Colloid Polym Sci 273:598–602 (1995)

ORIGINAL CONTRIBUTION

M. Hebrant
A. Bouraine
A. Brembilla
P. Lochon
C. Tondre

Extraction kinetics and ultrafiltration removal of Nickel (II) by long chain alkoxypicolinic acids in cationic and mixed micelles

Received: 18 November 1994
Accepted: 24 February 1995

Dr. M. Hebrant (✉) · A. Bouraine
C. Tondre
Laboratoire d'Etude des Systémes
Organiques et Colloidaux (LESOC)*
Unité associée au CNRS no 406
Université Henri Poincaré – Nancy 1
B.P. 239
54506 Vandoeuvre-lés-Nancy Cedex, France

A. Brembilla · P. Lochon
Laboratoire de Chimie Physique
Macromoléculaire (LCPM)
Unité associeé au CNRS no. 494
ENSIC-INPL – BP 451
1 rue Grandville
54001 Nancy Cedex, France

* Institut Nancéien de Chimie Moléculaire (I.N.C.M.)

Abstract Micellar particles can solubilize lipophilic extractants similarly to the organic phase in classical biphasic extraction. This analogy is used here to investigate the kinetics of complex formation between Ni^{2+} ions and long chain 5-alkoxypicolinic acids (C_n-PIC, with $n = 12, 15, 18$) solubilized in different types of micelles, namely cetyl trimethylammonium bromide (CTAB), hexaethyleneglycol-dodecylether ($C_{12}EO_6$) and CTAB/$C_{12}EO_6$ mixed micelles. In the case of CTAB micelles, the interaction between the carboxylic function of the extractant and the polar head of surfactant molecules was expected to decrease the rate of complex formation so as to make possible kinetic separation of mixtures of metal ions. The observed rate constants for complex formation at pH 4.5 or 7.0 are indeed much smaller in CTAB micelles than in $C_{12}EO_6$ or mixed micelles, but they still remain too high for the previous purpose, although the influence of the surfactant concentration demonstrates, as expected, a much stronger partitioning in the case of CTAB in comparison to $C_{12}EO_6$. On the other hand, it is shown that, once complex formation has occurred the removal of Ni^{2+} ions can be achieved using ultrafiltration. The yield of extraction increases with n, with the mole fraction of $C_{12}EO_6$, and with the ligand to metal ratio.

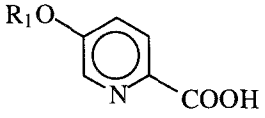
Key words Micellar extraction – complexation kinetics – mixed micelles – ultra- filtration

Introduction

Several recent publications have shown that systems involving hydrophobic ligands solubilized in micelles or in microemulsions [1–4] can be used for practical extraction of metal ions. It has also been demonstrated that it is possible to separate metal ions on the basis of their kinetics of reaction [4–5]. The principle of this kind of separation process is resting on the fact that the rate-limiting step of the reaction of complex formation is the removal of one water molecule from the inner-shell of solvation of the cation. Since the work of Eigen [6], it is indeed well known that the rate of exchange of water molecules around a metal ion depends on the nature of this cation. This means that, when there is a mixture of two cations having different rates of reaction, one of them will undergo complexation before the other. Provided that we can stop the reaction at a given time, it is then possible to trap one cation species whereas the other will remain free, even though both would be complexed in equilibrium conditions. This was shown to be possible using micellar systems [4–5] to slow down the reaction, whereas the separation of the micellar pseudophase solubilizing the complex and the pseudo-aqueous phase containing the free ions was achieved by ultrafiltration.

In order to improve these separation techniques it is thus important that the reaction be as slow as possible.

That is the reason why we considered the C_n-PIC series of complexing agents with which we expected some specific effects, due to the interaction of the carboxylic function with the polar head of cationic surfactant, such as cetyltrimethylammonium bromide (CTAB). This interaction through ion-pair formation, added to the hydrophobic interactions due to the alkyl chain should make metal complex formation more difficult than with neutral or negatively charged surfactants. This could be an interesting means to prevent the diffusion of the complexing agent in the aqueous phase, thus decreasing the rate of reaction with metal ions. Ideally, the characteristic time of the complexation step should be in the order of minutes to hours for such metal separation process to be feasible.



