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Transition Metal Complexes with 8-Hydroxyquinoline and Kelex 100 in Micellar Systems. Stoichiometry of the Complexes and Kinetics of Dissociation in Acid Media

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ABSTRACT

Complexation of metal ions by micelle-solubilized extractants can be used for the development of new extraction processes. Metal extraction in micellar systems is in many respects analogous to solvent extraction if one considers the use of ultrafiltration as a means to separate the micellar pseudophase from the continuous aqueous phase. The present paper is intended to further characterize the nature of the complexes obtained in micellar systems (especially their stoichiometry and their stability as a function of pH) and to compare the results with those previously obtained in classical biphasic systems. The extractant molecules considered in this work were 8-hydroxyquinoline (HQ) and its alkylated analogue (C_{11}-HQ) derived from Kelex 100. Their complexes with Ni^{2+}, Co^{2+}, and Cu^{2+} have been investigated in micellar solutions made of cetyltrimethylammonium bromide (CTAB), 1-butanol, and water. The stoichiometry of the complexes was determined using Job's continuous variation method, and their kinetics of dissociation was investigated with the stopped-flow technique. Practical selective recovery of the different metal ions from their complexes in micelles was shown to be possible using ultrafiltration.

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INTRODUCTION

A great deal of work has been devoted during the past few years to the applications of organized systems in the field of metal extraction (1–7). As a first step it has been recognized that microemulsions may form in certain solvent extraction systems (8), resulting in a considerable improvement of the extraction rates (9). These observations have contributed to initiate new research work aimed at determining the role of reverse micelles or microemulsions in hydrometallurgical processes. Parallelly direct micelles were used in order to mimic the part played by the organic phase in classical solvent extraction (10–15). Indeed, the hydrophobic core of micelles (or of oil-in-water microemulsions) can solubilize hydrophobic extractants, and the rate of metal complexation (equivalent to the rate of extraction of the metal ions by the micellar pseudophase) can be investigated in perfectly homogeneous conditions using spectrophotometric techniques, although the intimate nature of the system is microheterogeneous. Finally, the analogy between solvent extraction and "micellar extraction" has been pushed to a point where the feasibility of metal extraction by micellar systems has been clearly demonstrated (16–18). These new processes involve the coupling of metal complexation by micelle-solubilized extractants and membrane ultrafiltration (19–21).

Micellar extraction has some advantages worth considering. The first one resides in the fact that it is a purely aqueous process which does not require the presence of an organic solvent. This may be of interest from the point of view of the preservation of the environment. A second advantage can be found in the possibility of achieving kinetic separations (17, 18) of metal ions by taking advantage of the specific interactions existing between the micellar entities and the metal ions. Finally, micellar extraction offers a way of simultaneously removing undesirable metal ions and organic pollutants (22, 23), provided they are soluble in the oil-like micellar core.

The approach is, of course, different depending on whether the objective is the total elimination of the undesirable metal ions present (purification of water streams) or the selective recovery of a particular metallic species. In the former case there is no need of a specific complexing agent since anionic micelles can bind metal ions by themselves, especially multivalent cations. On the other hand, backextraction may be a problem in both cases. The development of micellar-based extraction processes requires this problem to be solved. Contrary to the conditions of extraction, which are now well documented in the literature, very little is known about the stripping conditions in these kinds of systems. We have recently reported some preliminary data tending to demonstrate that, from a thermodynamic point of view, the extraction/deextraction of metal ions in a micellar pseudophase behaves very similarly to the more classical solvent extraction (18).

The stability of the complexes formed is normally related to their structure and to the nature of the metal ion involved. One important question concerns the precise structure of the complexes solubilized in micellar entities: Is this structure comparable to what would be obtained in an organic solvent, such as those classically used in liquid–liquid extraction? This kind of question has not been addressed so far, except in occasional circumstances, and it will constitute one of the objectives of this paper.

