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ORIGINAL CONTRIBUTION

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Kinetics of metal ion complex formation in micellar media. A comparison between normal and polymerized micelles

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Abstract Micellar media can be used to investigate the rate of complex formation between hydrophobic extractants and metal ions. Acceleration or retardation effects may be obtained, depending on factors such as the nature of the surfactant, the hydrophilic/lipophilic character and ionization state of the extractant, etc. The present work was aimed at studying the influence of some specific parameters in producing retardation effects, which have potential application for performing separation of metal ions on a kinetic basis. The stopped-flow technique was used to measure the rate of complex formation between Cu^{2+} and complexing agents with varying alkyl chain length. Micelles made of the nonionic surfactants $C_{12}EO_6$, Triton X-100 and Brij 35 were first considered, which did not show any direct correlation between the rate of complex formation and the thickness of the hydrophilic layer constituted by the polar heads of the surfactant molecules.

In a second approach, we have used polymerized micelles obtained from undec-10-enyltrimethyl ammonium bromide, which we assumed to be more rigid than normal micelles. Although the absence of CMC was confirmed, the rates measured in these polymerized micelles were larger than those obtained in micellar solutions of CTAB and DTAB. The results are discussed in relation with the nature of the hydrophobic domains in the different situations.

Key words Complexation kinetics – micelles – polymerized micelles – micellar extraction

Introduction

Separation processes based on organized systems (such as micelles [1–8], microemulsions [9–10], vesicles [11], etc.) are currently the subject of intensive research, especially due to their potential applications in the field of environmental chemistry. For instance, the elimination of metal ions [1–8], dyes [12] or organic pollutants [13] from aqueous solutions can be achieved by coupling micellar extraction with ultrafiltration. These processes take advantage of the microheterogeneous nature of micellar solutions which can behave as pseudo-biphasic systems. Whereas in classical aqueous/organic biphasic extraction large amounts of organic solvents are usually required, it becomes thinkable to design new extraction processes operating in almost totally aqueous media.

Another potential development of such processes concerns the separation of metal ions on the basis of their kinetics of complexation. This has been shown to be possible for mixtures of Ni^{2+} and Co^{2+}, provided that the rate of complex formation can be made slow enough

[4, 14]. This requirement was fulfilled when highly hydrophobic complexing agents were solubilized in the hydrophobic core of nonionic, or even better, cationic micelles. In the experimental conditions considered, the complexation of the Co^{2+} ions was complete in a few minutes, whereas a much longer time was needed for the Ni^{2+} ions [9]. If the micellar solution is treated by ultrafiltration in a very short time after the reaction has started, the removal of Co^{2+} ions can be achieved whereas the Ni^{2+} ions remain in solution and can be collected in the permeate [4, 14].

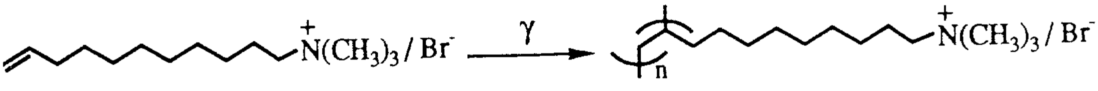
Extending this method to other mixtures of metal ions would be interesting, but unfortunately, for many metal ions, the rate of complex formation is faster than that of Co^{2+} [15]. For this reason we thought it useful to examine how we could further slow down the rate of complex formation. Different factors affecting this rate have been determined in previous studies: the hydrophilic/lipophilic balance of the complexing agent, the pH which governs its ionization state, the nature of the surfactant and especially the electric charge and chemical structure of the polar head [7, 16–18]. Electrostatic repulsions between the metal ions and the surface of the micelles play an important part in the case of cationic surfactants, but steric effects such as those found with polyethoxylated nonionic surfactants may also be considered.

The present work was aimed at examining two different ways of retarding metal ion complexation. One possibility is to increase the steric hindrances to make more difficult the approach of the complexing agent solubilized in the hydrophobic core by the metal ion. This can be done by increasing the number of ethyleneoxide units in the hydrophilic chain of nonionic surfactants in order to increase the thickness of the hydrophilic layer separating the interior of the micelle from its surface. Another idea is to decrease the mobility of the complexing agent in the micelle by the use of polymerized micelles. The dynamic nature of normal micelles is indeed well established [19] and it is also well known that the same kind of dynamics also applies to solubilized probes [20]. For instance, the exit rates of a bulky and hydrophobic molecule, such as pyrene, from sodium dodecyl sulfate (SDS) or cetyltrimethylammonium bromide (CTAB) micelles were found to be respectively 1.7×10^3 and 4.1×10^3 s^{-1}, whereas for benzene the corresponding values are 4.4×10^6 and 7.5×10^5 s^{-1} [20]. Exchange processes are known to be much slower in vesicular systems which are more rigid than micelles [21]. By freezing the micelle dynamics we expected that a solubilized probe, like here the complexing agent, will be more strongly associated with the micelles, as demonstrated by the comparison of solubility measurements in normal micelles and polymerized micelles respectively [22]. As mentioned before, we expected that polymerization will amplify the micellar properties.