C_n-PIC

$R_1 = C_{12}H_{25}$-, $C_{15}H_{31}$-, $C_{18}H_{37}$-

Besides these kinetic aspects which may be relevant for selective extraction of metal ions, we also investigated the extraction of Ni^{2+} under equilibrium conditions. Our aim was to evaluate more specifically the effectiveness of C_n-PIC compounds to achieve the practical extraction of metal ions using micellar processes.

Experimental part

The synthesis of the long chain 5-alkoxypicolinic acids has been reported elsewhere [7]. Cetyltrimethylammonium bromide (CTAB), purchased from Fluka, was twice recrystallized from methanol/diethylether. Hexaethyleneglycol-*n*-dodecylether ($C_{12}EO_6$) was obtained from Nikko Chemicals (Japan). All other reagents were of analytical grade.

The stopped-flow kinetic experiments were performed at 25 °C with a Durrum D-110 apparatus. The kinetic curves were recorded on a Gould 1602 storage oscilloscope interfaced with a Victor V 286 PC.

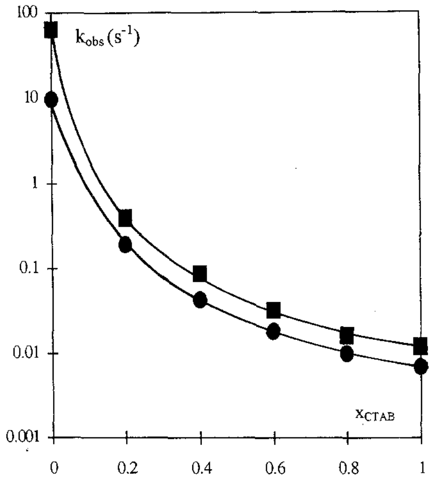
The ultrafiltration experiments were carried out with an Amicon cell (volume of 10 ml) at room temperature. Millipore cellulosic disc membranes were used, with molecular weight cut off 10000 dalton and the applied pressure was 3.5 bar. The metal ion content in the filtrate was analyzed by atomic absorption spectrometry with a Varian A.A. – 1275 apparatus. The amount of metal ion extracted was determined by assuming that the concentration of free species (i.e., all metal species not retained in the micellar pseudophase) was the same in the filtrate and in the retentate. Details of the procedures used can be found in a previous publication [2].

Results and discussion

Figure 1 shows the variation of the observed rate constant k_{obs} for complexation of C_{12}-PIC with Ni^{2+}, with the molar fraction of CTAB in mixtures of CTAB and $C_{12}EO_6$ (nonionic surfactant). The results were collected for two pH's: 4.5 and 7. Complex formation is slower at pH 4.5 than at pH 7, due to the change of the state of protonation of the ligand with the pH: the ligand, in its neutral form, is much less reactive than in its anionic form. This pH effect is quite large even though it is not well demonstrated in the logarithmic scale used in Fig. 1.

On the other hand, a so large difference (about three orders of magnitude) between the observed rate constants in pure micelles of either $C_{12}EO_6$ or CTAB was not observed so far. It should be recalled that in the case of 6-[(alkylamino) methyl] -2-(hydroxymethyl) pyridine extractants, in a positively charged form [8], the apparent rate constants characterizing the complexation of copper ions were found to have quite similar values in CTAB and $C_{12}EO_6$, respectively. The variation of k_{obs} with the micelle composition (Fig. 1) clearly demonstrates the effect of the electric charge of the micelle surface on the rate of complex formation. This is confirmed by the influence of the surfactant concentration reported in Fig. 2 for both surfactants. The absence of variation in case of CTAB indicates a very