Another point which has not been extensively studied and which deserves some attention concerns the conditions in which the decomplexation of metal ions occurs in micellar systems. The kinetic aspects are also of importance, and generally much less attention has been paid to the problem of complex dissociation compared to complex formation, even in purely aqueous media. Experiments have been done in this work in order to determine more precisely the effect of the nature of the metal ion and of the hydrophobicity of the extractant on the rate of dissociation in acid media.

Finally, the pH range in which the release of a particular metal ion takes place will be confirmed by ultrafiltration experiments, leading to practical recovery of metal ions in conditions of selectivity.

EXPERIMENTAL

Chemicals

The two complexing agents used had the following origins: 8-Hydroxyquinoline (HQ) was obtained from Fluka (puriss) and used without further purification; Kelex 100, from Schering (Germany), was thoroughly purified by chromatographic separations (10) to get pure 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline (C_{11}-HQ). The metal chlorides had different origins: $CuCl_2 \cdot 2H_2O$ (Prolabo, France); $CoCl_2 \cdot 6H_2O$ (UCB, Belgium), and $NiCl_2 \cdot 6H_2O$ (Fluka). Cetyltrimethylammonium bromide (CTAB), from Fluka, was twice recrystallized in methanol/diethylether. 1-Butanol (puriss) had the same origin. The complexing agents were solubilized in CTAB/butanol mixed micelles. As in previous studies, the stock solutions were prepared from doubly distilled water containing 0.1 M triethanolamine (TEA/HCl) at pH 6.5.

Techniques

The equilibrium measurements to obtain the stoichiometry of the complexes in micellar systems were performed with a Varian DMS-100 UVvisible spectrophotometer. A Metrohm pHmeter with a combined glass electrode was used for the pH measurements.

The kinetics of dissociation of the extractant/metal complexes were carried out with a stopped-flow spectrophotometer (Hi-Tech SF-3L, England) with a 2-mm optical path. In a typical experiment, one syringe contained a microemulsion of the following composition (24): CTAB (0.9%)/butanol (0.9%)/C_{11}-HQ or HQ (0.2%)/water, 0.1 M TEA (98%), in which the metal ion had been dissolved to form the extractant/metal complex (the extractant was in large excess compared to the metal-ion concentration, 3.4×10^{-4} M). The second syringe contained an acidified micellar solution of the same composition, except that the extractants and metal ions were omitted. The pH values indicated are the values measured after mixing the two solutions. The kinetics of complex dissociation was monitored at different wavelengths depending on the nature of the complex considered: 391 nm for HQ/Ni^{2+} and HQ/Co^{2+}, 490 nm for C_{11}-HQ/Ni^{2+}, 442 nm for C_{11}-HQ/Co^{2+}, and 430 nm for C_{11}-HQ/Cu^{2+}. The kinetic curves were either purely first order or biexponential. Data acquisition was performed through a Biomation 805 transient recorder interfaced with a computer. The relaxation times characterizing the kinetic curves were computed from nonlinear least-squares fitting of the experimental curves with mono- or biexponential functions.

Ultrafiltration experiments were performed with a stirred cell (Amicon) of 10 mL volume, using cellulosic disc membranes with a molecular weight cut-off of 10,000, following a previously described procedure (16, 18).

RESULTS AND DISCUSSION

Equilibrium Measurements

The stoichiometries of a series of extractant/metal complexes were determined using Job's continuous-variation method (25). For this purpose two solutions of, respectively, the metal ions and the extractants at equivalent concentrations (3.4×10^{-3} M) were mixed in different ratios. The solutions were composed of 0.45% CTAB, 0.45% butanol, and 99% water (0.1 M TEA, pH 6.5). Figure 1 is relative to the results obtained for the complexation of HQ with Ni^{2+} and Co^{2+}, respectively. The position of the maximum of absorbance corresponds in both cases to a metal/(metal + extractant) ratio of 0.33, which indicates the existence of a 1:2 complex (1 metal ion for 2 HQ molecules). This result is to be compared with the complex composition determined by Stary (26) from biphasic extraction in chloroform. The extracted species in the case of Ni^{2+} was $NiOx_2$ and that for Co^{2+} was $CoOx_2 \cdot 2HOx$, where HOx represents 8-hydroxyquinoline (equivalent to HQ) and Ox is the oxinate. There is thus a perfect