Experimental part

Chemicals

The surfactants used had the following origins: the nonionic surfactants Triton X-100 (polyethylene glycol tert-octylphenyl ether) and Brij-35 (polyethylene glycol dodecylether) were obtained from Fluka, whereas hexaethylene glycol *n*-dodecylether ($C_{12}EO_6$) was purchased from Nikko Chemicals (Japan). The two first cited have a statistical distribution of ethyleneoxide units, whose average numbers are 10 and 23 for Triton X-100 and Brij-35 respectively. In $C_{12}EO_6$ the hydrophilic chain is monodisperse and it contains 6 ethylene oxide units. They were used as received. The cationic surfactants, cetyltrimethylammonium bromide (CTAB) and dodecyltrimethyl ammonium bromide (DTAB) were from Fluka. They were twice recrystallized either from methanol/diethyl ether or from ethyl acetate/anhydrous ethanol (95: 5, v/v). The synthesis of undec-10-enyltrimethyl ammonium bromide has been described previously [22, 23]. The polymerized surfactant (I) was obtained from γ-irradiation. Its average molecular weight obtained from light scattering measurements (see below in Techniques) was found to be 8000 g·mol^{-1} (average of two independent determinations). For some experiments, aqueous solutions of the polymer were extensively dialyzed against distilled water in order to remove low molecular weight components or impurities. Cellulose membranes (Visking) with average pore diameters of 24 Å were used for this purpose. The concentration of the dialyzed solution was determined both from dry content measurements and from the bromide concentration obtained from conductimetric titration with $AgNO_3$.



I

The complexing agents 6-[(alkylamino) methyl]-2-(hydroxymethyl) pyridines($C_nNHMePyr$ with n varying from 4 to 16) were kindly supplied by Dr. P. Scrimin and P. Tecilla (University of Padua). Their synthesis was reported before [24] and these compounds proved to be very useful to study the mechanisms of copper complexation and extraction in micellar media [5, 18, 25]. Copper chloride ($CuCl_2, 2H_2O$) was from Prolabo (France). The pH of the solutions was adjusted with drops of diluted HCl. It was measured with a combined glass electrode. The pH values given in the figures refer to the equilibrium pH, measured after mixing of the solutions.

Techniques

The rate of complex formation was measured with a stopped-flow apparatus with optical detection. The experiments were run at 25 °C with a Biologic SFM-3 stopped flow (Grenoble, France), totally computer-controlled (Tandon PC ASL/486-110) with Biokine Software. The apparatus is equipped with three mixing syringes. Two of them were used for the automatic variation of the copper chloride concentration before the resulting solution was mixed with the extractant solution contained in the third syringe. The absorbance change due to complex formation was detected at 300 nm. The kinetic curves were pseudo first-order and the observed rate constants k_{obs} were obtained from least-squares fitting with an exponential function (the accuracy on the values of k_{obs} was $\pm 10\%$ and the reported values are averages over six experiments or more). The concentration of micelles or polymer was identical in all the solutions before and after mixing and the metal ion concentration ($10^{-3} - 10^{-2}$ M) was in large excess over the extractant concentration (10^{-4} M).

The fluorescence measurements were carried out on a Shimadzu RF 450 spectrofluorimeter. Pyrene was introduced in the solutions as described by Chu and Thomas [26] so as to obtain a final pyrene concentration of 2×10^{-6} M. The excitation wavelength was 240 nm.

The light scattering experiments were performed with a modified Sofica apparatus using a laser beam at 6320 Å(He-Ne). The polymer was solubilized in water with added sodium chloride in order to screen the electrostatic interactions. Two independent determinations were carried out with salt concentrations respectively 2×10^{-2} and 0.1 M. The polymer concentration was varied in the range 1.7×10^{-3} to 7×10^{-3} $g \cdot cm^{-3}$. The refractive index increment with concentration (dn/dc) was 0.155.

