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Kinetic evidence for the solubilization of pyridine-2-azo-*p*-dimethylaniline in alkanediyl-α,ω-bis(dimethylcetylammonium nitrate) surfactants. Role of the spacer chain length

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The incorporation of the bidentate ligand pyridine-2-azo-*p*-dimethylaniline (PADA) into micellar aggregates of the dimeric cationic surfactants propanediyl-, hexanediyl- and dodecanediyl-α,ω-bis(dimethylcetylammonium nitrate) (16-3-16,2NO_3^-, 16-6-16,2NO_3^- and 16-12-16,2NO_3^-, respectively) has been studied at 25 °C by examining the kinetics of the complexation reaction of the Ni(II) ion with this ligand. For comparison, cetyltrimethylammonium nitrate (CTAN), which can be considered as the "monomeric" surfactant of 16-3-16,2NO_3^-, has also been used. The kinetic data have shown that, for 16-3-16,2NO_3^- and CTAN, at a surfactant concentration below the critical micelle concentration (cmc) the rate of the complex formation reaction does not significantly depend on the surfactant concentration, while it slightly decreases in the presence of the other two gemini surfactants. Beyond this critical value, in all cases examined, the rate constant is conspicuously inhibited by the presence of surfactant. The results below the cmc have been explained in the light of conductometric measurements, which have evidenced that both 16-6-16,2NO_3^- and 16-12-16,2NO_3^- form premicellar aggregates while 16-3-16,2NO_3^- and CTAN do not. The kinetic data above the cmc conform to a reaction mechanism that implies partitioning of the ligand only between the aqueous and the micellar pseudo-phases. The quantitative analysis of the kinetic data allows us to estimate the binding of PADA to the cationic micellar aggregates used. Solubilization of PADA in the micelles markedly depends on the nature of the surfactant used and, in particular, decreases on either increasing the spacer chain length or changing the surfactant type, namely conventional or gemini. These trends have been ascribed to the change in the shape of the micellar aggregates and, consequently, the hydrophobic character of the micelles, which can be modulated either by insertion of the spacer in the micellar interior or by using a conventional surfactant. The incremental free energy of transfer of a methylene group in the spacer chain from the aqueous to the micellar pseudo-phase has also been determined. The present data evidence that binding of PADA to micellar aggregates is primarily governed by hydrophobic interactions and the solubilization capability of gemini aggregates is superior to that of conventional micelles.

Introduction

Among the different applications[1] of aqueous micelle-forming surfactant solutions, such as in the soap industry, for mineral flotation, medical and pharmaceutical applications and remediation of aquifer basins contaminated by apolar liquids, one of the most exploited is their capability to enhance the solubility of hydrophobic compounds that are otherwise only slightly soluble in water. Several physical methods[2] have been used to study the solubilization process of substrates of widely different characteristics in both ionic and non-ionic micellar aggregates and to determine the predominant binding sites of the organic compounds in such aggregates. The study of the solubilization in aqueous micellar solutions[3] of sparingly soluble substances dates back to the beginning of the last century.

Only recently a new class of surfactants,[4] the alkanediyl-α,ω-bis(dimethylalkylammonium bromides) of general chemical formula $(CH_3)_2C_mH_{2m+1}N^+(CH_2)_sN^+C_mH_{2m+1}(CH_3)_2,2Br^-$, namely gemini surfactants, have attracted researchers' attention. Usually, they are represented by the abbreviation *m*-*s*-*m*,2Br^-, where *m* and *s* are the alkyl chain and the hydrophobic spacer lengths, respectively. These surfactants differ in their chemical nature from the above mentioned surfactants having a single chain and a polar head group, so-called "conventional" ones. Gemini surfactants consist of two hydrophobic alkyl chains and two hydrophilic head groups covalently connected by a hydrocarbon spacer, which may be rigid or flexible. These surfactants form in aqueous solution different types of aggregated systems[5] whose structure and properties significantly depend on the nature of the alkyl chain, head group and spacer. These parameters can be independently varied and, as a consequence, both the shape and size of the aggregated systems can be easily modulated.

While quite a large amount of work dealing with the determination of the physico-chemical properties[4c,4i,6] of surfactant aggregates of gemini surfactants has been done, solubilization[4f,4h] in gemini micelles has not been examined in detail. In addition, scarce attention[7] has so far been paid to the effects of these organized assemblies on the rate and mechanism of chemical reactions. To our knowledge no kinetic studies on the influence of gemini surfactants on the kinetics of complexation

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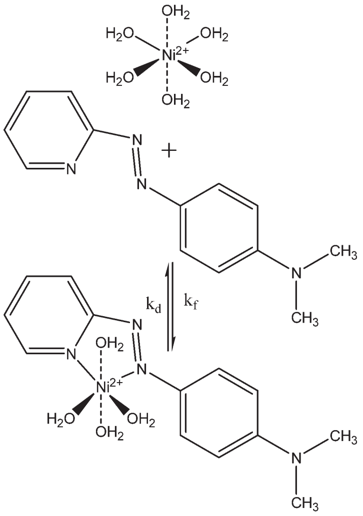
reactions exist. A systematic kinetic study in the presence of aggregated systems offers the twofold advantage of providing valuable information on both reactivity and reaction mechanisms in these media, as well as on the solubilization of reagents, and, in some cases, location of the solute in the micellar structure.