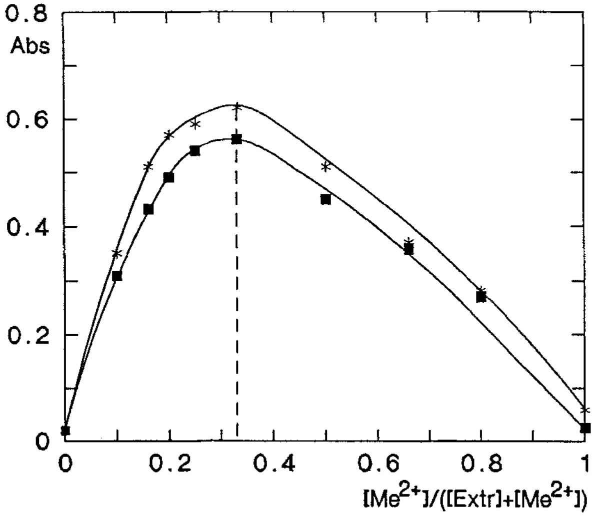

FIG. 1 Absorbance versus mole fraction of Me^{2+} ($[Me^{2+}]/([extractant] + [Me^{2+}])$) at 391 nm (Job's plots) in the CTAB/butanol micellar solution, pH 6.5. Analytical extractant and metal ion concentrations: 3.4×10^{-3} M. (*): HQ/Co^{2+}; (■): HQ/Ni^{2+}.

similarity in the case of Ni^{2+} between the complexes formed in chloroform and in the micellar solution. In the case of Co^{2+}, Job's method in micellar solutions does not allow us to say if there is additional solvation by two more molecules of extractant.

The corresponding results for the alkylated extractant C_{11}-HQ are represented in Fig. 2, in which the complex with Cu^{2+} has also been considered. The metal/(metal + extractant) ratio at maximum absorbance is clearly 0.25 for Co^{2+} and 0.33 for Cu^{2+}, which indicates a 1:3 stoichiometry in the former case and a 1:2 stoichiometry in the latter case. The case of Ni^{2+} is not as clear-cut since a flat maximum was obtained, but its position is close to 0.33, as for Cu^{2+}, which suggests a 1:2 stoichiometry.

We can thus conclude that the complexes of Ni^{2+} with HQ and C_{11}-HQ are equivalent and have the same stoichiometry as previously obtained in methanol (10) (this was no longer true in microemulsions of SDS/pentanol/dodecane/water in which a 1:2 stoichiometry was obtained for HQ/Ni^{2+}, whereas Job's curve for C_{11}-HQ/Ni^{2+} was bimodal, with maxima around 0.3 and 0.6) (10). On the other hand, the complexes of Co^{2+} have different stoichiometries depending upon whether the extractant is HQ or C_{11}-HQ. This will be seen below to have implications for the dissociation of the complexes.