Results and discussion

The first set of experiments was concerned with the influence of steric hindrances in the case of nonionic surfactants. We recall that the rate of complexation of a metal ion with a lipophilic extractant solubilized in the hydrophobic core of a micelle can be slowed down by electrostatic repulsions (case of cationic micelles) but also by steric hindrances due to the existence of the hydrophilic layer (case of nonionic surfactants) [18]. Our purpose here is to see how a change in the thickness of this hydrophilic layer (determined by the number of ethylene oxide (EO) units of the surfactant molecule) will affect the rate of complexation. For these experiments we considered a complexing agent with a long hydrophobic chain (C_{16}NHMePyr), for which a strong partitioning in favor of the micelles has been demonstrated [18, 27]. The rate of complex formation with copper was investigated at pH 3.5 in 0.02 M surfactant solutions of Triton X-100 (10 EO units) and Brij-35 (23 EO units). The values measured for the observed rate constants versus the analytical copper concentration are compared in Fig. 1 with those previously obtained in similar conditions with $C_{12}EO_6$ [18]. A direct comparison is strictly valid between $C_{12}EO_6$ and Brij 35 which have similar chemical structures whereas the hydrophobic moiety of Triton X-100 is not the same. The surfactant concentration used was in all cases largely above the CMC. A linear behaviour was expected for the variation of k_{obs} versus the copper concentration. Although this was indeed observed for Triton X-100 and $C_{12}EO_6$, a strong curvature was nevertheless found in the case of Brij-35. For this reason we have also measured the variation of the observed rate constant when the added ionic strength was kept constant by adding mixtures of $CuCl_2$ and $CaCl_2$ instead of $CuCl_2$ alone. Considering that the stability constants of complexes involving Ca^{2+} are usually much smaller than those for Cu^{2+}, we assume that

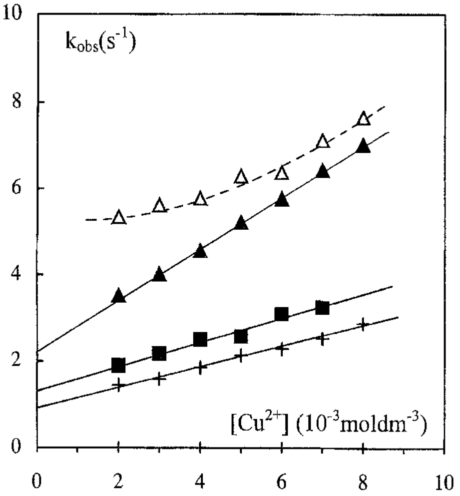


Fig. 1 Observed rate constant k_{obs} for the reactions of C_{16}NHMePyr with Cu^{2+} versus the analytical concentration of Cu^{2+} in different media: (+) Triton × 100, (■) $C_{12}EO_6$, (▲) Brij with $[CaCl_2] + [CuCl_2] = 8 \times 10^{-3}$ M, (△) Brij. $[\text{Surfactant}] = 2 \times 10^{-2}$ M, pH = 3.5 ± 0.2, $T = 25$ °C, $[C_{16}\text{NHMePyr}] = 10^{-4}$ M

there is no competition between the two ions. This procedure allows a fairly good linearization of the previous plot, as shown in Fig. 1.

For the interpretation of these data, we will assume that the rate of complex formation is not affected by some kind of interaction between the metal ions and the EO units of the nonionic surfactant. Such interactions are known to occur in organic solvents like methanol [28], but they are much weaker for open-chain polyether than for crown ether [29], and they become almost undetectable for linear polyether in aqueous solutions. It can thus be deduced from the preceding results that there is no direct correlation between the rate of complex formation and the thickness of the hydrophilic layer of the nonionic surfactants. Whereas we expected a decrease of the reaction rate with Brij-35, it turned out that the kinetics are faster than those with $C_{12}EO_6$ whether the added ionic strength is kept constant or not. In fact the micelles of Brij-35 are characterized by extremely long hydrophilic chains as compared to a small hydrophobic core. For this reason i) the site of solubilization of the complexing agent may not be the same as in $C_{12}EO_6$ micelles; ii) the internal compactness of the hydrophobic core may be weaker. The result of these two effects is thus opposite to the expected effect of steric hindrance. In addition the penetration of water molecules (which are expected to hydrate the ethylene oxide units) in these long hydrophilic hairs, may be affected by the change of salinity, since it is well known that there exists a competition between the hydration of ionic species and the hydration of the ethylene oxide units (the phenomenon of cloud point is an illustration of this effect) [30]. This may furnish an explanation to the curvature in the plot of k_{obs} versus $CuCl_2$ concentration when the added ionic strength was not fixed. On the other hand, for Triton X-100 the kinetics is slower than for $C_{12}EO_6$, but the presence of a phenolic group in the surfactant molecule may be responsible for specific interactions with the complexing agent.