Fig. 1 Effect of the mole fraction of CTAB in mixtures of CTAB and $C_{12}EO_6$ on the kinetics of complexation of Ni^{2+} ions with C_{12}-PIC. (●) pH = 4.5 ± 0.5; (■) pH = 7.0 ± 0.5. Overall surfactant concentration 2×10^{-2} M; $[C_{12}\text{-PIC}] = 10^{-4}$ M; $[Ni^{2+}]_0 = 10^{-3}$ M



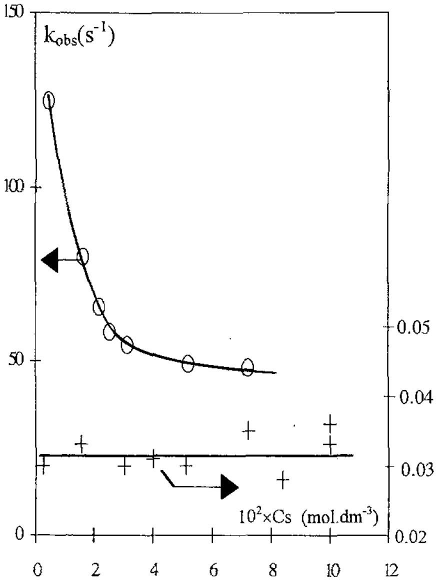


Fig. 2 Effect of the surfactant concentration on the observed rate constants k_{obs} for complexation of Ni^{2+} ions with C_{12}-PIC at pH = 7 ± 0.5: (o) $C_{12}EO_6$, left scale (+) CTAB, right scale $[C_{12}\text{-PIC}] = 10^{-4}$ M; $[Ni^{2+}]_0 = 10^{-3}$ M

strong partitioning of the extractant in favor of the micellar pseudo-phase, where the maximum solubilization exists from the very first surfactant concentration. The decrease of k_{obs} in case of $C_{12}EO_6$ points out a progressive solubilization of the extractant in the micelles, which is an indication that the partition coefficient is not as high as that in CTAB.

Since the overall surfactant concentration was always excessively large compared to their respective CMC's (6.8×10^{-5} M for $C_{12}EO_6$ [9] and 9.2×10^{-4} M for CTAB [10]), we can assume that the average composition of the mixed micelles is close to that of the surfactant mixture except when one component is in excessively weak concentration compared to the other [11], which was not the case in the present experiments. In addition, we do not expect that the rate of complex formation could be affected by some kind of interaction between Ni^{2+} ions and the ethylene oxide (EO) units of the nonionic surfactant. Such interactions between oxygen atoms of EO units and cations are known to occur in organic solvents like methanol [12], but i) they are much weaker for open-chain polyether than for crown ether [13], and ii) they become almost undetectable for linear polyether in aqueous solutions.

The decrease of k_{obs} with the molar fraction of CTAB (Fig. 1) is thus related to the increase of the average number of charges per surface unit of the mixed micelle, i.e., to the electrostatic potential at the surface of the micelle [14]. However, even in pure CTAB, the reaction rates measured here are significantly higher than those obtained in a CTAB/*n*-butanol/C_{11}HQ system (where C_{11}-HQ is an alkylated analogue of hydroxyquinoline which was used in its neutral state) [15], which was previously considered to perform the kinetic separation of Ni^{2+} and Co^{2+}. In the present case, the very large decrease of the observed rate constant, due to the ion-pairing effect, when we go from non-ionic to cationic micelles is thus over-compensated by the increase of the reaction rate in the aqueous phase when an anionic extractant replaces a neutral one (note that the observed reaction rate of the picolinic acid in water was too high to be determined by the stopped flow technique). Because of the preceding observations we have not further attempted to use these complexing agents in view of kinetic separations.