In pursuit of these goals we have studied the effects of the dimeric cationic surfactants propanediyl-, hexanediyl- and dodecanediyl-α,ω-bis(dimethylcetylammonium nitrate) referred to as 16-3-16,2NO_3^-, 16-6-16,2NO_3^- and 16-12-16, 2NO_3^-, respectively, on the kinetic of the complexation reaction (1) of the nickel(II) ion and the ligand pyridine-2-azo-*p*-dimethylaniline (PADA):



(1)

For comparison, the effects of the cationic surfactant cetyltrimethylammonium nitrate (CTAN), which can be considered the "monomeric" analog of 16-3-16,2NO_3^-, have also been examined. In reaction (1), k_f and k_d represent the formation and dissociation rate constants, respectively. The kinetic experiments have been carried out at 25 °C over a wide range of surfactant concentrations. This reaction has been chosen because the mechanism in water,[8] in other solvent media[9] and in the presence of conventional micelle-forming surfactant[10] systems is well-established.

In addition to the rate experiments we have performed conductivity measurements to estimate both the critical micelle concentration (cmc) of the surfactants and the micelle ionization degree (α), which allow us to gain very helpful information for the interpretation of the kinetic data.

The findings of this work allow for a broad insight into the effects of both gemini and conventional surfactants on the rates of reaction and, as a consequence, on the solubilization ability of the two different classes of micelle-forming surfactants.

Experimental

Materials and general methods

The cationic surfactant cetyltrimethylammonium nitrate (CTAN) has been obtained[11] by slowly adding in the dark an $AgNO_3$ methanol–water (1:1 ratio) solution to an aqueous solution of cetyltrimethylammonium bromide (Merck). The obtained suspension has been stored in the dark, for one week at low temperature, and, then, to remove the AgBr, has been filtered with a Millipore™ system with a pore diameter of 1 micron. The solvents from the final solution have been partially removed by means of a rotating evaporator and then completely eliminated by using a vacuum oven. The surfactant, obtained as a white powder, has been recrystallized two times from methanol. Elemental analysis of the final product revealed the absence of impurity as AgBr. The dimeric cationic surfactants propanediyl-, hexanediyl- and dodecanediyl-α,ω-bis(dimethylcetylammonium nitrate) have been synthesized accordingly to literature methods[12] from the dimethylhexadecylamine and the appropriate dibromoalkane. The ionic exchange from bromide to nitrate anion was attempted using the same procedure reported above for CTAN but in these cases the elemental analysis revealed the presence of AgBr impurities. Thus, the ionic exchange has been carried out by using an ionic hydroxide exchanger (Merck) and titrating the final solution with HNO_3. This second method proved to be better than the first one. In fact, no impurities were present as the elemental analysis showed.[13]

Pyridine-2-azo-*p*-dimethylaniline [$C_5H_5N–N_2–C_6H_4–N(CH_3)_2$, PADA] was used as received from Sigma. Stock solution containing Ni(II) ion was prepared from $Ni(NO_3)_2·6H_2O$ (Carlo Erba) and its concentration was estimated by complexometric titration with EDTA. Stock solutions of all chemicals used in the present work were prepared by weight before use. Deionized water from reverse osmosis (Elga, model Option 3), having a resistivity higher than 1 MΩ cm, was used to prepare all solutions. Solubilization of 16-3-16,2NO_3^- in pure water required heating, while the other two surfactants could be readily dissolved in pure water. In all cases, once the surfactant was solubilized the final solutions were optically transparent. The 16-3-16,2NO_3^- aqueous solutions were stable for 1 day while those of 16-6-16,2NO_3^- and 16-12-16,2NO_3^- were stable for several weeks. However, for all measurements carried out in this work we have used freshly prepared solutions. In addition, it was not possible to perform measurements with 16-3-16, 2NO_3^- at concentrations higher than 1×10^{-3} mol dm^{-3} because the solutions were viscous and this caused practical difficulties in both their preparation and for the kinetic measurements.

Kinetic measurements

A HI-TECH SF-61 stopped-flow spectrophotometer has been used to carry out the kinetic measurements. The surfactants were added to both solutions of PADA and Ni(II) before their mixing in the stopped-flow apparatus, which was equipped with thermostatted compartments at 25.0 ± 0.1 °C and interfaced to a computer for both data collection and analysis.

In order to verify the stability of the reactants and the products of reaction in the presence of the surfactants used in this work, UV-vis spectra of the solutions as a function of both the surfactant concentration and time have been monitored. It has been found that, in all cases examined, the spectra do not show any significant changes with respect to those obtained in aqueous solutions. The rates of complex formation were followed at a wavelength of 550 nm.