In a second step we have examined the case of cationic surfactants, and more specifically the influence of surfactant polymerization. For different practical reasons the polymerized surfactant we had at our disposal was issued from a monomer having an undecenyl chain. We needed to study, as a reference, normal micelles with a structure as close as possible to that of the polymerized micelles. We have chosen to use DTAB, which was commercially available, although the alkyl chain has 12 carbon atoms instead of 11. Since most of the previous experiments were carried out in CTAB micelles, we have compared the rates of complex formation in CTAB and DTAB respectively, in order to determine the part played by the length of the alkyl chain of the surfactant itself. We have used for these experiments two complexing agents with alkyl chain lengths comprising 10 and 12 carbon atoms respectively (C_{10}NHMePyr and C_{12}NHMePyr). In Fig. 2, the change of k_{obs} for copper complexation versus DTAB concentration has been plotted for both ligands. Before the CMC (0.015 M) [31] the rate measured in pure water remains almost unaffected by the presence of the surfactant. Above the CMC a decrease of k_{obs} due to the partitioning of the complexing agents between the aqueous phase and the micellar pseudo-phase is observed. This decrease is compared in Figs. 3 and 4 (corresponding to C_{12}NHMePyr and C_{10}NHMePyr respectively) with the data previously obtained with CTAB [18]. For both ligands, we observe a steeper initial decrease of k_{obs} in the case of DTAB as compared to CTAB, but the values measured at high surfactant concentration are larger for DTAB than for CTAB. At first sight it is surprising that the results at low surfactant concentration indicate a stronger partitioning of both ligands in DTAB than in CTAB. The result is to be put in relation with the effect of ionic strength on the variation of k_{obs} vs CTAB concentration in the case of C_{12}NHMePyr (see Fig. 5 in ref. [25]). The addition of 0.1 M NaBr resulted in a transformation of the curve, which is comparable, at least qualitatively, to the transformation observed in Fig. 3 from CTAB to DTAB. In that case we assumed that the shielding of the electrostatic interactions due to salt addition was responsible for a stronger partitioning of the complexing agent (in a protonated form) in favor of the micelles. The CTAB micelles then behave almost exactly as the nonionic micelles did [18, 25]. In the present case we can thus conclude that the presence of a much higher concentration of monomeric

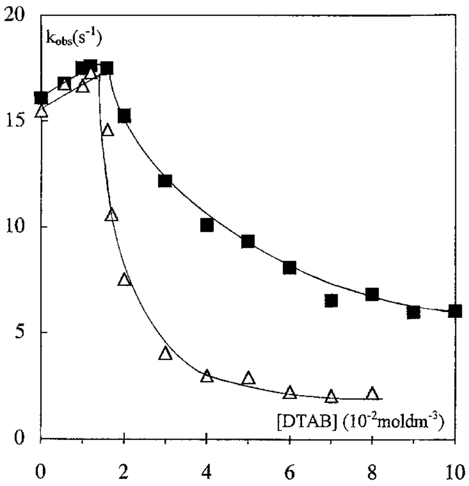


Fig. 2 k_{obs} for the reaction of C_{10}NHMePyr (■) and C_{12}NHMePyr (△) with Cu^{2+} ions versus the concentration of DTAB. [C_nNHMePyr] = 10^{-4} M, [Cu^{2+}] = 5×10^{-3} M, pH = 3.5 ± 0.2, $T = 25\,°C$

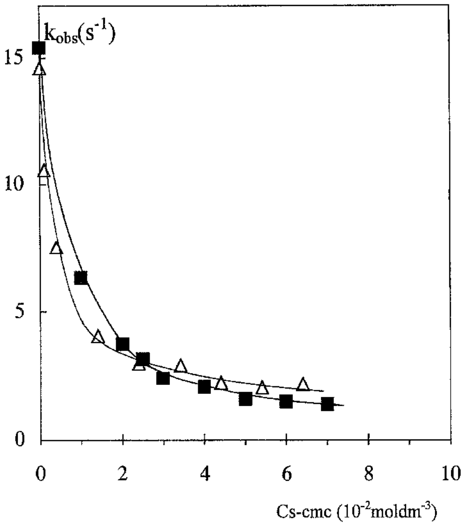


Fig. 3 k_{obs} for the reaction of C_{12}NHMePyr with Cu^{2+} ions versus the concentration of micellized surfactant Cs-CMC. (△) DTAB, (■) CTAB. $[C_{12}NHMePyr] = 10^{-4}$ M, $[Cu^{2+}] = 5 \times 10^{-3}$ M, pH = 3.5 ± 0.2, $T = 25\,°C$