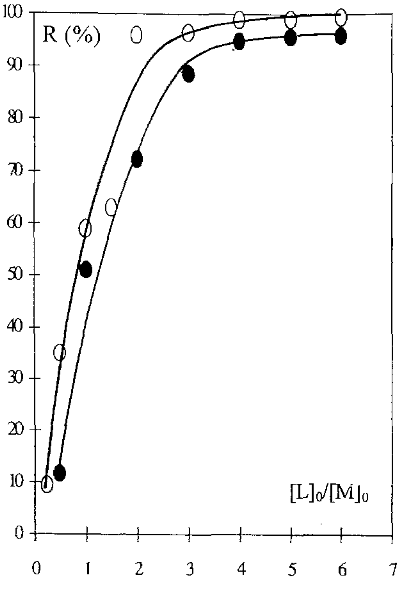
In the second part of this work we have investigated the practical extraction of nickel ions by these C_n-PIC under equilibrium conditions, using an ultrafiltration technique. The yield of metal ion extraction is expressed as

$$R\% = 100 \times \frac{[Ni^{2+}]_0 - [Ni^{2+}]_{fil}}{[Ni^{2+}]_0},$$

where $[Ni^{2+}]_0$ is the initial nickel ion concentration and $[Ni^{2+}]_{fil}$ is the concentration found in the filtrate. The influence of the micelle composition, the hydrophobicity of the extractant (value of n) and the ligand to metal ratio ($[L]_0/[M]_0$) where considered.

Figure 3 shows the effect of the nature of the micelles solubilizing the ligand and complex species. Whatever

Fig. 3 Yield of Ni^{2+} ions extraction versus extractant to metal ratio for C_{12}-PIC. (●) [CTAB] = 2.5×10^{-2} M; (o) mixed micelles (40% CTAB, 60% $C_{12}EO_6$, overall surfactant concentration 2×10^{-2} M). pH = 7.0 ± 0.5; $[Ni^{2+}]_0 = 10^{-4}$ M



pure CTAB micelles or mixed CTAB/$C_{12}EO_6$ micelles are used very high yields (> 95%) are obtained for large $[L]_0/[M]_0$ ratios. It is clear that the yields obtained in mixed micelles containing 60% of $C_{12}EO_6$ are greater than those in pure CTAB micelles. Furthermore, it must be emphasized that, in the case of pure CTAB micelles, the concentration of surfactant was 2.5×10^{-2} M, whereas in the case of mixed micelles the overall concentration of surfactant was only 2×10^{-2} M. Since it has been shown that the partitioning of the complex in the micelles is increasing when the surfactant concentration increases [16], one can conclude that the extraction is strongly favored in the mixed micelles containing $C_{12}EO_6$.

This observation is confirmed for the three different alkyl chain lengths (Fig. 4). The yield significantly improves when the increase of the alkyl chain length induces a stronger partitioning in favor of the micellar pseudophase. This is especially well demonstrated for the lower mole fraction of $C_{12}EO_6$, or in pure CTAB, but this effect tends to decrease for the larger mole fraction. When the alkyl chain length of the ligand is increased for different $[L]_0/[M]_0$ ratios (results given in table 1) the yield increases, particularly for the lowest $[L]_0/[M]_0$ ratios. Above $[L]_0/[M]_0 = 4$ there is no significant effect of the alkyl chain length, all the values being larger than 95% or very close to it.

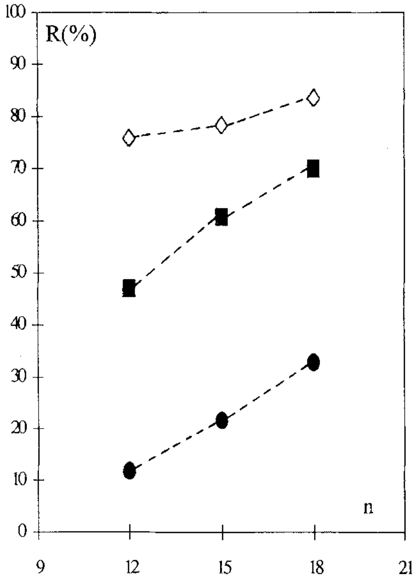


Fig. 4 Yield of Ni^{2+} ions extraction versus the number of carbon of the alkyl chain of C_n-PIC. (●) [CTAB] = 2.5×10^{-2}; (■) 60% CTAB, 40% $C_{12}EO_6$, overall surfactant concentration 2×10^{-2} M; (◇) 20% CTAB, 80% $C_{12}EO_6$, overall surfactant concentration 2×10^{-2} M; pH = 7.0 ± 0.5; [C_n-PIC] = 10^{-4} M; $[Ni^{2+}]_0 = 10^{-4}$ M

