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ENHANCED SOLVENT EXTRACTION WITH WATER-IN-OIL MICROEMULSIONS

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ABSTRACT

This paper examines theoretically the conditions which favor enhanced extraction when a microemulsion phase containing a surfactant and a chelating agent is used as the solvent extraction organic phase. A general thermodynamic model of liquid-liquid distribution in reversed micellar systems is presented. The model treats the reversed micellar aggregates of the surfactant HA as a pseudophase and considers (a) the partition of a chelating extractant (HL) between the continuous organic phase and the reversed micellar pseudophase, (b) transfer of the metal ion M^{z+} into the continuous organic phase via reaction with HA monomers, (c) partition of the M^{z+}-HA complex between the continuous organic phase and the reversed micellar pseudophase, (d) reaction of the M^{z+}-HA complex with HL in the reversed micellar pseudophase, and (e) partition of the HL-containing complex between the reversed micellar pseudophase and the continuous organic phase. Quantitative expressions are derived that permit one to identify the chemical parameters that influence the liquid-liquid transfer process and therefore permit one to undertake the rational design of microemulsion formulations for specific applications.

INTRODUCTION

At relatively high concentrations, aqueous-soluble surfactants self-associate to form micelles which are aggregates characterized by a nonpolar core inhabited by the hydrocarbon groups and an outer polar surface consisting of the polar functional groups (1,2). A similar phenomenon occurs when the surfactant is present in an anhydrous organic solvent. However, in this case, reversed micelles form, i.e., the polar groups constitute the inner region. The term microemulsion is used when the micelles solubilize hydrocarbon molecules in their nonpolar core (oil-in-water or o/w microemulsion) or reversed micelles solubilize water molecules (water-in-oil or w/o microemulsion) (3,4).

Microemulsions are thermodynamically stable isotropic solutions that typically consist of four components: a surfactant (e.g. salts of long chain carboxylic, phosphoric, and sulfonic acids; long chain alkylammonium salts), a cosurfactant (e.g. a medium chain length alcohol), oil (e.g. a hydrocarbon) and water (or aqueous salt solution). Three-component microemulsions are also known; these are generally based on double-chain ionic surfactants (e.g. Aerosol OT, i.e., di-2-ethylhexyl sodium sulfosuccinate), oil and water or on nonionic surfactants (e.g., polyoxyethylene alkylphenyl ethers), oil and water.

The application of microemulsions in tertiary oil recovery has stimulated considerable research into their interfacial activity, phase behavior and structural characteristics. Currently, several new applications of microemulsions are under consideration and are the focus of much active research. As Friberg has pointed out (5), many potential applications of microemulsions are yet to be developed. One such potential application concerns metal separations in microemulsion media and forms the subject of this paper. In a paper presented at ISEC '80, Chin-kwang et al (6) presented experimental data that demonstrated that w/o microemulsions form when conventional acidic solvent extraction reagents are saponified (i.e. converted to salts of alkali or alkaline earth metals) and used in combination with long-chain alcohols. During the same conference, Osseo-Asare and Keeney (7) drew attention to the ability of reversed micelles to catalyze solvent extraction reactions and suggested that with proper selection of reagents and extraction conditions, reversed micellar catalysis could be used advantageously in liquid-liquid metal separation processes.

Solvent extraction reagents are necessarily amphiphilic: the hydrophobic organic groups ensure organic phase solubility while the hydrophilic moieties provide the functional groups needed for complexation reactions (8-10). As a result of this hydrophobic-hydrophilic coupling, there is a tendency for certain extraction reagents and/or their salts to aggregate in the organic

phase (8,10,11). The fact that these aggregates are generally water-saturated reversed micelles means that the organic phase is in actuality a microemulsion phase.