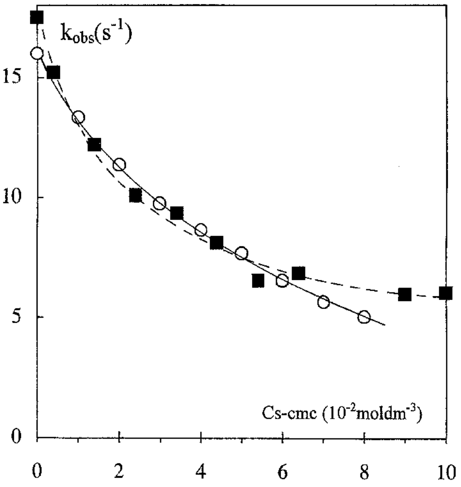


Fig. 4 k_{obs} for the reaction of C_{10}NHMePyr with Cu^{2+} ions versus the concentration of micellized surfactant Cs-CMC. (■) DTAB, (○) CTAB. $[C_{10}NHMePyr] = 10^{-4}$ M, $[Cu^{2+}] = 5 \times 10^{-3}$ M, pH = 3.5 ± 0.2, $T = 25\,°C$

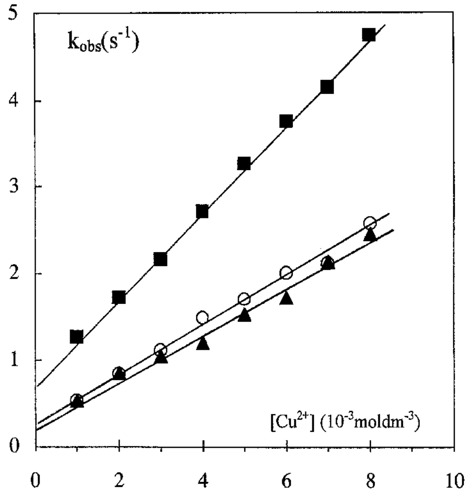


Fig. 5 k_{obs} versus the analytical concentration of Cu^{2+} for the C_nNHMePyr extractant in DTAB micelles (▲) $n = 16$, (○) $n = 14$, (■) $n = 12$. pH = 3.5 ± 0.2, $[C_nNHMePyr] = 10^{-4}$ M, [DTAB] = 4×10^{-2} M, $T = 25\,°C$

Table 1 Values of the apparent rate constants k_f^{app} ($M^{-1}\,s^{-1}$) for complex formation between Cu^{2+} and the extractants C_nNHMe Pyr ($n = 12$, 14 and 16) in CTAB and DTAB

	C_{12}	C_{14}	C_{16}
CTAB 0.025 M [18]	240	136	128
DTAB 0.04 M	506	293	268

surfactant in the case of DTAB comparatively to CTAB, is in some way equivalent to the presence of an added salt. Beside that point the quantitative effects obtained are not so much different in CTAB and DTAB, so far as the ligands in C_{10} or C_{12} are concerned (note that the alkyl chain lengths of the ligands are smaller or equal to the surfactants ones).

We have also determined the apparent rate constants for complex formation in DTAB for C_nNHMePyr with $n = 12$, 14 and 16. The results are represented in Fig. 5 and the values of the kinetic constants are compared in Table 1 with those previously obtained in CTAB [18]. The surfactant concentration was 0.025 M in CTAB and 0.04 M in DTAB in order to take into account the difference in the CMC's. As previously observed in CTAB, the decrease of the rate is much more significant between $n = 12$ and $n = 14$ than between $n = 14$ and $n = 16$, where an asymptotic behavior occurs (see Fig. 7). On the other hand, in the conditions used, the k_f^{app} values measured in DTAB are systematically about twice as large as those in CTAB. The latter surfactant thus appears to be the more efficient to retard the rate of complex formation. Nevertheless the comparison between the two surfactants was made at the same concentration of micellized surfactant and not at the same concentration of micelles, since the aggregation numbers are different.

From the preceding results we know that shortening the alkyl chain of the surfactant results in a reduction of the retarding effect. This point was important to clarify before considering the polymerized surfactant, since it implies that we will have to keep in mind the fact that the

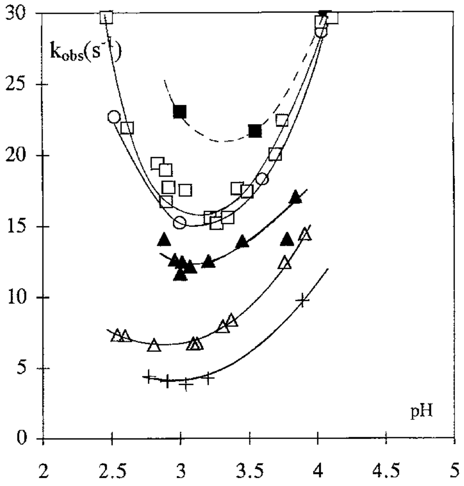


Fig. 6 Variation of k_{obs} with pH for the reaction of Cu^{2+} with $C_nNHMePyr$ in different media. (□) $n = 4$ in water; (■) $n = 10$ in non-dialyzed polymer solutions, (+) $n = 16$, (△) $n = 14$, (▲) $n = 12$, (○) $n = 10$ in dialyzed polymer solutions, $[polymer] = 2 \times 10^{-2}$ M, $[Cu^{2+}] = 5 \times 10^{-3}$ M, $T = 25$ °C

