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On a Possible Role of Microemulsions for Achieving the Separation of Ni^{2+} and Co^{2+} from Their Mixtures on a Kinetic Basis

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Abstract

Complexation of Ni^{2+} or Co^{2+} with extractant molecules is usually a very fast process. A separation of the two metals from their mixtures on a kinetic basis would require a considerable slowing down of the rates of complexation. We show here that this can be achieved with microemulsions of a lipophilic extractant by taking advantage of the electrostatic repulsions between the metal ions and the charged surface of the dispersed particles. The effects of pH, extractant concentration, and purity are examined.

INTRODUCTION

Several recent publications have shown that microemulsion systems have potential applications in the field of metal recovery by liquid-liquid extraction (*1–7*). A generally accepted idea is that microemulsions can improve the rate of extraction of metal species. It has also been demonstrated that they can serve as model systems to study the kinetics and mechansim of reactions (particularly interfacial reactions) occurring between lipophilic extractants and metal ions (*6*).

On the other hand, it is often considered that the pure complexation

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step is the rate-limiting step in a liquid-liquid extraction process when the hydrodynamic conditions are such that a "kinetic regime" is established (*8*). This implies a high enough stirring speed to ensure the disappearance of the diffusional processes. The rate of complexation itself is known to be essentially governed by the rate of removal of the first water molecule in the inner solvation shell of the metal ion (*9–11*). The rate constant for complex formation is thus proportional to the rate constant for water exchange at the metal ion, which can be obtained from NMR measurements.

For most univalent and bivalent metal ions, complex formation in homogeneous solutions occurs rapidly, typically on the time scale of milliseconds for Co^{2+} and of several tenths of seconds for Ni^{2+} at the millimolar concentration level. Although the Co^{2+} ions react some 50 times faster than the Ni^{2+} ions, one cannot take advantage of this difference in separation processes because the time scale involved is rather short.

A separation on a kinetic basis would require a considerable slowing down of the rates of complexation so that the reaction can be stopped at the moment where most of the fast complexing metal has reacted. The purpose of the present work was to demonstrate that this can possibly be achieved by the use of well-chosen microemulsions. Contrary to what is usually done, we have formulated a microemulsion with a cationic surfactant in order to create coulombic repulsions between the metal ions and the positively charged oil microdroplets into which the lipophilic extractant is incorporated.

EXPERIMENTAL PART

Chemicals

Cetyltrimethylammonium bromide (CTAB) from Fluka was twice recrystallized in methanol/diethylether (*12*). Butyl alcohol (puriss) and triethanolamine (TEA, pro analysi) were obtained from Fluka and Merck, respectively. The industrial extractant Kelex 100 was from Schering (FRG). Its purification procedure to obtain 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline has been described elsewhere (*13*). Hexahydrated nickel and cobalt nitrates were from Prolabo (France).

Formulation of Microemulsions

Hydrocarbons can be solubilized in CTAB/water solutions provided that butanol is added as a cosurfactant. A pseudo-ternary phase diagram including *n*-hexadecane has been published by Hermansky and Mackay (*14*). We have previously shown that the industrial extractant Kelex 100 can play the part of the oil in microemulsion systems containing sodium dodecylsulfate (*15*). In the present case we tried to replace hexadecane by the extractant and we were able to obtain a microemulsion of Kelex 100 in CTAB/butanol micelles with the following composition (values in weight %): CTAB (13.5)/butanol (13.5)/Kelex (3.0)/water (70.0). The microemulsion obtained was densely colored and its UV-visible absorption was so high that it was impossible to detect the change of transmitted light upon complexation with metal ions. For this reason we diluted it with water to bring the Kelex concentration to 1% (or less in some cases), which gives the following composition: CTAB (4.5)/butanol (4.5)/Kelex (1.0)/water (90.0). As the complexation reaction rates are pH-dependent (*6*, *13*), due to the possible ionization of the extractant, we added a buffer to adjust the pH of the solutions. The water component of the microemulsion was thus in fact a 0.1 *M* TEA/HCl buffer. Most experiments were performed with the crude extractant and a few with a purified sample.