The aggregation behavior of extraction reagents has been known for some time (8). However it is only relatively recently that the unique potential of the microemulsion phase as a solvent extraction medium has begun to attract scientific and technological attention. The fact that the aqueous microdrops present in water-in-oil microemulsions are capable of solubilizing hydrophilic macromolecules provides a mechanism for transferring enzymes from an aqueous phase to an organic phase and vice-versa (12,13). In the case of metal ion separations, the ability of reversed micelles to solubilize both hydrophilic aqueous species and hydrophobic extractants creates conditions that can lead to enhanced equilibrium liquid-liquid distribution equilibria as well as improved kinetics (6,7,10,14-24). A number of different microemulsion formulations have been prepared based on conventional solvent extraction reagents such as dinonylnaphthalene sulfonic acid (HDNNS or HD), versatic acid, naphthenic acid, di-2 ethylhexyl phosphoric acid (HDEHP), and Aliquat 336 (6,14,18-21). Formulations containing classical surfactants such as long chain sulfates (e.g. sodium dodecylsulfate, SDS), sulfonates (e.g. sodium dodecylbenzene sulfonate, SDBS), and carboxylates have also been reported (15-18,23). Use of these microemulsion media has permitted separations to be achieved which are otherwise (a) not feasible from an equilibrium standpoint or (b) too slow to be of practical interest.

The physicochemical basis of this promising separation process is little understood at this time. However, examination of the various reaction steps proposed in the literature reveals that an important requirement for enhanced solvent extraction is the ability of the microemulsion to solubilize both the metal ion and the extractant. In addition, a mechanism is needed to transfer the aqueous species to the macroscopic organic/aqueous interface or into the continuous organic phase before the reversed micelle-based reactions can occur. It appears that whereas with a conventional organic phase, transfer of a metal ion into the organic phase often requires dehydration, such is not the case for microemulsion systems since the reversed micelle core itself contains water and is therefore friendly to a hydrated solubilizate. This is one of the most significant factors responsible for enhanced solvent extraction, i.e., the ability to transfer hydrophilic solutes from the aqueous phase into the microemulsion phase thereby circumventing the usually slow dehydration step at the macroscopic organic/aqueous interface.

A quantitative analysis of liquid-liquid distribution equilibria in reversed micellar solvent extraction processes is not presently available. Such an analysis would permit systematic

speculation and therefore assist in the rational design of enhanced solvent extraction separations. In this paper, the micellar pseudophase model developed by Berezin et al. (25-27) is further extended to the problem of liquid-liquid distribution equilibria in reversed micellar systems. The corresponding treatment of extraction kinetics is the subject of a separate paper (28). In a recent publication from this laboratory (29), a pseudophase model was presented for the case where the organic phase contains a surfactant dissolved in a hydrocarbon diluent. The present paper considers the more complicated situation of a mixed extractant system consisting of a surfactant and a chelating agent.

THEORY

Reversed Micellar Pseudophase Model

The liquid-liquid system will be viewed as a water-in-oil microemulsion phase adjacent to a macroscopic aqueous phase. It shall be assumed that the microemulsion is of the reversed micellar type, i.e., there are distinct hydrophilic and hydrophobic domains. The reversed micelle-forming surfactant located in the organic phase will be designated as HA with an aggregation number of x. The organic phase also contains an extractant HL which is considerably less surface active than HA and does not self-aggregate. At the beginning of the distribution experiment, the aqueous phase contains the extractable hydrophilic species M^{z+}.

Following Berezin et al. (25-27), the reversed micelles will be treated as a distinct pseudophase that is uniformly distributed in the organic phase. The total organic phase, the bulk organic phase (i.e., the reversed micelle-free continuous organic phase), and the reversed micellar pseudophase will be identified with the labels "o", "b" and "m" respectively. A further simplifying assumption is that the volume of water in the reversed micelle core is negligible compared with the total reversed micelle volume. Thus the volume (V_m) of the reversed micelle pseudophase may be related to the total volume V_o of the organic phase as:

$$V_m = v_s C_s V_o \tag{1}$$

where v_s is the molar volume of the surfactant and C_s is the concentration of reversed micellar surfactant (based on the total volume of the organic phase) i.e.,

$$C_s = x\,[(HA)_x]_o \tag{2}$$

In the analysis below, dilute solutions will be considered, and in particular, it shall be assumed that $V_w \ll V_o$. In the following discussion, the term "organic phase" refers to the entire microemulsion phase, i.e., the sum of the bulk organic phase and the reversed micelle pseudophase. It will be assumed that no M^{z+} complexes exist in the aqueous phase and that the

concentration of M^{z+} in the organic phase is sufficiently low as not to significantly influence the size and concentration of the reversed micelles, or the mass balance of HL. Further, it will be assumed that the presence of HL does not significantly alter the aggregation characteristics of HA.