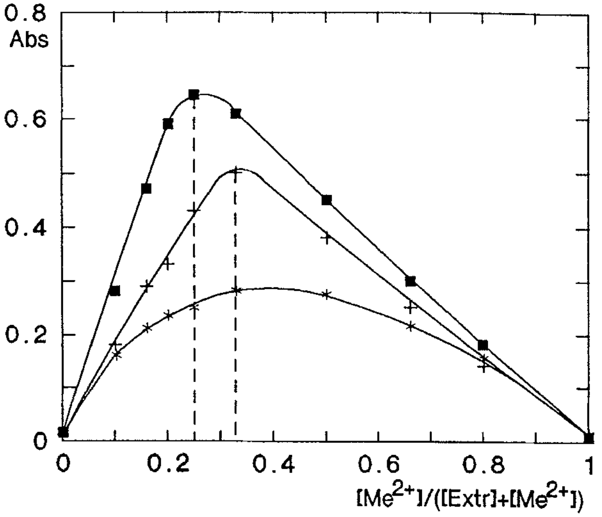

FIG. 2 Absorbance versus mole fraction of Me^{2+} ($[Me^{2+}]/([extractant] + [Me^{2+}])$) at the wavelengths indicated in the text in the CTAB/butanol micellar solution, pH 6.5. Analytical extractant and metal ion concentrations: 3.4×10^{-3} M. (■): $C_{11}HQ/Co^{2+}$; (+): C_{11}-HQ/Cu^{2+}; (∗): C_{11}-HQ/Ni^{2+}.

It should be emphasized that the above analysis of Job's plots totally ignored the pseudobiphasic nature of the micellar system, which was considered in a similar way to homogeneous solvents. In the case mentioned before where bimodal Job's plots were obtained, different kinds of complexes may coexist in the continuous and in the micellar pseudophases.

Kinetic Measurements

The second set of data is relative to stopped-flow studies of the kinetics of dissociation of preformed complexes in micellar solution. We have considered the complexes of Ni^{2+}, Co^{2+}, and Cu^{2+} with HQ and with C_{11}-HQ in the conditions given in the Experimental Section. For two of the systems investigated, namely HQ/Cu^{2+} and HQ/Co^{2+}, the dissociations of the complexes were too fast to be measured by the stopped-flow technique, and we can only give a lower limit of the observed rate constants [equivalent to the reciprocal relaxation times $1/\tau$ (s^{-1})]. An opposite situation was found with C_{11}-HQ/Co^{2+}, whose complex was so stable that its destruction was never observed, so that in this case only an upper limit can be given. For the three remaining complexes, the results obtained from least-squares analysis of the relaxation curves are given in Tables 1 and 2. These curves were best fitted with biexponential functions when

TABLE 1

Results Obtained from Least-Squares Analysis of the Kinetic Curves for Dissociation of the Complexes HQ/Ni^{2+} and C_{11}-HQ/Ni^{2+} in Micellar Solutions (variation of absorbance of the form Absorbance = $A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + c^{te}$); A_1 and A_2 in OD Units: $1/\tau_1$ and $1/\tau_2$ in s^{-1}

		pH								
System		2.7	2.94	3.28	3.80	3.85	4.0	4.2	4.5	4.55
HQ/Ni^{2+}:	A_1				0.13		0.21	0.19		0.11
	$1/\tau_1$				13.2		7.4	6.1		4.93
	$A2$				0.04		0.12	0.12		0.10
	$1/\tau_2$				0.98		0.35	0.34		0.35
C_{11}-HQ/Ni^{2+}:	A_1	0.27	0.37	0.42		0.23			0.16	
	$1/\tau_1$	2.17	1.01	0.53		0.22			0.056	
	A_2	—	—	—		0.24			0.29	
	$1/\tau_2$	—	—	—		0.088			0.010	

the final pH was above 3.5, but purely monoexponential absorbance changes were always found at pHs below this value. Since all the complexes treated here have a 1:2 stoichiometry, we can assume that the dissociation proceeds in two steps, as suggested in similar situations (27, 28):

$$L_2Me + H^+ \xrightarrow{k_1} LMe^+ + LH \qquad (1)$$

$$LMe^+ + H^+ \xrightarrow{k_2} Me^{2+} + LH \qquad (2)$$

The first step can be split into a fast protonation of the complex, followed by its dissociation. When the pH is acid enough, the reaction appears to proceed in a single step and the free extractant is expected to be instantaneously bis-protonated to give LH_2^+. A classical kinetic treatment of the