To avoid shape transitions of the micellar aggregates induced by salts the kinetic measurements in the presence of surfactants were performed without keeping the ionic strength constant, such as by adding supporting electrolyte ($NaNO_3$). Preliminary kinetic measurements were carried out in aqueous solution in the presence of increasing amounts of $NaNO_3$ (1×10^{-3}–0.1 mol dm^{-3}). In this salt concentration range the rate constants do not appreciably depend on the concentration of added salt. This result is reliable because an uncharged reacting species is involved in the chemical process.

All reactions were studied under pseudo-first-order conditions with the nickel ion concentration (in the range 5×10^{-5} to 1×10^{-3} mol dm^{-3}) greater than the concentration of the PADA (5×10^{-6} mol dm^{-3}). The observed pseudo-first-order rate constants, k_{obs}, were reproducible to within ±5%. Under the experimental conditions used in the present work k_{obs} is related[8–10] to the formation (k_f) and dissociation (k_d) rate constants in reaction (1) by eqn. (2):

$$k_{obs} = k_f[\mathrm{Ni(II)}] + k_d \qquad (2)$$

This equation enables both k_f and k_d to be evaluated by plotting k_{obs} as a function of the stoichiometric nickel(II) concentration and, hence, the equilibrium constant K_{eq} is obtained from the ratio k_f/k_d. In all cases examined, the plots derived from the experimental data were good straight lines. These trends are not shown for the sake of space.

Conductivity measurements

The critical micelle concentration of the surfactants and the micelle ionization degree were determined in the absence and presence of Ni(II) and PADA, under the same experimental conditions used for the kinetic runs, by means of a digital Amel 160 conductimeter (cell constant 0.998 cm^{-1}). The critical micelle concentrations of the surfactants used were obtained from the plots of the specific conductivity (κ) as a function of the surfactant concentration ([surf]). The cmc values were taken from the intersection of the two straight lines drawn before and after the inflection point in the κ *vs.* [surf] plot, while α was calculated as the ratio of the slopes of the conductivity lines above and below the cmc.

The measurements were performed in a temperature-controlled double-walled glass cylinder with circulation of water connected to a thermostat at 25.0 ± 0.1 °C. For the conductivity runs the aqueous surfactant solutions at the desired concentration were obtained by adding appropriate aliquots of a stock solution to 15 ml of pure water. Additions were made by a burette with an accuracy of 1 μL. The final solution were stirred for 5 min to allow the system to equilibrate and then the conductivity was measured. The conductivity was measured to within 0.01 μS for conductivity values lower than 20 μS and to within 0.1 μS for higher values. As a consequence of the experimental method used for increasing the surfactant concentration the conductivity measurements are not sufficiently accurate to be analyzed in a quantitative manner.[14] However, the conductivity data show qualitative differences on varying the surfactant nature and this allows us to draw significant conclusions regarding their behaviour in aqueous solution, which were very helpful for the interpretation of the kinetic data.

Results and discussion

Conductivity data

The complete course of the specific conductivity (κ) for the three gemini surfactants examined, as a function of the surfactant concentration, is illustrated in Figs. 1 to 3. In addition, in the same figures the variation of the molar conductivity $\Lambda = (\kappa - \kappa_0)/[\mathrm{surf}]$ with $[\mathrm{surf}]^{0.5}$ is also shown. For comparative purpose, the results for the surfactant CTAN are shown in Fig. 4.

Perusal of these figures evidences different regions of behaviour. At low surfactant concentrations ([surf] < cmc) the κ value sharply increases on increasing surfactant concentration and, then, after the inflection point, a further increase in the surfactant concentration leads to an increase in the κ values but with a lower slope with respect to that observed at low surfactant concentration. These trends are indicative of micelle formation. In the plots of Λ as a function of $[\mathrm{surf}]^{0.5}$ striking differences in the behaviour of the surfactants used can be seen. In particular, for 16-6-16,$2NO_3^-$ and 16-12-16,$2NO_3^-$, the Λ values increase on increasing $[\mathrm{surf}]^{0.5}$ and reach a maximum, this maximum being more pronounced for 16-6-16,$2NO_3^-$, at a concentration value very close to that corresponding to the inflection point in the plots of κ *vs.* [surf]. It is now well-established[14b,15] that the appearance of a maximum in the plot of Λ *vs.* $[\mathrm{surf}]^{0.5}$ indicates that premicellar association of the surfactant in aqueous solution takes place. For CTAN and 16-3-16,$2NO_3^-$, the absence of a maximum in the plot of Λ on increasing $[\mathrm{surf}]^{0.5}$ demonstrates that premicellar association does not occur for these surfactants. Premicellar aggregates of anionic and cationic gemini surfactants have been evidenced by Menger *et al.*[4a,4e] and similar trends to those shown in the present work have also been obtained by Zana[15b] for a wide number of dimeric cationic surfactants.

The cmc and α values obtained from the conductivity measurements are collected in Table 1. It has also been found that both the cmc and α values are not significantly affected by the presence of the $NiPADA^{2+}$ complex (data not shown).