Kinetic Experiments

The kinetic experiments were carried out with a stopped-flow spectrometer (Hi-Tech SF-3L, England) with a 2-mm optical path. The apparatus was on-line with a data acquisition system (Biomation 805 transient recorder) interfaced with a NM 4/30 computer-automation set-up (Yrel, France). The kinetic curves were either transferred from the computer to a Tektronix 4662 digital plotter or directly recorded on a Tracelab recorder.

One of the syringes contained the microemulsion with the extractant and the other one contained a buffered aqueous solution with the metal ions. The microemulsion remained perfectly clear during and after mixing. The extractant concentration (3.3×10^{-3} to 1.6×10^{-2} *M*) was always in large excess over the total metal ion concentration (3.4×10^{-4} to 1.5×10^{-3} *M*). We systematically compared the results obtained in three different situations: complexation of Ni^{2+} alone, complexation of Co^{2+}

alone, complexation of a mixture of Ni^{2+} and Co^{2+}. Difficulties have sometimes been encountered in reproducing exactly the starting point of the three kinetic curves to be compared. This was likely due to the adsorption of impurities of Kelex on the glass walls of the stopped-flow optical cell. All the concentrations given refer to the concentrations after mixing.

RESULTS AND DISCUSSION

In previous experiments performed in this laboratory with the same extractant/metal ion couple (*6*, *13*), we worked with a large excess of metal ions to ensure pseudo-first-order conditions. The reverse conditions were used in the present work to bring the experiments closer to the situation encountered in metal extraction processes. We still expect pseudo-first-order kinetics when a large excess of extractant exists. In fact, biexponential curves were obtained in both cases with Kelex. We checked that the pseudo-first-order rate constant associated with the main process and attributed to Ni^{2+} complexation was practically independent of the Ni^{2+} ions concentration in the range 1×10^{-4} to 2×10^{-3} *M* when using crude Kelex at a concentration of 0.5% and pH 8.0.

Figure 1 gives an example of the UV-visible spectra obtained for the Kelex-containing microemulsion alone and for the complexes formed with Ni^{2+}, Co^{2+}, and their mixture. The kinetics of complexation was followed at 400 nm where the absorption obtained for either metal is about the same.

The following factors which influence the rate of complexation have been investigated: pH, concentration of the extractant, and purity of the extractant. They will be examined successively.

We know from previous experiments (*6*, *13*) that a neutral or even slightly acidic pH is much more favorable *for slow complexation* than a basic pH. Some experiments were attempted at pH 3.5–4 with acetate buffer as well as in the absence of buffer, but we did not obtain any usable results. These are the lower acceptable pH's if we consider that the yield of extraction with 8-hydroquinoline (which is a nonalkylated analog of Kelex) decreases below pH 4 (*16*). More interesting results have been found at pH 6.5 with a TEA/HCl buffer ($HClO_4$, which was used to adjust the pH in our previous work, caused precipitation with the microemulsion system used here). Examples are given in Fig. 2 (crude extractant) and in Fig. 3 (purified extractant).