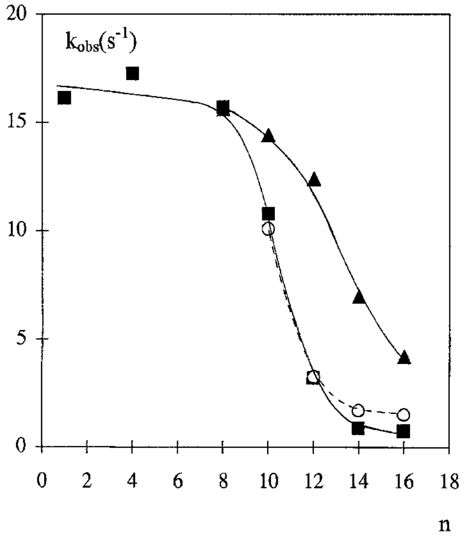


Fig. 7 Variation of k_{obs} for copper complexation versus n in different reaction media. (■) $[CTAB] = 2.5 \times 10^{-2}$ M, (○) $[DTAB] = 4 \times 10^{-2}$ M; (▲) $[polymer] = 2 \times 10^{-2}$ M. pH = 3.5 ± 0.2, $[C_n NHMePyr] = 10^{-4}$ M, $[Cu^{2+}] = 5 \times 10^{-3}$ M

shortening of the alkyl chain length may compensate the effect of rigidification expected from polymerization. As we know from previous works that the observed rate constant goes through a minimum when the pH is varied [32], we have checked the effect of pH in different situations, which are reported in Fig. 6.

In all the experiments the concentration of polymerized surfactant was 2×10^{-2} M and the concentrations of $CuCl_2$ and ligands $C_nNHMePyr$ were respectively 5×10^{-3} M and 1×10^{-4} M. The result previously obtained in pure water [32] for the ligand with $n = 4$ is also shown for the sake of comparison. To our surprise the values of k_{obs} measured in the polymerized surfactant for ligand $C_{10}NHMePyr$ were larger than those for $C_4NHMePyr$ in water (we recall that the rate constants for complex formation measured in water were only weakly affected by the length of the alkyl chain of the ligand). Therefore, there is no retarding effect associated with the use of polymerized micelles in that case, but rather a slight increase of k_{obs} comparatively to pure water. For this reason we have attempted to dialyze the polymer solution in order to remove all the low molecular weight contaminants, using membranes with molecular weight cut off of about 6000 Dalton. Then we investigated the effect of the ligand chain length in solutions of the dialyzed polymer. This time the k_{obs} values for $C_{10}NHMePyr$ were found slightly smaller than those of $C_4NHMePyr$ in water. The increase of the alkyl chain length showed a definitive decrease of the rate. Note that the minimum of the curves is shifted towards lower pH values when n increases, going from about 3.4 to 3.0. The existence of a minimum in such curves was theoretically accounted for in previous publications in which it was shown that it is the result of a mechanism involving both the neutral ligand and its protonated form [32]. It is likely that in the presence of the polymerized micelles the shift of the pH at minimum is related to the change of partitioning of the ligand species, combined with the effect of local pH at the surface of the particle.