The overall extraction process is envisaged as the net result of several steps:

1. Aggregation of the surfactant HA:

$$xHA(o) = (HA)_x(o) \tag{3}$$

$$K_x = [(HA)_x]_o/[HA]_o^x \simeq [(HA)_x]_o/[HA]_b^x \tag{4}$$

In Equation 4, the assumption that $V_m \ll V_o$ has been invoked.

2. Partition of the hydrophobic reagent HL between the bulk organic phase and the reversed micellar pseudophase:

$$HL(b) = HL(m) \tag{5}$$

$$P_{HL} = [HL]_m/[HL]_b \tag{6}$$

This type of expression has been found (26-28) to be satisfactory in describing the binding characteristics of hydrophobic substrates. Given the assumption that the concentration of M in the organic phase is extremely low compared with the concentration of HL, Equations 1 and 6 can be combined with a mass balance on the HL concentration in the organic phase to give:

$$[HL]_b = [HL]_{to}/[1 + K_{HL}C_s] \tag{7}$$

where $[HL]_{to}$ is the total analytical concentration of HL in the organic phase, and K_{HL} is a binding constant defined (26-28) as:

$$K_{HL} = [P_{HL} - 1]v_s \tag{8}$$

3. Transfer of the hydrophilic species M^{z+} into the bulk organic phase via reaction with monomeric HA:

$$M^{z+}(a) + zHA(b) = MA_z(b) + zH^+(a) \tag{9}$$

$$K_{co} = [MA_z]_b\,[H^+]_a^z/[M^{z+}]_a\,[HA]_b^z \tag{10}$$

4. Partition of the M-A complex between the bulk organic phase and the reversed micellar pseudophase:

$$MA_z(b) + zHA(m) = MA_z(m) + zHA(b) \tag{11}$$

$$K_{so} = [MA_z]_m [HA]_b^z / [MA_z]_b [HA]_m^z \quad (12)$$

Given the assumption of negligible concentration of M in the organic phase, the concentration of monomeric HA in the micellar pseudophase can be taken as constant ($=1/v_s$), and thus a new parameter K'_{so} may be defined as:

$$K'_{so} = [MA_z]_m [HA]_b^z / [MA_z]_b \quad (13)$$

where

$$K'_{so} = K_{so}[HA]_m^z = K_{so}/v_s^z \quad (14)$$

5. Reaction of HL with the M-A complex in the reversed micellar pseudophase. Several different reaction stoichiometries are possible. For the purposes of the present discussion, the case that will be considered is that in which HL reacts with the M-A complex to give a final M-HL-A complex which contains both HL and the surfactant:

$$yHL(m) + MA_z(m) = M(HL)_yA_z(m) \quad (15)$$

$$K_{c1} = [M(HL)_yA_z]_m / [HL]_m^y [MA_z]_m \quad (16)$$

6. Partition of the M-HL-A complex between the bulk organic phase and the reversed micellar pseudophase.

$$M(HL)_yA_z(b) + zHA(m) = M(HL)_yA_z(m) + zHA(b) \quad (17)$$

$$K_{s1} = [M(HL)_yA_z]_m [HA]_b^z / [M(HL)_yA_z]_b [HA]_m^z \quad (18)$$

Again, a new parameter K'_{s1} may be defined as

$$K'_{s1} = K_{s1}[HA]_m^z = K_{s1}/v_s^z \quad (19)$$

It should be noted that an equilibrium state is path independent. Thus, for example, the transfer of M^{z+} into the bulk organic phase may be treated in terms of the dissolution of HA into the aqueous phase followed by aqueous phase complexation of M^{z+} and liquid-liquid distribution of MA_z. Alternatively, the complexation reaction may be considered to occur at the liquid/liquid interface. In this case pertinent equilibrium steps would involve the adsorption of HA from the bulk organic phase followed by the interfacial complexation of M^{z+} and the desorption of the resulting MA_z complex into the bulk organic phase. The point here is that whatever the mix of steps chosen, the final result (e.g., the distribution of M^{z+} between the macroscopic organic and aqueous phases) should be the same.

In the above analysis, the surface activity of HA implies the presence of an adsorbed layer at the macroscopic liquid/liquid

interface. It has been assumed for the sake of simplicity, however, that the amount of HA tied up at the interface is negligible compared with that in the bulk organic phase and in the reversed micelles. This assumption can be relaxed without negating the basic arguments of this analysis; an appropriate mass balance can be readily incorporated into the mathematical treatment. Similar considerations pertain for the case where there is significant liquid-liquid distribution of HA.