Conclusion

In view of retarding the rate of complexation between micelle-solubilized extractants and metal ions, we have attempted to increase the partitioning of the extractant by adding to the normal hydrophobic effect an electrostatic interaction between the complexing site and the polar head of the surfactant. We have shown that the ion-pairing between an anionic extractant and a micellized cationic surfactant considerably affects the rate of complex formation. This is demonstrated by comparison with the kinetics measured in the case of nonionic micelles. Unfortunately, the rate remains larger than with previously studied extractants because of the presence of a negative charge on the extractant. This fact led us to conclude that alkoxypicolinic extractants are not good candidates to perform kinetic separations, in comparison with other types of hydrophobic complexing agents in neutral or positively charged states.

Parallel studies conducted in equilibrium conditions have been carried out to evaluate the actual removal of Ni^{2+} ions using the ultrafiltration technique to separate the micellar pseudophase from the bulk aqueous phase. This process has appeared to be very efficient, attaining high yield of Ni^{2+} extraction provided that the experimental conditions are well chosen.

Table 1 Yield of Ni^{2+} ions extraction in CTAB micelles for different alkyl chain lengths of the extractant. $[M]_0 = 10^{-4}$ M; pH = 7.0 ± 0.5

	$[L]_0/[M]_0$						
C_nPIC	0.5	1	2	3	4	5	6
C_{12}PIC	11.6	50.8	72.2	88.5	94.8	95.7	96.0
C_{15}PIC	21.5	57.0	76.6	86.5	97.3	98.7	99.2
C_{18}PIC	32.65	60.4	77.3	82.7	96.0	96.8	97.0

References

1. Pramauro E, Bianca A, Barni E, Viscardi G, Hinze WL (1992) Colloids Surfaces 63:91
2. Tondre C, Son S-G, Hebrant M, Scrimin P, Tecilla P (1993) Langmuir 9:950
3. Dharmawardana UR, Christian SD, Taylor RW, Scamehorn JF (1992) Langmuir 8:414
4. Ismael M, Tondre C (1993) J Colloid Interface Sci 160:252
5. Ismael M, Tondre C (1992) Langmuir 8:1039
6. Eigen M (1963) Pure Appl Chem 6:97
7. Faivre V, Roizard D, Brembilla A, Lochon P (1991) Bull Soc Chim Fr 128:278
8. Son S-G, Hebrant M, Tecilla P, Scrimin P, Tondre C (1992) J Phys Chem 96:11072
9. from the manufacturer, Nikko Chemicals Co, LTD (Tokyo) technical notice
10. Critical Micelle Concentration of Aqueous Surfactant Systems, Mukerjee P, Mysels KJ, Ed, Nat Stand Ref Data Ser, Nat Bur Stand (US) 1971
11. Clint JH (1975) J Chem Soc Faraday Trans 1 71:1327
12. Burger-Guerrisi C, Tondre C (1987) J Coll Interface Sci 116:100
13. Früh PU, Simon W (1973) "Protides of the Biological Fluids" 20th Colloquium (Peeters H Ed), Pergamon, Elmsford, New York, 1973
14. Hebrant M, Bouraine A, Tondre C, Brembilla A, Lochon P (1994) Langmuir 10:3994
15. Kim HS, Tondre C (1989) Sep Sci Technol 24:7
16. Tondre C, Hebrant M (1992) J Phys Chem 96:11079