In Fig. 7, the results obtained in this work in DTAB and in the polymerized surfactant are compared with those previously obtained in CTAB. The data were taken at pH 3.5(± 0.2) except for the polymerized surfactant for which the values plotted were read on the curves of Fig. 6 at pH 3.2, value which is the closest possible to all the minima obtained. As mentioned above, we can see that the decrease of the rate associated with an increase of the number of carbon atoms of the ligand is slightly more important with CTAB than with DTAB, both appearing more efficient than the polymerized surfactant. We can thus conclude that the polymer considered here does not meet the requirements for performing kinetic separation of metal ions. The reason for this may be twofold : i) considering that the skeleton of the polymer contains itself two carbons of the original monomeric surfactant, we are left with hydrophobic chains comprising only nine carbon atoms which may not be enough ; ii) we can wonder about the existence of true hydrophobic domains in these particles. This can be probed by measuring the absorbance of a dye like pinacyanol chloride [33] or the fluorescence of pyrene [34]. The absorbance of pinacyanol chloride is known to change abruptly when micelles form in solution. As demonstrated in Fig. 8 the variations of absorbance as a function of the concentration of either the polymerized surfactant or the monomer, show a totally different behavior, indicating that the dye is in an hydrophobic environment at concentrations around 2×10^{-2} M for the polymer and only at around 10^{-1} M for the monomer. A confirmation of these observations was obtained by comparing the pyrene fluorescence change measured in the solutions of the polymer and DTAB respectively (note that the CMC of the unsaturated monomer is expected to be much higher than that of DTAB). It is well known that the main features of the fluorescence spectrum of pyrene depend on the properties of the medium where it is solubilized [34]. The ratio of the first and third vibronic peaks I_1/I_3 can be used to qualify the polarity of the solubilizing site. The results of such determinations are reported in Fig. 9 for DTAB and for the polymerized surfactant. The change of polarity of the solubilization site of pyrene at the CMC of DTAB is well demonstrated : the ratio I_1/I_3 goes from 1.65 (solubilization in water) to 1.25 (solubilization in the hydrophobic domains of the micelles). In the case of the polymerized surfactant, we observe a continuous decrease of I_1/I_3, whose value becomes comparable to that of DTAB only when the concentration becomes close to the CMC of DTAB. The absence of CMC in the polymerized surfactant is confirmed, but the hydrophobic domains, which undoubtedly exist at the concentration used (2×10^{-2} M) appear to be the result of a progressive aggregation process. For this reason the actual concentration of hydrophobic domains may not be as high as in DTAB, since we used for the latter a concentration 4×10^{-2} M in order to compensate for the high value of the CMC. The fact that the change of I_1/I_3 versus concentration is much less abrupt with the polymerized surfactant than with the normal micelles is in agreement with previously reported results concerning the comparison between 3-hexadecyl-1-methylimidazole bromide (HMIB) and its polymerized analogue $PC_{16}VI$ [35]. The present result can also be put in relation with the work of Nika et al. [36] concerning the aggregational character of two methacrylate functionalized micelle- forming quaternary ammonium salts leading respectively to head and tail polymers. The tail polymer, which was comparable to the polymerized surfactant considered here, was found to have a degree of polymerization (DP) of only 10 from vapor pressure osmometry, whereas an aggregation number of 46 was obtained from static fluorescence quenching measurements. This discrepancy points out how difficult it is to distinguish between single polymerized entities and aggregates resulting from the association of the previous entities. A new approach, using well defined telomers, has been recently proposed to characterize the aggregation properties of similar particles from viscosity measurements [37]. The reported DP were in the range 33–42. The molecular weight obtained in our case (see Experimental Section) for the polymerized micelles indicates a DP (or aggregation number) of the order of 30. This value is consistent with that reported for micelles of surfactants having alkyl chains with nine carbon atoms (see Table IV in ref. [19]). Such a small size of the hydrophobic domains could explain the small effect obtained in our complexation studies when the polymerized surfactant replaced CTAB or DTAB micelles.

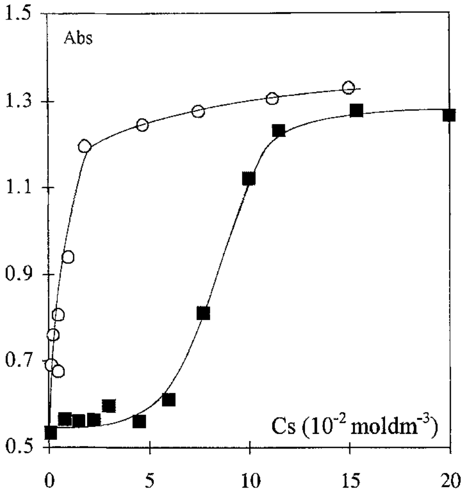


Fig. 8 Absorbance of pinacyanol chloride versus surfactant concentration. (■) monomer, (○) polymer; $\lambda = 610$ nm, $T = 25\,^{\circ}$C, [dye] $= 1.05 \times 10^{-5}$ M

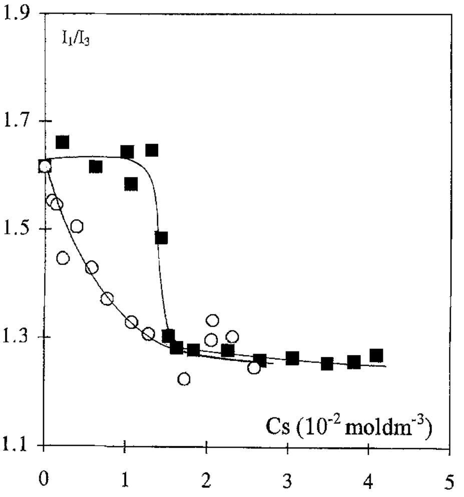


Fig. 9 Intensity ratio I_1/I_3 of pyrene fluorescence plotted versus surfactant concentration (■) DTAB, (○) polymer; $\lambda_{ex} = 240$ nm, [pyrene] $= 2 \times 10^{-6}$ M, $T = 25\,^{\circ}$C

In conclusion, although we have brought new information concerning the rate of metal ion complexation in micellar systems, further experiments will be needed to find the conditions permitting to produce more significant retardation effects. The steric effect introduced by the thick layer of ethylene oxide units, when complex formation takes place in nonionic micelles, does not appear to play the part expected since there is no clear correlation between the thickness of this layer and the rate measured. On the other hand the information gained by using the polymerized surfactant (*I*) suggests that the hydrophobic domains were probably too small and their rigidity not high enough. In this respect, polymerized micelles with longer alkyl chains may prove more efficient in order to further reduce the mobility of solubilized hydrophobic extractants.