The Observed Distribution Coefficient

An important parameter in solvent extraction studies is the experimental or observed distribution coefficient (D_{obs}) defined as,

$$D_{obs} = [M]_{to}/[M]_{ta} \tag{20}$$

where $[M]_{to}$ and $[M]_{ta}$ represent the total analytical concentrations of the solute M in the organic and aqueous phases respectively.

The total concentration of M^{z+} in the organic phase (i.e., $[M]_{to}$) is the sum of contributions from the M-HL-A and M-A complexes present in both the bulk organic phase and the reversed micellar pseudophase:

$$[M]_{to}V_o = [MA_z]_bV_b + [MA_z]_mV_m + [M(HL)_yA_z]_bV_b + [M(HL)_yA_z]_m V_m \tag{21}$$

By using the expressions obtained above for $[M]_{to}$, the corresponding expressions can be derived for D_{obs} in terms of the several concentration variables and the relevant equilibrium parameters. As noted above, it is assumed that there are no M^{z+} complexes in the aqueous phase, i.e., $[M]_{ta} = [M^{z+}]_a$. Thus,

$$D_{obs} = \alpha_o [1 + \beta_o C_s] C_s^{z/x}/[H^+]_a^z + \alpha_o \alpha_1 [1 + \beta_1 C_s][HL]_{to}^y C_s^{z/x}/[H^+]_a^z[1 + K_{HL}C_s]^y \tag{22}$$

where

$$\alpha_o = K_{co}/(xK_x)^{z/x} \tag{23}$$

$$\alpha_1 = K_{c1}K_{so}P_{HL}^y/K_{s1} \tag{24}$$

$$\beta_o = [K'_{so}\ (xK_x/C_s)^{z/x-1}]v_s \tag{25}$$

$$\beta_1 = [K'_{s1}\ (xK_x/C_s)^{z/x-1}]v_s \tag{26}$$

The first term on the right hand side of Equation 22 was derived previously (29) and represents the distribution

coefficient (D_o) in the absence of HL. Thus the observed distribution coefficient obtained in the presence of HL can be considered as the sum of two terms:

$$D_{obs} = D_o + D_m \tag{27}$$

where D_m represents the contribution due to the complexation reaction of HL in the presence of the reversed micelles. It follows from Equations 22 and 27 that

$$D_m = \alpha_o \alpha_1 [1 + \beta_1 C_s][HL]_{to}^y C_s^{z/x}/[H^+]_a^z[1 + K_{HL}C_s]^y \tag{28}$$

DISCUSSION

The Effects of Surfactant Concentration on the Distribution Coefficient.

The M-HA System. This case is discussed in detail elsewhere (29). When β_o is relatively small (i.e., under conditions where the MA_z complex has little affinity for the reversed micellar pseudophase), D_o becomes:

$$D_o = \alpha_o C_s^{z/x}/[H^+]_a^z \tag{29}$$

Thus under these conditions, a plot of log D_o vs log C_s at constant $[H^+]_a$ gives a straight line with a slope of (z/x). On the other hand when β_o is relatively large (i.e., under conditions where the MA_z complex partitions preferentially into the reversed micellar pseudophase), D_o reduces to:

$$D_o = (K_{co}K_{so}/v_s^{z-1})C_s/[H^+]_a^z \tag{30}$$

Therefore for this situation, a plot of log D_o vs log C_s at constant $[H^+]_a$ gives a slope of unity.

The M-HL-A Complex System. In considering the influence of the surfactant concentration on the distribution coefficient expression of Equation 28 it should be recalled that the parameter β_1 is dependent on surfactant concentration (see Equation 26). When the final M-HL-A complex resides exclusively in the bulk organic phase, β_1 is negligibly small and therefore $\beta_1 C_s \ll 1$. Equation 28 then reduces to

$$D_m = \alpha_o \alpha_1 [HL]_{to}^y C_s^{z/x}/[H^+]_a^z[1 + K_{HL}C_s]^y \tag{31}$$

It can be seen from Equation 31 that when C_s is relatively low, the distribution coefficient is given by

$$D_m \simeq \alpha_o \alpha_1 [HL]_{to}^y C_s^{z/x}/[H^+]_a^z \tag{32}$$

On the other hand when C_s is relatively large, Equation 31 becomes:

$$D_m \simeq (\alpha_o \alpha_1 / K_{HL}^y)[HL]_{to}^y / [H^+]_a^z C_s^{y-z/x} \quad (33)$$