We can observe that α monotonically increases as the length of the spacer increases whereas the cmc value first increases with increasing spacer chain length (*s*) and then decreases with a further increase in the *s* value. Similar trends[4c,5c] were

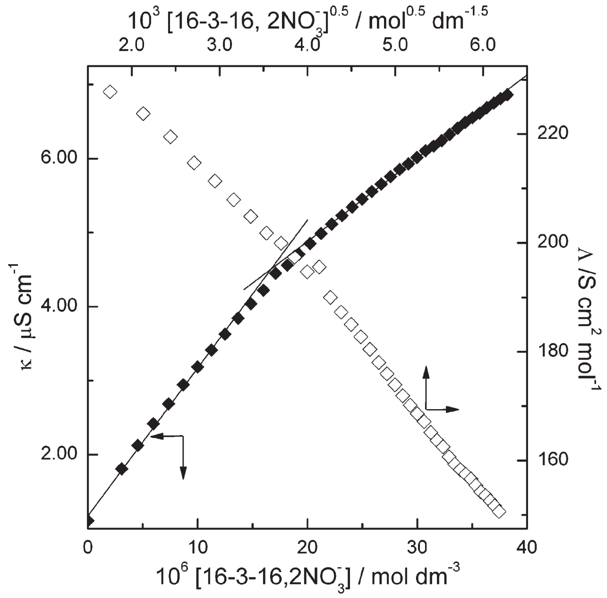


Fig. 1 Plot of the specific conductivity κ as a function of 16-3-16, $2NO_3^-$ concentration and of the molar conductivity Λ *vs.* [16-3-16, $2NO_3^-]^{0.5}$ at $T = 25.0$ °C.

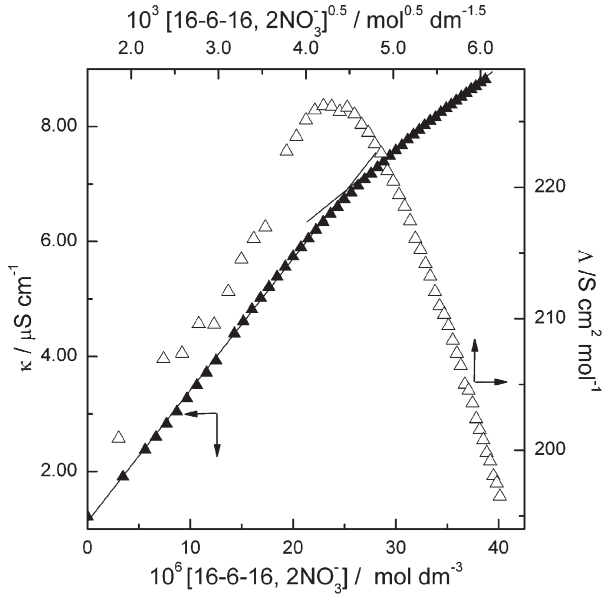


Fig. 2 Plot of the specific conductivity κ as a function of 16-6-16, $2NO_3^-$ concentration and of the molar conductivity Λ *vs.* [16-6-16, $2NO_3^-]^{0.5}$ at $T = 25.0$ °C.

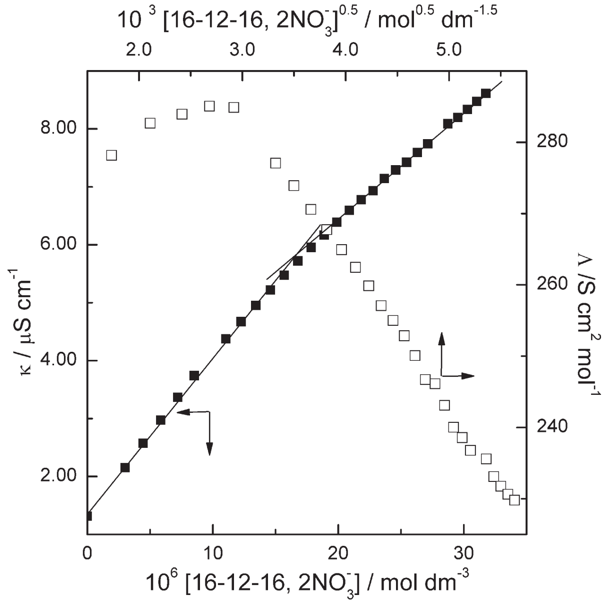


Fig. 3 Plot of the specific conductivity κ as a function of 16-12-16, $2NO_3^-$ concentration and of the molar conductivity Λ *vs.* [16-12-16, $2NO_3^-$]$^{0.5}$ at $T = 25.0\,^{\circ}C$.

obtained previously for the same dicationic surfactant with bromide as counter ion. Comparison among the cmc and α values obtained in this work and those reported in the literature reveals a slight difference, probably due to the experimental conditions used (lower temperature) and not to the diverse counter ions (nitrate instead of bromide).