The rate of reaction is expected to decrease when the extractant

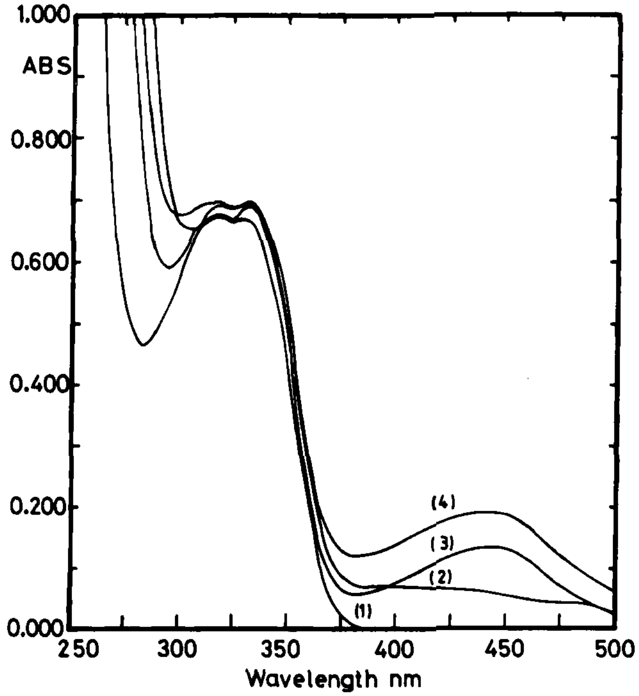

FIG. 1. UV-visible spectra of a microemulsion of purified Kelex and complexes with Ni^{2+}, Co^{2+}, and Ni^{2+}/Co^{2+} mixture (optical path: 1 mm). Microemulsion composition (wt%): CTAB/butanol/Kelex/water (0.1 *M* TEA/HCl): 0.45/0.45/0.1/99, pH 6.5. (1) No metal; (2) $[Ni^{2+}] = 1.7 \times 10^{-4}$ *M*; (3) $[Co^{2+}] = 1.7 \times 10^{-4}$ *M*; (4) $[Ni^{2+}] = 1.7 \times 10^{-4}$ and $[Co^{2+}] = 1.7 \times 10^{-4}$ *M*.

concentration decreases. This is verifed in Table 1 where it can be observed that the time after which all the Co^{2+} ions are complexed goes from about 2.5 to 12 s when the crude extractant concentration varies from 0.5 to 0.1%. The time bases available for sampling the kinetic curve with the Biomation 805 A/D converter did not allow for completion of Ni^{2+} complexation. For this purpose we had to use a conventional plotter (Tracelab recorder).

As we knew that (a) complexation by 8-hydroxyquinoline in microemulsions is about 30 times faster than complexation with its alkylated homolog 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline (*6*), and (b) crude Kelex 100 contains about 0.5% of 8-hydroxyquinoline and some 17% of other impurities (*17*), we felt it necessary to do some experiments

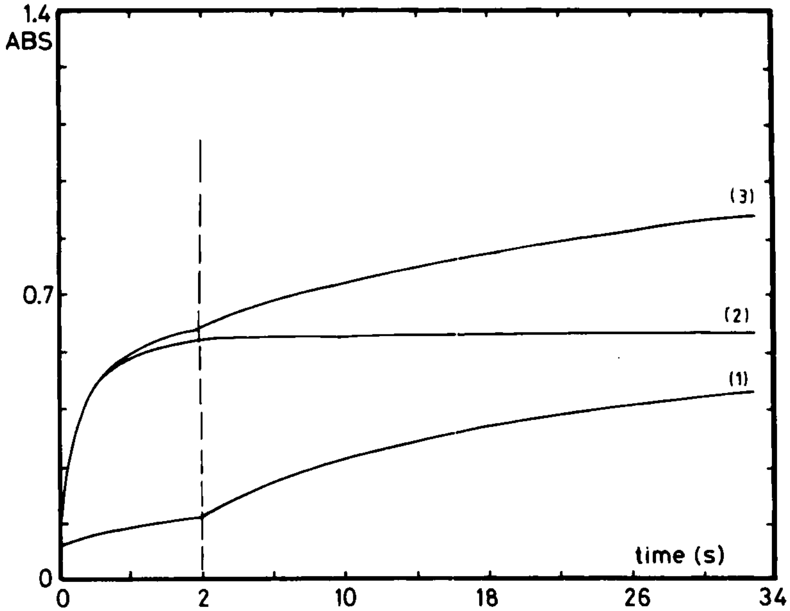

FIG. 2. Kinetic curves for complexation at pH 6.5 of crude Kelex in a microemulsion containing 0.5% Kelex. O.D. versus time at 400 nm. (1) $[Ni^{2+}] = 1 \times 10^{-3}$ *M*; (2) $[Co^{2+}] = 5 \times 10^{-4}$ *M*; (3) mixture. Two time bases have been used in this recording: time intervals for the sampling are 5 ms for the first 400 points and 20 ms for the remaining 1600 points.