Thus it follows that the distribution coefficient (D_m) passes through a maximum as the surfactant concentration is increased. This effect is characteristic of systems in which the reactants are preferentially solubilized in the micellar pseudophase (2,26,27). The initial increase in D_m with C_s is attributable to increasing solubilization of HL and MA_z^m by the reversed micellar pseudophase. The subsequent decrease in D_m with increase in C_s is the result of a dilution effect, i.e., once all the reactants have entered the reversed micellar pseudophase, further increase in the volume of the pseudophase only results in a decrease in the effective concentrations of the reactants.

In principle, it should be possible to predict D_{obs} (Equation 22) from knowledge of the relevant equilibrium parameters. Figure 1 presents a log D vs log C_s plot for a hypothetical liquid-liquid system. Values of the relevant equilibrium parameters are collected in Table I. It can be seen from this diagram that with

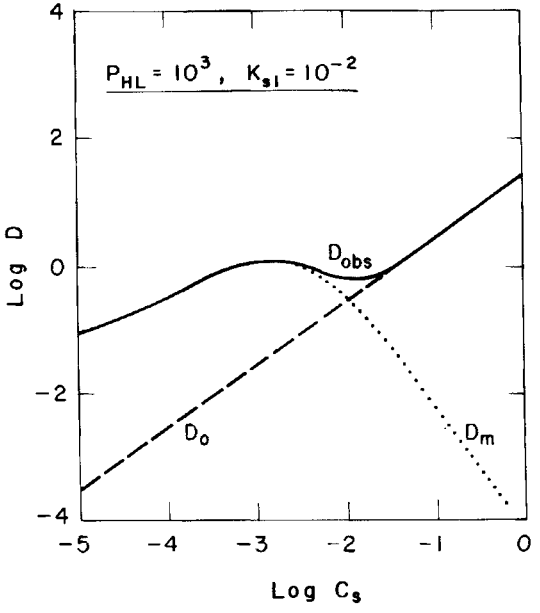

Figure 1. Effect of surfactant concentration on D_{obs}, showing the contributions of D_o and D_m: the M-HL-A complex system with $P_{HL} = 10^3$ and $K_{s1} = 10^{-2}$; see Table I.

Table I. Constant Values of Selected Parameters Used in Figures 1 and 2

$K_x = 10^{25}$	$x = 10.0$	$[HL]_{to} = 0.01$ mol dm^{-3}
$K_{so} = 1.0$	$y = 3.0$	$[H^+]_a = 0.1$ mol dm^{-3}
$K_{co} = 0.1$	$z = 2.0$	
$K_{cl} = 0.1$	$v_s = 0.35$ dm^3 mol^{-1}	

increase in surfactant concentration, D_{obs} first increases to a maximum, then passes through a minimum and then increases again. It is clear from Figure 1 that these trends in D_{obs} are a result of the combined effects of D_m and D_o. It must be noted that whether a maximum and/or a minimum is observed depends on the relative magnitudes of the various equilibrium and stoichiometric parameters. For example, it can be seen from Figure 2 that with decrease in P_{HL} the maximum D_{obs} becomes less pronounced.

Effects of the Equilibrium Parameters on the Distribution Coefficient

Examination of Equation 22 reveals that the observed distribution coefficient is dependent on several equilibrium parameters. These parameters may be determined by applying parameter estimation techniques to the model equations and experimental liquid-liquid distribution data. Correspondingly, a parametric analysis of the above equations can yield further insight into the effects of the reversed micellar pseudophase on the overall extraction process. Thus it follows from Equations 22-33 that,

1. The distribution coefficient D_o increases with increase in K_{co} and K_{so}, i.e., solute transfer into the organic phase is favored by complex formation between M^{z+} and A (i.e., large K_{co}), and preferential solubilization of the M^{z+}-A complex by the reversed micellar pseudophase (i.e., large K_{so}).

2. The distribution coefficient D_m increases with increase in the ability of the surfactant HA to transfer M^{z+} into the organic phase (i.e., large K_{co}), as well as with increase in the ability of HL to interact with the MA_z complex (i.e., large K_{cl}).