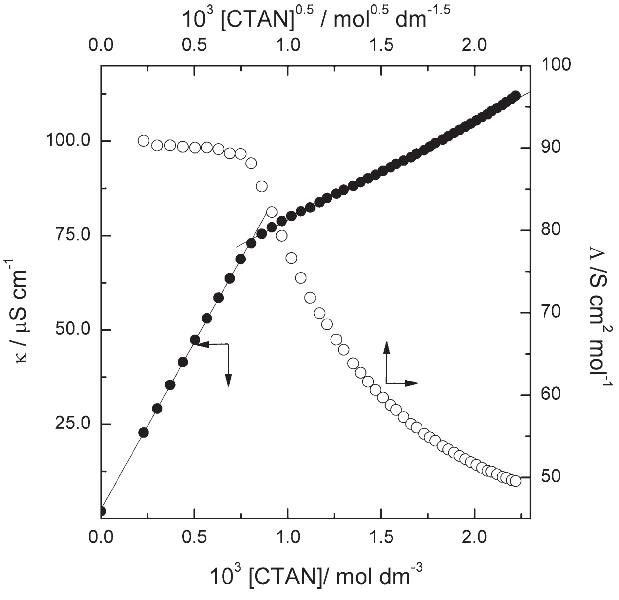


Fig. 4 Plot of the specific conductivity κ as a function of CTAN concentration and of the molar conductivity Λ vs. [CTAN]$^{0.5}$ at $T = 25.0\,^{\circ}C$.

Table 1 Critical micelle concentration (cmc) and dissociation degree (α) for the CTAN and 16-*s*-16,$2NO_3^-$ micelles in aqueous solution ($T = 25.0\,^{\circ}C$)

Surfactant	10^4 cmc/mol dm^{-3}	α
CTAN	8.1	0.29
16-3-16,$2NO_3^-$	0.18	0.54
16-6-16,$2NO_3^-$	0.25	0.61
16-12-16,$2NO_3^-$	0.16	0.68

The observed cmc and α dependence on the spacer chain length have been previously[4c,5c] attributed to conformational changes of the polymethylene spacer chain within the dimeric surfactant ion and gradual penetration of a significant part of the polymethylene segment into the micellar interior. Consequently, this insertion causes a progressive change in the shape of the micellar aggregates and implies that micelles formed by surfactants with long and flexible spacers have a less hydrophobic character with respect to those formed by surfactants with short spacers. Small angle neutron scattering studies and microviscosity measurements have evidenced[5c,5f] that 16-3-16,$2Br^-$ micelles are disk-like in shape while gemini surfactants having a spacer chain length greater than 4 form prolate ellipsoidal aggregates. We reasonably believe that the shape of aggregates formed by the 16-*s*-16,$2NO_3^-$ gemini surfactants do not differ significantly from those formed by the 16-*s*-16,$2Br^-$ series.

Kinetic data

The kinetics of reaction (1) have been extensively studied and it has been found that eqn. (2) is valid[8–10a] in both aqueous media and in the presence of surfactant. Under the experimental conditions used in the present work, the estimated rate and equilibrium constants in the absence of surfactant are: $k_{f,w} = (12.1 \pm 0.1) \times 10^2$ dm^3 mol^{-1} s^{-1}, $k_{d,w} = (7.1 \pm 0.4) \times 10^{-2}$ s^{-1} and $K_{eq} = (1.7 \pm 0.1) \times 10^4$ dm^3 mol^{-1}. If allowance is made for the different experimental conditions, these values are in good agreement with those previously[10a] reported.

The kinetics of complex formation in reaction (1) has been studied in the presence of 16-*s*-16,$2NO_3^-$ over a wide surfactant concentration range. For comparison, a kinetic study in the presence of CTAN has also been carried out. For all surfactants used, it has been found that eqn. (2) is valid. In the presence of surfactant we use the notation $k_{f,app}$ and $k_{d,app}$ for the apparent (overall) formation and dissociation rate constants, respectively, to distinguish them from the corresponding rate constants in water denoted by the w subscript. The apparent rate and equilibrium constants obtained at varying concentrations of CTAN and 16-*s*-16,$2NO_3^-$ are collected in Tables 2 to 5.

These data show that the complex formation rate appreciably depends on both the surfactant nature and surfactant concentration, while the dissociation rate constant is almost unaffected by the presence of surfactant. As a consequence, the equilibrium constant varies with the surfactant concentration in the same way as $k_{f,app}$ does.

The observed absence of significant effects of both types of cationic surfactants, that is conventional and gemini, on the dissociation rate of the NiPADA^{2+} complex can be easily

Table 2 Rate and equilibrium constants for reaction (1) in the presence of CTAN ($T = 25.0\,^{\circ}C$)

10^3 [CTAN]/ mol dm^{-3}	10^{-2} $k_{f,app}$/ dm^3 mol^{-1} s^{-1}	10^2 $k_{d,app}$/ s^{-1}	10^{-3} K_{app}/ dm^3 mol^{-1}
0.01	12.0	9.0	13.3
0.10	12.1	7.2	16.8
0.30	11.7	7.6	15.3
0.70	8.2	7.9	10.3
0.85	6.8	9.2	7.4
1.0	6.0	8.1	7.4
2.0	3.07	7.3	4.2
3.5	1.80	7.1	2.55
5.0	1.28	7.0	1.83
6.5	1.01	7.0	1.45
8.5	0.80	7.2	1.12
10	0.74	6.5	1.14

Table 3 Rate and equilibrium constants for reaction (1) in the presence of 16-3-16,2NO$_3^-$ ($T = 25.0\,°C$)