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References

1. Scamehorn JF, Christian SD, Ellington RT in Surfactant-Based Separation Processes; Surfactant Science Series Vol. 33; Scamehorn JF, Harwell JH Eds (1989) Marcel Dekker, New York
2. Dharmawardana UR, Christian SD, Taylor RW, Scamehorn JF (1992) Langmuir 8:414
3. Pramauro E, Prevot AB, Pelizzetti E, Marchelli R, Dossena A, Biancardi A (1992) Anal Chim Acta 264:303
4. Ismael M, Tondre C (1992) Langmuir 8: 1039
5. Tondre C, Son SG, Hebrant M, Scrimin P, Tecilla P (1993) Langmuir 9:950
6. Reiller P, Lemordant D, Moulin C, Beaucaire C (1994) J Colloid Interface Sci 163:81
7. Hebrant M, Bouraine A, Tondre C, Brembilla A, Lochon P (1994) Langmuir 10:3994
8. Scamehorn JF, Christian SD, El-Sayed DA, Uchiyama H, Younis SS (1994) Sep Sci Technol 29:809
9. Kim HS, Tondre C (1989) Sep Sci Technol 24:485
10. Derouiche A, Tondre C (1990) Colloids and Surfaces 48:243
11. Walsh AJ, Monbouquette HG (1993) J Membrane Sci 84:107
12. Pramauro E, Prevot AB, Savarino P, Viscardi G, De La Guardia M, Cardells EP (1993) Analyst 118:23
13. Christian SD, Scamehorn JF in Surfactant-Based Separation Processes (see ref 1)
14. Ismael M, Tondre C (1993) J Colloid Interface Sci 160:252
15. Eigen M (1963) Pure Appl Chem 6:97
16. Tondre C, Boumezioud M (1989) J Phys Chem 93:846
17. Boumezioud M, Kim HS, Tondre C (1989) Colloids and Surfaces 41:255
18. Son SG, Hebrant M, Tecilla P, Scrimin P, Tondre C (1992) J Phys Chem 96:11072
19. Aniansson EAG, Wall SN, Almgren M, Hoffmann H, Kielmann I, Ulbricht W, Zana R, Lang J, Tondre C (1976) J Phys Chem 80:905
20. Almgren M, Grieser F, Thomas JK (1979) J Am Chem Soc 101:279
21. Almgren M (1980) Chem Phys Lett 71:539
22. Boyer B, Lamaty G, Leydet A, Roque JP, Sama P (1992) New J Chem 16:883
23. Boyer B, Lamaty G, Leydet A, Roque JP, Sama P (1992) New J Chem 16:887
24. Scrimin P, Tecilla P, Tonellato U (1991) J Org Chem 56:161
25. Tondre C, Hebrant M (1992) J Phys Chem 96:11079
26. Chu DY, Thomas JK (1986) J Am Chem Soc 108:6270
27. Hebrant M, Tondre C (1992) J Colloid Interface Sci 154:378
28. Burger-Guerrisi C, Tondre C (1987) J Coll Interface Sci 116:100
29. Früh PU, Simon W (1973) "Protides of the Biological Fluids" 20th Colloquium (Peeters H Ed), Pergamon, Elmsford, New York, p 505
30. Schott H, Han SK (1975) J Pharm Sci 64:658
31. Critical Micelle Concentrations of Aqueous Surfactant Systems (1971) Mukerjee P, Mysels KJ Ed., Nat Stand Ref Data Ser, Nat Bur Stand (US)
32. Hebrant M, Son SG, Tondre C, Tecilla P, Scrimin P (1992) J Chem Soc Faraday Trans 88:209
33. Menger FM, Portnoy CE (1967) J Am Chem Soc 89:4698
34. Binana-Limbele W, Zana R (1987) Macromolecules 20:1331
35. Damas C, Brembilla A, Baros F, Viriot ML, Lochon P (1994) Eur Polym J 30:1215
36. Nika G, Paleos CM, Dais P, Xenakis A, Malliaris A (1992) Progr Colloid Polym Sci 89:122
37. Boutevin B, Robin JJ, Boyer B, Roque JP, Senhaji O, Eur Polym J (in press)