TABLE 2

Results Obtained from Least-Squares Analysis of the Kinetic Curves for Dissociation of the Complexes C_{11}-HQ/Cu^{2+} in Micellar Solutions (variation of absorbance of the form Absorbance = $A \exp(-t/\tau) + c^{te}$); A in OD Units and $1/\tau$ in s^{-1}

		pH					
System		0.5	0.7	0.93	1.03	1.16	1.25
C_{11}-HQ/Cu^{2+}:	A	0.16	0.16	0.25	0.23	0.06	0.02
	$1/\tau$	91.0	90.6	47.7	37.4	14.4	12.0

preceding mechanism is consistent with the biexponential changes observed in some cases. The reciprocal relaxation times in that case are expressed by

$$1/\tau_x = k_x[H^+]$$

where $x = 1$ or 2.

This expression, which is, in principle, strictly correct when the proton concentration is in excess of the complex concentration, is verified for the fast relaxation times, as shown in Fig. 3 for the case of C_{11}-HQ/Ni^{2+}. The proton concentrations plotted in this figure were directly obtained from the pH values, assuming they are equivalent to proton activities. The data relative to the slow relaxation times do not allow a check of the validity of the previous expression. Only the values of the fast relaxation times are shown in Fig. 4 for the sake of comparison of the six systems investigated. The following observations can be made from Fig. 4.

With the HQ extractant, the fastest complexing cations (29, 30) (Cu^{2+} and Co^{2+}) are also those for which the dissociation is the more rapid, since it is too fast to be measured by stopped-flow, contrary to the dissociation of the Ni^{2+} complex. For C_{11}-HQ, the same observation can be made by considering the cases of Cu^{2+} and Ni^{2+}, leaving aside the case of Co^{2+} which is very special. The high stability of the latter complex

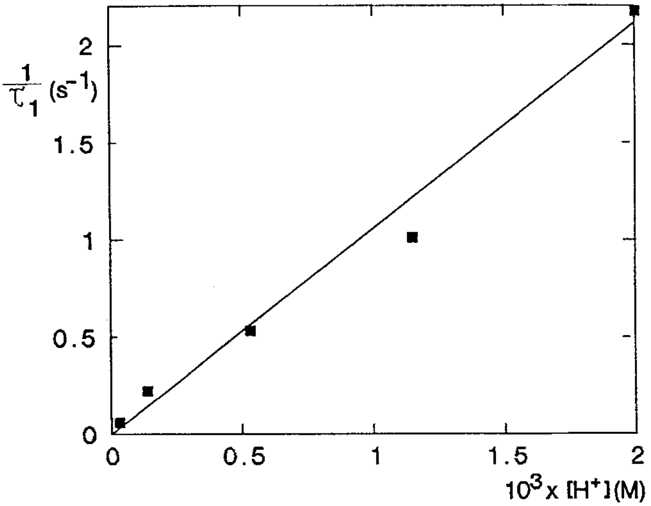

FIG. 3 Plot of $1/\tau_1$ versus the proton concentration for C_{11}-HQ/Ni^{2+} complex dissociation in the CTAB/butanol micellar solution. Analytical extractant and metal ion concentrations: 3.4×10^{-3} M and 1.7×10^{-4} M, respectively.