10^3 [16-3-16,2NO$_3^-$]/ mol dm^{-3}	10^{-2} $k_{f,app}$/ dm^3 mol^{-1} s^{-1}	10^2 $k_{d,app}$/ s^{-1}	10^{-3} K_{app}/ dm^3 mol^{-1}
0.001	11.3	8.1	13.9
0.01	10.1	11	9.2
0.05	10.1	12	8.5
0.10	9.2	8.9	10.4
0.30	6.9	7.3	9.5
0.50	5.3	6.3	8.4
0.70	3.8	7.9	4.9
0.85	3.4	7.3	4.7
1.0	2.99	7.4	4.1

understood by considering that both the complex and the micelle are positively charged, as a consequence electrostatic repulsions confine the complex in the bulk aqueous region. Moreover, it has been previously[10a] found that, despite the strong hydrophobicity of the coordinated ligand (PADA), no interactions between the NiPADA^{2+} complex and non-ionic Triton X-100 [$C_8H_{17}C_6H_4(OC_2H_4)_{9,10}OH$] micelles occur. Thus, the hydrophilic interactions predominate over the hydrophobic ones.

From the kinetic data obtained in the presence of CTAN and 16-3-16,2NO$_3^-$, it is seen that the $k_{f,app}$ values remain substantially unchanged with increasing surfactant concentration until a given surfactant concentration is reached. This surfactant concentration value is very close to the cmc value conductometrically estimated. Beyond this critical surfactant concentration value the formation rate constant sharply decreases, tending to attain a limiting value at high surfactant concentrations. A different behaviour of $k_{f,app}$ as a function of surfactant concentration can be noticed when the other two gemini surfactants, 16-6-16,2NO$_3^-$ and 16-12-16,2NO$_3^-$, are used. In fact, the apparent formation rate constants always decrease on increasing surfactant concentration, even though at low surfactant concentration the inhibitory effect is less marked. The trends in rate at surfactant concentrations below the cmc can be explained in the light of the conductometric results (see above). In fact, we have found that 16-3-16, 2NO$_3^-$ surfactant and its corresponding monomer (CTAN) do not form premicellar aggregates while the other two gemini surfactants do. Thus, the slight decrease of $k_{f,app}$ on increasing surfactant concentration is consistent with the presence of premicellar aggregates that interact with the reacting species, that is the hydrophobic PADA and the hydrophilic Ni(II) ions.

Table 4 Rate and equilibrium constants for reaction (1) in the presence of 16-6-16,2NO$_3^-$ ($T = 25.0\,°C$)

10^3 [16-6-16,2NO$_3^-$]/ mol dm^{-3}	10^{-2} $k_{f,app}$/ dm^3 mol^{-1} s^{-1}	10^2 $k_{d,app}$/ s^{-1}	10^{-3} K_{app}/ dm^3 mol^{-1}
0.01	10.7	8.2	13
0.05	9.3	8.9	10
0.10	8.7	9.5	9.1
0.30	6.8	6.9	9.8
0.50	5.1	7.7	6.7
0.70	4.6	6.5	7.1
0.85	3.9	8.0	4.9
1.0	3.7	7.2	5.1
3.0	1.42	6.8	2.07
5.0	0.93	7.4	1.25
7.0	0.58	8.4	0.69
8.5	0.50	7.6	0.67
10	0.42	7.4	0.57

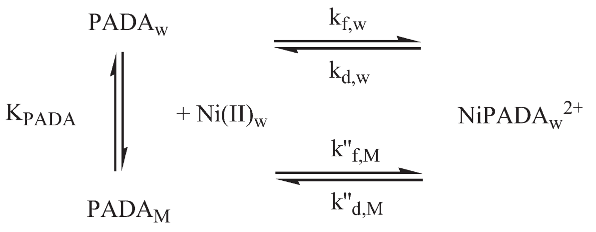
Table 5 Rate and equilibrium constants for reaction (1) in the presence of 16-12-16,2NO$_3^-$ ($T = 25.0\,°C$)

10^3 [16-12-16,2NO$_3^-$]/ mol dm^{-3}	10^{-2} $k_{f,app}$/ dm^3 mol^{-1} s^{-1}	10^2 $k_{d,app}$/ s^{-1}	10^{-3} K_{app}/ dm^3 mol^{-1}
0.002	9.0	1.0	8.7
0.01	8.7	7.8	11
0.02	8.3	9.4	8.8
0.05	8.2	1.3	11
0.10	8.2	7.1	11
0.15	7.6	7.6	10
0.50	6.6	6.5	10
1.0	4.9	8.5	5.7
3.0	2.41	7.6	3.2
5.0	1.82	7.5	2.42
7.0	1.37	7.2	1.89
10	0.86	7.5	1.15