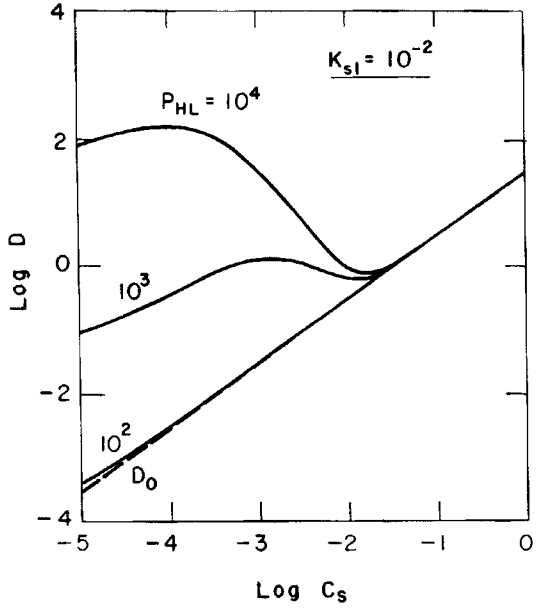

Figure 2. Effect of increasing P_{HL} on the log D_{obs} vs log C_2 profile: the M-HL-A complex system with $K_{sl} = 10^{-2}$; see Table I.

3. Since both MA_2 and HL must be present in the reversed micellar pseudophase for reaction to occur, preferential solubilization of MA_2 (i.e., large K_{sQ}) and HL (i.e., large P_{HL}) leads to high D_m^z values. However, when the surfactant concentration is relatively high, D_m becomes insensitive to P_{HL}; under these conditions there is virtually complete solubilization of HL and therefore, further increase in P_{HL} provides no additional benefit.

4. The effect of K_{sl} is opposite to that of P_{HL}, i.e., with increase in K_{sl}, D_m first decreases and then attains a constant value. This effect is related to increasing inaccessibility of the entire organic phase for liquid-liquid partition, as the value of K_{sl} increases.

Comparison of Theoretical Model with Experimental Data

The literature does not presently contain a sufficiently large pool of systematic experimental data base that can be used for a detailed evaluation of the theoretical analysis presented in this

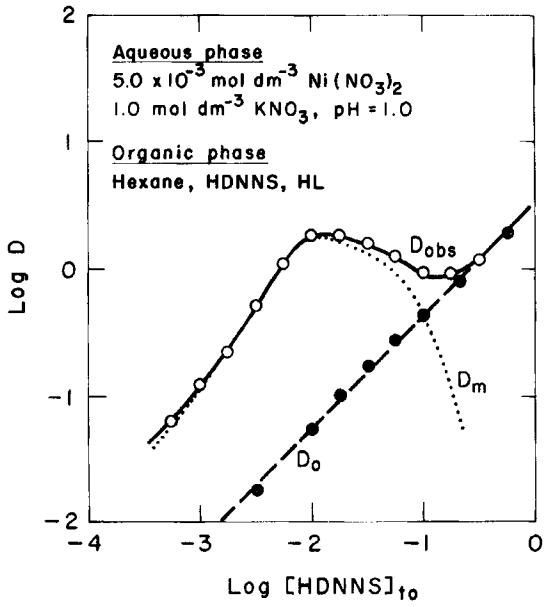

Figure 3. Effect of total HDNNS concentration, $[HDNNS]_{to}$ on nickel distribution in the HDNNS-HL-hexane/$Ni(NO_3)_2$ system, showing the contributions of D_m and D_o to D_{obs}; HL represents 5,8-diethyl-7-hydroxy-6-dodecanone oxime, the active extractant in LIX63. The D_{obs} and D_o data are taken from ref. 20.

paper. Nevertheless the available data are in qualitative agreement with the theoretical trends discussed above. Figure 3 shows log D vs log $[HA]_{to}$ data for nickel distribution (20). In this case HA is dinonylnaphthalene sulfonic acid (HDNNS) while HL is 5,8-diethyl-7-hydroxy-6-dodecanone oxime (the active extractant in LIX63). The sulfonate HDNNS is a liquid-cation-exchanger which readily forms reversed micelles in nonpolar organic solvents, e.g., the CMC of this reagent is in the neighborhood of 10^{-3} mol dm^{-3} and aggregation numbers in the range of 6 to 20 have been reported (30-32). In the absence of HL, the log D_o vs log $[HDNNS]_{to}$ curve shows a straight line with a positive slope of unity which is consistent with Equation 30. This indicates that the $Ni(DNNS)_2$ complex is solubilized within the reversed micellar HDNNS pseudophase. It can also be seen that in the presence of the hydroxyoxime (HL), the log D_{obs} vs log $[HDNNS]_{to}$ curve exhibits the same trend as that shown in the corresponding theoretical curve in Figure 1. Subtraction of the distribution data obtained