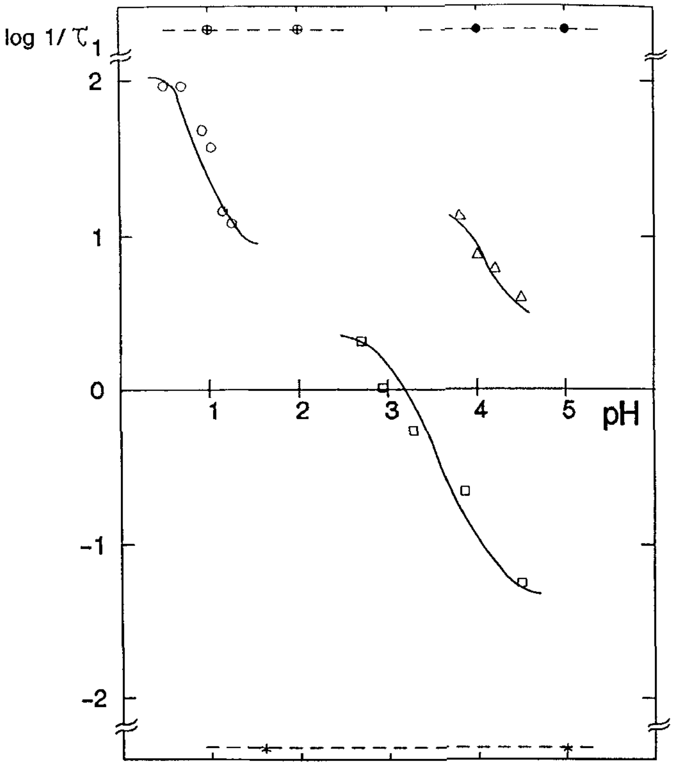

FIG. 4 Logarithmic plots of $1/\tau_1$ (s^{-1}) versus pH for the dissociation of the complexes in the CTAB/butanol micellar solutions. (○): C_{11}-HQ/Cu^{2+}; (△): HQ/Ni^{2+}; (□): C_{11}-HQ/Ni^{2+}. The broken lines indicate lower limits [(⊕): HQ/Cu^{2+}; (●): HQ/Co^{2+}] or upper limits [(*): C_{11}-HQ/Co^{2+}]. See text for more details.

was previously reported to also occur in a kerosene organic phase (31). The present results further confirm the strong similitude between micelles and organic solvents with respect to their extraction properties. The stability of the Co^{2+} complex is related to the 1:3 stoichiometry reported in the first part of this paper. The alkyl chains of the three extractant molecules may create a hydrophobic shell around the Co^{2+} ion, totally preventing the approach of a proton. Furthermore, this strongly hydrophobic complex is expected to be buried in the core of the micelles, whose positively charged surface repels protons. This exceptional stability could also come from the possible oxidation of Co(II) in Co(III), although this has not been demonstrated in the present case.

By comparing in Fig. 4 the results obtained with HQ and C_{11}-HQ for the same metal ion, we notice that decomplexation is considerably slower for C_{11}-HQ, in agreement with what was previously reported for the complexation of Ni^{2+} by those two extractants (10, 11). This can probably again be attributed to steric constraints making access of H^+ ions more difficult to protonation sites. Nevertheless, whereas it was shown before that complexation can be made so slow as to make possible metal separations on a kinetic basis (17, 18, 24), the characteristic times measured for decomplexation are not long enough to offer a similar possibility. However, the data clearly indicate that a selective decomplexation could be easily obtained by adjusting the pH; in the case of C_{11}-HQ, for instance, the release of copper will take place at a much more acidic pH than the release of nickel. This is demonstrated in the next section.

Ultrafiltration Experiments

The range of pH where complex dissociation occurs (Fig. 4) can be correlated with the practical recovery of the metal ions considered by using ultrafiltration. Figure 5 collects the results of three different experiments, each of them involving a mixture of two metal ions and either HQ or C_{11}-HQ. Five milliliters of the micellar solutions containing the complexes were mixed in the ultrafiltration cell with 5 mL of an acidified micellar solution so as to obtain the final pH indicated on the X-axis in Fig. 5 (the micellar concentration was thus kept constant during mixing). A nitrogen pressure of approximately 4 bars was applied until 20–30% of the initial volume was collected. This filtrate was analyzed by atomic absorption spectrometry for its metal content. The results, plotted in Fig. 5, are expressed in the form of the ratio of the metal ion concentration in the filtrate divided by the initial concentration of the same metal ion (as a percentage). They confirm the possibility of selectively recovering metal ions from micellar solutions by a procedure quite similar to the stripping step in classical biphasic extraction.