We can also see from Tables 2 to 5 that the inhibitory effect depends on both the type of surfactant and the spacer chain length. In particular, it can be calculated that the 16-3-16, 2NO$_3^-$ gemini surfactant causes a two times rate retardation with respect to CTAN over the whole surfactant concentration range examined. In addition, at a given gemini surfactant concentration, the rate constant $k_{f,app}$ decreases following the order 16-3-16,2NO$_3^-$ > 16-6-16,2NO$_3^-$ > 16-12-16,2NO$_3^-$. For instance, addition of 1×10^{-3} mol dm^{-3} of surfactant causes the formation rate constant to decrease with respect to k_w by a factor *ca.* 4, 3 and 2.5 for 16-3-16,2NO$_3^-$, 16-6-16, 2NO$_3^-$ and 16-12-16,2NO$_3^-$, respectively. These inhibitory effect trends can be ascribed to the change[5c] in the shape of the micellar aggregates. In fact, by modulating the hydrophobic micellar character, either by using the conventional CTAN surfactant that forms spherical micelles or by increasing the spacer chain length in the gemini dicationic surfactant, the rate of complex formation is inhibited to an extent that reflects the capability of the aggregated systems to solubilize the hydrophobic PADA in their interior. Thus, the higher the solubilization of PADA the less favoured is complex formation.

The observed rate-retarding effects of the surfactant are consistent with the reaction scheme (Scheme 1) proposed previously[10a] for the same reaction in the presence of other aggregated systems. This reaction scheme implies that only the hydrophobic ligand PADA is partitioned between water (w) and the micellar pseudo-phase (M), with a "binding" constant K_{PADA} ($[PADA]_M/[PADA]_w \cdot C$, where $C = [surf] - cmc$ is the micellized surfactant concentration), while the hydrophilic Ni(II) is confined in the aqueous pseudo-phase. Thus, two reaction paths may contribute to the overall rate of complex formation, namely the reactions of the Ni(II) ion in the bulk water with the PADA solubilized in both the aqueous and micellar pseudo-phases. The rate constants $k_{f,w}$ and $k''_{f,M}$ of these pathways are related to the apparent (overall) formation rate constant and to the micellized surfactant concentration by eqn. (3):

$$k_{f,app} = \frac{k_{f,w} + k''_{f,M} K_{PADA} C}{1 + K_{PADA} C} \qquad (3)$$



Scheme 1

The particular variation of $k_{f,app}$ as a function of C depends upon the relative importance of each term in eqn. (3) and can be easily weighed up by considering the plot of $1/k_{f,app}$ *vs.* C. In particular, such a plot will show a linear trend if the term $k_{f,w} >> k''_{f,M}K_{PADA}C$, while a curved plot, tending to reach a plateau at high C values, will be obtained when the term $k''_{f,M}K_{PADA}C$ is not negligibly small compared with $k_{f,w}$. Non-linear least squares analysis of the kinetic data has shown that, for all surfactants used, the term $k''_{f,M}K_{PADA}C$ can be neglected with respect to $k_{f,w}$. Thus, we can rearrange eqn. (3) and obtain:

$$\frac{1}{k_{f,app}} = \frac{1}{k_{f,w}} + \frac{K_{PADA}}{k_{f,w}}C \qquad (4)$$

We can see from Fig. 5 that the plots of $1/k_{f,app}$ *versus* C are linear. This behaviour indicates that the second-order rate constant $k''_{f,M}$ is markedly smaller than that ($k_{f,w}$) of the complexation path occurring in water, consistent with the difficulty of approach of the Ni(II) cation to the positively charged micellar surface. Similar inhibiting effects have also been previously[2d,2e,10,16] obtained for some chemical reactions involving one of the reactant species solubilized in the micellar pseudo-phase and the other one in the aqueous pseudo-phase.

The plots in Fig. 5 allow us to evaluate $k_{f,w}$ from the intercept ($1/k_{f,w}$) and the binding constants (K_{PADA}) from the slopes ($K_{PADA}/k_{f,w}$). The $k_{f,w}$ value evaluated from the intercept is in fair agreement with that obtained by independent kinetic measurements. The estimated K_{PADA} values are reported in Table 6.

The data show that the solubilization of the PADA in the micellar pseudo-phase markedly depends on the type of surfactant used. In particular, it decreases in the order 16-12-16,2NO_3^- < 16-6-16,2NO_3^- < 16-3-16,2NO_3^- and CTAN < 16-3-16,2NO_3^-. The decreased solubilizing capacity of the cationic micelles towards PADA, in line with the microviscosity results[5c], reflects the less hydrophobic character of the aggregated system achieved on either increasing the spacer chain length or changing the surfactant type, either conventional or gemini. It has also been previously[4f] found that within the gemini 12-*s*-12,2Br^- series, the capacity to solubilize toluene decreases with increasing spacer chain length. In addition, the ability of gemini aggregates to solubilize organic compounds is higher than that of conventional micelles formed by surfactants having the same alkyl chain length.