with a purifed sample. The results obtained (Fig. 3) can be compared in Table 1 with those obtained for the crude product (Fig. 2). The complexation of the totality of the Co^{2+} ions requires about 10 times more time with the purified extractant. A recording of the transmission change of the solution on a long time scale is presented in Fig. 4. It shows that, with the indicated experimental conditions, 2 min are required for a total complexation of Co^{2+}, within which time the complexation of Ni^{2+} remains negligibly small. In this case, complexation of Ni^{2+} is completed only after 1.5 h.

We have thus demonstrated that a tremendous slowing down of the rate of complexation can be achieved with cationic micelles. This is to be attributed to the combination of several factors: a pH favoring the neutral form of the extractant (note that the pH at the surface of the CTAB micelles is expected to be more basic than the measured one (*18*)), a purely lipophilic extractant ensuring that the reaction is strictly inter-

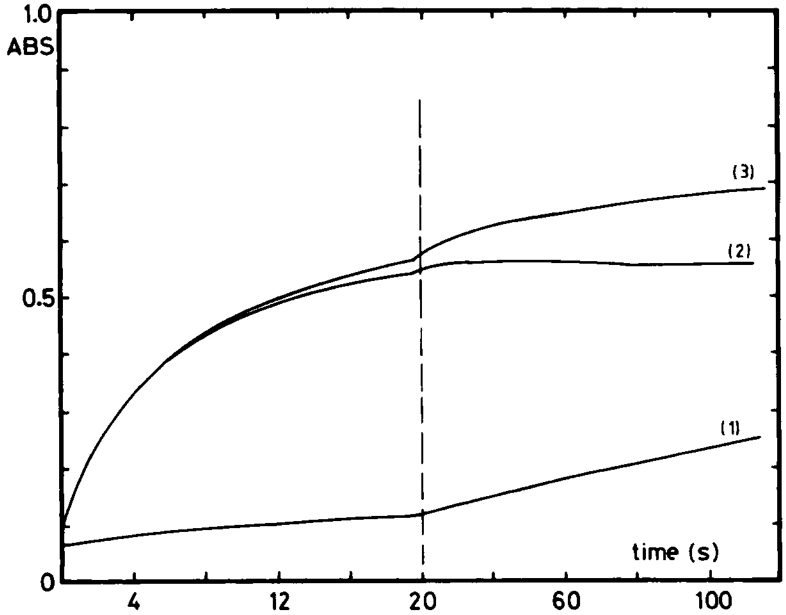

FIG. 3. Kinetic curves for complexation at pH 6.5 of purified Kelex in a microemulsion containing 0.5% extractant. O.D. versus time at 400 nm. (1) $[Ni^{2+}] = 1 \times 10^{-3}$ *M*; (2) $[Co^{2+}] = 5 \times 10^{-4}$ *M*; (3) mixture. Two time bases have been used in this recording: time intervals for the sampling are 20 ms for the first 1000 points and 100 ms for the remaining 1000 points.