The shapes of the curves in Fig. 5 intrinsically contain information regarding the structure of the metal/extractant complexes (32, 33). In particular, their steepness tells us the number of protons removed during complex formation. Unfortunately, our attempts to calculate these curves theoretically did not lead to the expected agreement with the experimental data. For these calculations we considered the micellar solution to be a simple solvent, and we have used concentrations instead of activities in the equilibrium relations since the activity corrections in such systems cannot be evaluated. These approximations may explain our difficulties in correctly fitting the data. Because the two curves obtained with HQ are much steeper than the two curves relative to C_{11}-HQ, the number of protons removed upon complex formation may be larger in the case of the HQ/Me^{2+} compared to C_{11}-HQ/Me^{2+} complexes.

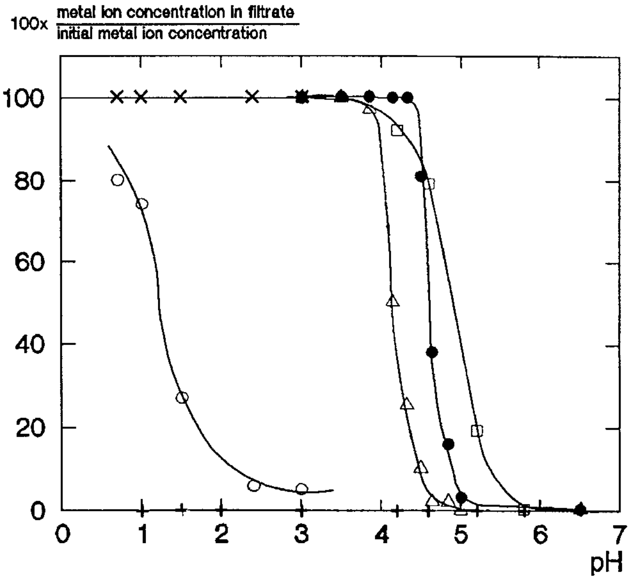

FIG. 5 Ultrafiltration experiments: percent of metal ion concentration found in the filtrate reported to the initial concentration versus pH after acid dissociation in the CTAB/butanol micellar solution. Analytical extractant and metal ion concentrations: 3.4×10^{-3} M and 1.7×10^{-4} M, respectively. HQ with Ni^{2+}-Co^{2+}: (△) Ni^{2+}; (●) Co^{2+} (slightly turbid solution at pH > 4.5). C_{11}-HQ with Ni^{2+}-Cu^{2+}: (×) Ni^{2+}; (○) Cu^{2+}. C_{11}-HQ with Ni^{2+}-Co^{2+}: (□) Ni^{2+}; (+) Co^{2+}.

CONCLUSION

Complexes of Ni^{2+} and Co^{2+} with HQ in micellar systems were shown to have a 1:2 stoichiometry, similar to the situation reported in organic solvents if the contribution of simply solvating extractant molecules is neglected. The same stoichiometry was also obtained for complexes involving C_{11}-HQ, with the exception of Co^{2+} which is characterized by a 1:3 complex. The rate of acid dissociation of the different complexes remains quite fast except for the above complex of cobalt with C_{11}-HQ which has an exceptional long-term stability. For the other metal ions investigated, the alkyl chain is responsible for a significant decrease of the rate of complex dissociation. Finally, we have shown that deextraction from micellar systems is equivalent to the stripping step in biphasic extraction. Ultrafiltration of the micellar pseudophase was carried out at different pHs to illustrate this purpose and demonstrate the feasibility of doing selective metal recovery.