with only HDNNS from the corresponding data obtained with the sulfonic acid-hydroxyoxime combination gives the D_m curve as shown in Figure 3. Again, this trend is reminiscent of the D_m curve in Figure 1. The implication is that in this metal-hydroxyoxime-sulfonic acid system, a mixed complex is formed that contains both the hydroxyoxime and the surfactant molecules. In fact, it has been demonstrated previously (20) that the extraction process yields a complex with the stoichiometry Ni/HL/HDNNS = 1/3/2.

In developing the above liquid-liquid distribution model, it was assumed that the organic phase concentration of the extracted solute is so low that it does not significantly influence the mass balance on HA and HL. This assumption does not hold for the experimental conditions used to generate the nickel distribution data (20). Therefore further quantitative analysis of the Ni-HL-HDNNS system must await the results of experiments based on more dilute metal ion concentrations. In addition, it is known that the hydroxyoxime self-aggregates (32)and that its presence shifts the CMC of HDNNS to higher total sulfonate concentrations (31). Work is currently in progress to incorporate these factors into the theoretical liquid-liquid distribution model.

CONCLUSIONS

In this paper, a quantitative analysis of equilibrium liquid-liquid distribution has been developed for a model system consisting of a surfactant HA, an extraction reagent HL, and a solute M^{z+}. It has been shown that analysis of liquid-liquid distribution data can yield quantitative information on extraction as well as solubilization parameters. Thus, systematic liquid-liquid distribution experiments can now be designed specifically to determine parameters such as aggregation constants, aggregation numbers, and solubilization or binding constants. It has also been shown that for the model system investigated, the observed distribution coefficient (D_{obs}) is the sum of the contributions by the M-A complex (i.e., D_o) and the M-HL-A complex (i.e., D_m). Thus, any factors that increase D_o and D_m will also increase D_{obs}.

NOTATION

CMC	critical micelle concentration of HA
C_s	concentration (based on the total volume of the organic phase) of micellar surfactant
D_o	distribution coefficient of M^{z+} in the absence of HL
D_m	distribution coefficient due to the micellar effect on the complexation reaction of HL.
D_{obs}	experimental (observed) distribution coefficient of M^{z+}
HA	micelle-forming surfactant
HL	hydrophobic extractant

K_{co}	equilibrium constant for complexation of M^{z+}(a) by HA(b) (Equation 10)
K_{cl}	equilibrium constant for MA_z-HL reaction to give M-HL-A complex (Equation 16)
K_{HL}	binding constant of HL (Equation 8)
K_{so}	equilibrium constant for solubilization of MA_z (Equation 12)
K'_{so}	equilibrium constant (Equation 14)
K_{sl}	equilibrium constant for solubilization of $M(HL)_yA_z$ (Equation 18)
K'_{sl}	equilibrium constant (Equation 19)
K_x	micellization constant (Equation 4)
M^{z+}	extractable solute
MA_z	extracted complex (Equation 9)
$M(HL)_yA_z$	extracted complex (Equation 15)
P_{HL}	partition coefficient of HL (Equation 6)
V^b	volume of the bulk organic phase
V^m	volume of the reversed micellar pseudophase
V^o	volume of the entire organic phase
v_s^o	molar volume of the surfactant HA
$[X]_b$	concentration of species X in the bulk organic phase
$[X]^m$	concentration of species X in the micellar pseudophase
$[X]^m_{to}$	total analytical concentration of X in the organic phase
$[X]_a$	concentration of species X in the aqueous phase
$[X]_{ta}$	total analytical concentration of X in the aqueous phase
x	aggregation number of HA
y	stoichiometric coefficient for reaction of HL with MA_z (Equation 15)
z	charge on the solute M^{z+}
α_o	equilibrium constant (Equation 23)
α_1	equilibrium parameter (Equation 24)
β_o	equilibrium parameter (Equation 25)
β_1	equilibrium parameter (Equation 26)

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