n-heptane. The observation of a separate water phase in the case of cobalt is consistent with the nonmeasurable (by FT-IR) bulk water. Upon equilibration with water, the Ni-HDEHP aggregates solubilized an appreciable quantity of bulk water as shown by the water absorption band at 3400 cm^{-1} in Fig. 8b. However, even upon equilibration, the Co-HDEHP aggregates did not solubilize any observable bulk water as shown in Fig. 9b. Therefore, the proposed model does not appear, at first hand, to apply to cobalt because the aggregates do not appear to solubilize bulk water in their interior core. Nevertheless, our earlier solvent extraction results indicated the formation of reversed micelles.

Thus, in order to resolve this question, the effect of sodium ions which can exist in practical solvent extraction systems (e.g., as the result of pH adjustment) was investigated. The HDEHP in n-heptane was first partially neutralized with sodium hydroxide to yield 2NaDEHP·HDEHP and then equilibrated with aqueous $NiCl_2$ (0.35M) and $CoCl_2$ (0.35M) solutions. Significantly, a water absorption band is observed in Figure 10b and shows that the organic phase which contains cobalt is now able to solubilize some bulk water. In our study, NaOH was used for pH adjustment of the solvent extraction systems such that sodium ions were present (and confirmed by atomic absorption spectroscopic measurements) in the organic phase, thereby yielding reversed micellar aggregates.

Zinc extraction by HDEHP is similarly very complicated. The zinc salt of HDEHP forms polymeric structures. Again, in the presence of sodium or 2-octanol, Zn-HDEHP aggregates can solubilize water. The effect of sodium ions is being studied further in our laboratory.

Consideration of the coordination chemistry of metal ions can assist in interpreting the aggregation behavior of the Ni-HDEHP, Co-HDEHP, and Zn-HDEHP complexes. In the case of nickel, octahedral coordination structures are formed with ligands including extractant and water molecules. Cobalt(II), however, can form either octahedral or tetrahedral coordination structures. In solvent extraction systems, even with sodium present, the tetrahedral structure is favored as demonstrated by VIS absorption spectroscopic measurements. The octahedral structure was observed only as the result of 2-octanol being used as a co-extractant. Clearly, for a given extractant, the chemical nature of the metal ion is of great importance to the formation of metal-extractant association microstructures.

Practical Significance

The above findings indeed support our earlier hypothesis that reversed micelles can form in the liquid/liquid extraction of metal ions by HDEHP. Solvent extraction studies in our laboratory with PC 88A and CYANEX 272 suggest that the formation of reversed micelles is a general phenomenon operative in hydrometallurgical systems which employ acidic organophosphorus extractants (39,40). Importantly, the amount and rate of metal ion extraction appear to become of practical significance under conditions of reversed micelle formation. Any mechanistic model of practical solvent extraction systems requires detailed knowledge of the nature of the extracted species in the bulk organic phase. Most certainly, more realistic models of extraction need to incorporate reversed micellar and other association microstructure effects.

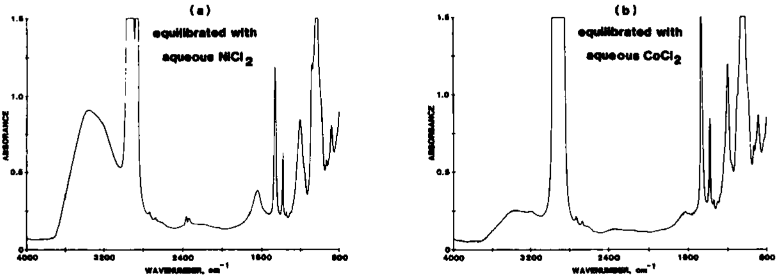

Fig. 10. FT-IR spectra of the model systems: (a) Ni/Na-HDEHP aggregates in n-heptane upon equilibration with 0.35 mol dm^{-3} $NiCl_2$ and (b) Co/Na-HDEHP aggregates in n-heptane upon equilibration with 0.35 mol dm^{-3} $CoCl_2$.

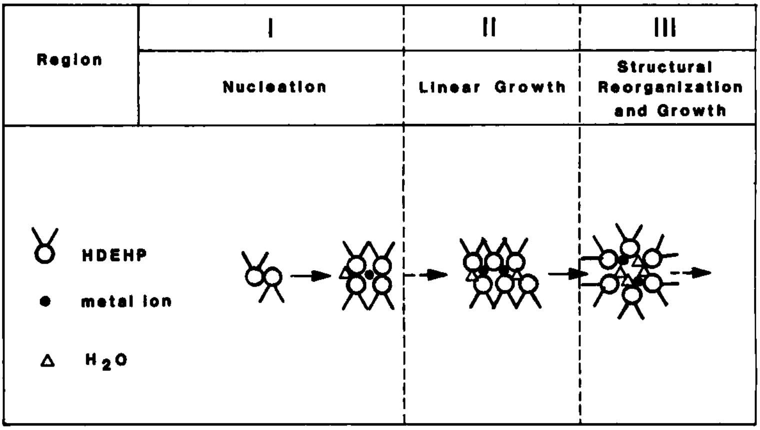

Fig. 11. Simplified model for aggregation of metal-extractant complexes in solvent extraction systems.

CONCLUSIONS

Colloid and surface science concepts have been employed to explain the results of various physicochemical, spectroscopic and light scattering measurements performed for the purpose of investigating the nature of the molecular aggregates in the organic phase of organophosphorus solvent extraction systems. As such, a simplified model for aggregation of metal-extractant complexes has been developed. The proposed model seems to be fairly general, nevertheless it is necessary to also invoke other concepts in coordination chemistry and polymer science to explain differences observed in the aggregation behavior of some extraction systems. Further studies characterizing the aggregates in greater detail are required to examine complexities associated with the solvent extraction process.

ACKNOWLEDGMENTS

This research was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, Department of Energy under Grant No. DE-FG05-85ER13357. The authors also acknowledge Dr. Zhi-Jian Yu for his contribution to the light-scattering measurements.

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