REFERENCES

1. K. Osseo-Asare and M. E. Keeney, *Sep. Sci. Technol.*, *15*, 999 (1980).
2. C. S. Vijayalakshmi, A. V. Annapragada, and E. Gulari, *Ibid.*, *25*, 711 (1990).
3. C. A. Savastano and E. S. Ortiz, *Chem. Eng. Sci.*, *46*, 741 (1991).
4. E. Paatero and J. Sjöblom, *Hydrometallurgy*, *25*, 231 (1990).
5. E. Paatero, J. Sjöblom, and S. Datta, *J. Colloid Interface Sci.*, *138*, 388 (1990).
6. K. Osseo-Asare and Y. Zheng, *Colloids Surf.*, *53*, 339 (1991).
7. R. D. Neuman, M. A. Jones, and N. F. Zhou, *Ibid.*, *46*, 45 (1990).
8. D. Bauer, P. Fourre, and J. Lemerle, *C. R. Acad. Sci., Ser. 2*, *292*, 1019 (1981).
9. P. Fourre and D. Bauer, *Ibid.*, *292*, 1077 (1981).
10. C. Tondre and M. Boumezioud, *J. Phys. Chem.*, *93*, 846 (1989).
11. M. Boumezioud, H. S. Kim, and C. Tondre, *Colloids Surf.*, *41*, 255 (1989).
12. Y. Miyake, M. Yamada, T. Kikuchi, and M. Teramoto, *J. Chem. Soc., Faraday Trans.*, *88*, 1285 (1992).
13. S. Muralidharan, W. Yu, S. Tagashira, and H. Freiser, *Langmuir*, *6*, 1190 (1990).
14. S.-G. Son, M. Hebrant, P. Tecilla, P. Scrimin, and C. Tondre, *J. Phys. Chem.*, *96*, 11072 (1992).
15. C. Tondre and M. Hebrant, *Ibid.*, *96*, 11079 (1992).
16. C. Tondre, S.-G. Son, M. Hebrant, P. Scrimin, and P. Tecilla, *Langmuir*, *9*, 950 (1993).
17. M. Ismael and C. Tondre, *Ibid.*, *8*, 1039 (1992).
18. M Ismael and C. Tondre, *J. Colloid Interface Sci.*, *160*, 252 (1993).
19. S. D. Christian, E. E. Tucker, J. F. Scamehorn, B.-H. Lee, and K. J. Sasaki, *Langmuir*, *5*, 876 (1989).
20. R. O. Dunn, J. F. Scamehorn, and S. D. Christian, *Colloids Surf.*, *35*, 49 (1989).
21. E. Pramauro, A. Bianco, E. Barni, G. Viscardi, and W. Hinze, *Ibid.*, *63*, 291 (1992).
22. J. F. Scamehorn and J. H. Harwell, in *Surfactants in Chemical/Process Engineering Surfactant Science Series*, Vol. 28 (D. T. Wasan, M. E. Ginn, and D. O. Shah, Eds.), Dekker, New York, 1988, p. 77.
23. E. Pramauro, A. B. Prevot, P. Savarino, G. Viscardi, M. De La Guardia, and E. P. Cardells, *Analyst*, *118*, 23 (1993).
24. H. S. Kim and C. Tondre, *Sep. Sci. Technol.*, *24*, 485 (1989).
25. P. Job, *Ann. Chim.*, *9*, 113 (1928).
26. J. Stary, *Anal. Chim. Acta*, *28*, 132 (1963).
27. R. N. Banerjee, S. Gangopadhyay, A. K. Banerjee, and D. Banerjea, *J. Coord. Chem.*, *12*, 287 (1983).
28. S. Guha and D. Banerjea, *Indian J. Chem.*, *30A*, 269 (1991).
29. M. Eigen, *Pure Appl. Chem.*, *6*, 97 (1963).
30. M. Eigen and R. G. Wilkins, in *Mechanism of Inorganic Reactions* (Adv. Chem. Ser., 49), 1965, p. 55.
31. V. I. Lakshmanan and G. J. Lawson, *J. Inorg. Nucl. Chem.*, *35*, 4285 (1973).
32. M. Rumeau, F. Persin, V. Sciers, M. Persin, and J. Sarrazin, *J. Membr. Sci.*, *73*, 313 (1992).
33. M. Hebrant, M. Mimouni, M. Tissier, Y. Pointud, and J. Juillard, *New J. Chem.*, *16*, 999 (1992).

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