TABLE 1

Time Scales Involved in the Kinetics of Complexation at pH 6.5 (0.1 *M* TEA/HCl) and 25°C (detection at 400 nm)

Extractant[a] and concentration[b] (in wt%)	Metal ion concentration[b] (mol/L)		Time after which all Co^{2+} is complexed	Total time observed	Remarks
	Ni^{2+}	Co^{2+}			
Crude 0.5%	1×10^{-3}	5×10^{-4}	2 s	34 s	Ni^{2+} complexation is far from being completed
Crude 0.1%	1.7×10^{-4}	1.7×10^{-4}	12 s	144 s	
Crude 0.2%	1.7×10^{-4}	1.7×10^{-4}	8 s	144 s	
Crude 0.3%	1.7×10^{-4}	1.7×10^{-4}	6 s	144 s	
Crude 0.5%	1.7×10^{-4}	1.7×10^{-4}	2.5 s	105 s	
Purified 0.5%	1×10^{-3}	5×10^{-4}	20 s	120 s	
Purified 0.1%	1.7×10^{-4}	1.7×10^{-4}	100–120 s	1.5 h	Tracelab recorder was used

[a] The "crude" extractant is the industrial Kelex 100 and the "purified" extractant is 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline

[b] Concentration given refers to concentration after mixing.

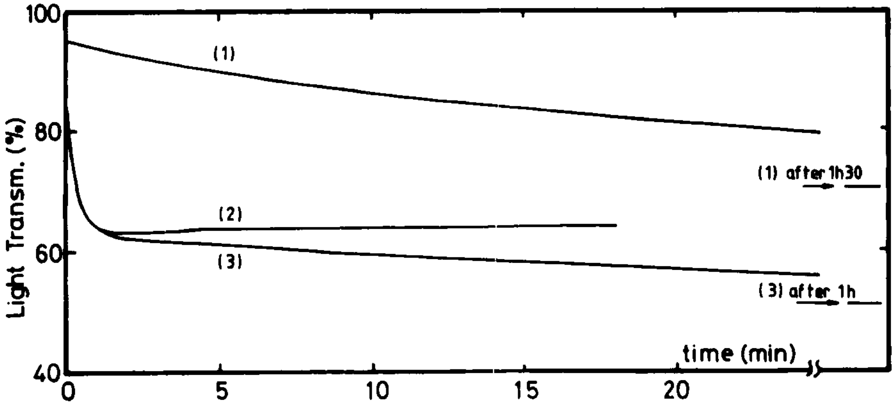

FIG. 4. Kinetic curves for complexation at pH 6.5 of purified Kelex in a microemulsion containing 0.1% extractant. (1) $[Ni^{2+}] = 1.7 \times 10^{-4}$ *M*; (2) $[Co^{2+}] = 1.7 \times 10^{-4}$ *M*; (3) mixture. Transmission change at 400 nm versus time recorded on a Tracelab recorder.

facial (this is not the case in the presence of nonalkylated impurities), and finally a repulsive effect on the incoming metal ions.

In a way similar to "polyelectrolyte catalysis," the inhibition effect observed here can be explained in terms of the local concentration of metal ions. The distribution of ions having the same sign as the micellar surface is given by a classical Boltzmann equation (*19*, *20*):

$$n_+ = n_0 \exp\left[-\frac{ze\psi}{kT}\right]$$

where n_+ is the number of positive ions per unit volume at points where the potential is ψ and n_0 is the corresponding bulk concentration. Depending on the ratio of the electric potential energy $ze\psi$ to the thermal energy kT, the concentration at the surface of the micelles can be very low. Moreover, the smaller the rate constant for water/ligand exchange at the metal ion, the less probable the reaction with the extractant during the short residence time of the metal ion at the charged surface of the microemulsion droplet. This can be assumed to be the reason for the well-separated kinetics of complexation of Ni^{2+}/Co^{2+} mixtures, even on a long time scale.

In conclusion, we have shown that the complexation of Co^{2+} and Ni^{2+} with the active component of Kelex 100 can be slowed down to such an extent that a separation of the two metals on a kinetic basis becomes worth considering. The problem will be how to recover in a matter of a few minutes the metal ions complexed in the first place. This goal could be attained by inducing a phase separation in the microemulsion or by replacing it by weakly stable emulsions.

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