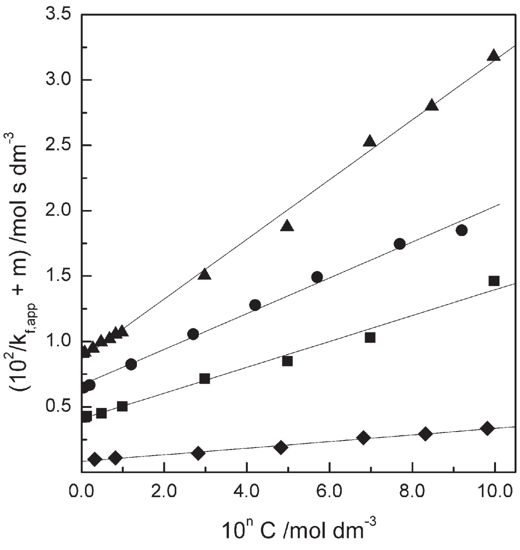


Fig. 5 Plot of $1/k_{f,app}$ *vs.* C for reaction (1) in the presence of: (◆) 16-3-16,2NO_3^- ($m = 0$, $n = 4$), (▲) 16-6-16,2NO_3^- ($m = 0.8$, $n = 3$), (■) 16-12-16,2NO_3^- ($m = 0.3$, $n = 3$) and (●) CTAN ($m = 0.5$, $n = 3$). The solid lines represent the least-squares fits. The parameter m is added to the ordinate axis to avoiding overlapping of lines.

Table 6 Binding constants of the ligand PADA in the presence of CTAN and 16-*s*-16,2NO_3^- micelle-forming surfactants ($T = 25.0$ °C)

Surfactant	10^3 K_{PADA}/dm^3 mol^{-1}
CTAN	1.7 ± 0.1
16-3-16,2NO_3^-	3.1 ± 0.2
16-6-16,2NO_3^-	2.8 ± 0.1
16-12-16,2NO_3^-	1.2 ± 0.2

The available K_{PADA} data as a function of the spacer chain length allow us to calculate the standard transfer free energy $\Delta\mu°(CH_2)$ of a methylene group in the spacer chain from water to micelles. As it is known,[17] the binding constant K_{PADA} is related to $\Delta\mu°$ by the expression $\Delta\mu° = -RT\ln(55.5\cdot K_{PADA})$, where $55.5\cdot K_{PADA}$ indicates the binding constant in the mole fraction scale. The plot of $\Delta\mu°$ as a function of the number of methylene groups in the spacer chain (Fig. 6) is linear with a positive slope.

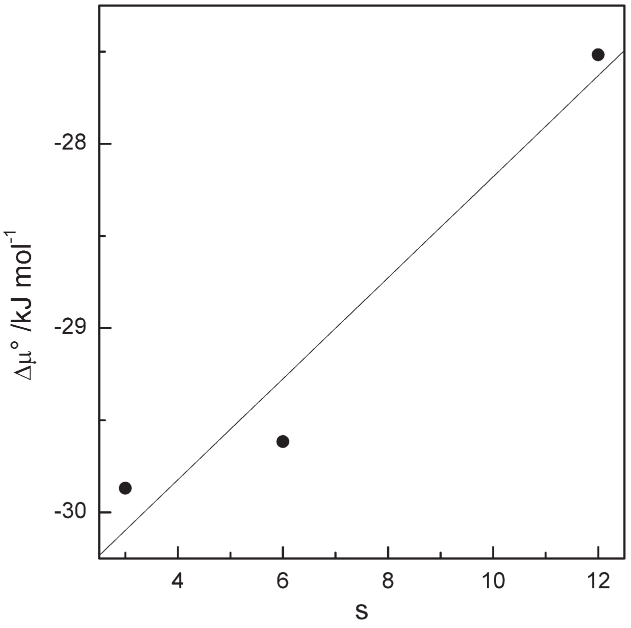


Fig. 6 Plot of $\Delta\mu°$ as a function of the number of carbon atoms (s) in the spacer chain.

Previous[2b,2d] kinetic determinations of the distribution constant of substituted ferrocenes as a function of the number of carbon atoms (n_s) in the alkyl chain of some alkyltrimethylammonium nitrate and alkylpoly(oxiethyleneglycol) monoethers have shown that the plots of $\Delta\mu°$ *vs.* n_s are linear with negative slopes. The opposite sign of the slope highlights that, even though a CH_2 group is added to both kind of surfactants, the effects brought about the methylene group depends on whether it is added to the surfactant alkyl chain or to the spacer chain. In particular, addition of a CH_2 group in the surfactant chain leads to micelles having a more hydrophobic character while in the spacer chain of the gemini surfactant it favours a smaller and less hydrophobic aggregated system.

Conclusions

The effects of both conventional and gemini cationic micelle-forming surfactants on the rate of the complexation reaction of Ni(II) ion with the bidentate ligand PADA have been studied over a wide surfactant concentration range. Some of the observations from this work are the following. (i) The presence of surfactant influences only the complex formation rate to an extent that depends on both the surfactant nature and concentration. (ii) Binding of PADA to both types of cationic micellar aggregates can be estimated by a quantitative analysis of the kinetic data. (iii) By modulating the shape of the micellar aggregates and, as a consequence their hydrophobic character, solubilization of PADA in the micelles significantly changes. (iv) The solubilization capability of gemini aggregated systems is superior to that of conventional micelles.

The present work shows that a systematic kinetic study is a powerful tool for obtaining information on the solubilization capabilities of microstructured systems.

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