

Physicochemical Properties of Mixed Anionic–non-ionic Micelles: Effects on Chemical Reactivity

Luis Freire,^a Emilia Iglesias,^{*a} Carlos Bravo,^b J. Ramón Leis^b and M. Elena Peña^b

^a Departamento de Química Fundamental e Industrial, Facultad de Ciencias, Universidad de La Coruña, 15071-La Coruña, Spain

^b Departamento de Química Física, Facultad de Química, Universidad de Santiago, 15076-Santiago de Compostela, Spain

Addition of the non-ionic surfactant C₁₆E₂₀ (C₁₆H₃₃ [OCH₂CH₂]₂₀-OH) to an aqueous acid solution of alkyl nitrites decreases its rate of acid hydrolysis. Kinetic data are analysed by using the pseudophase model, the partitioning of the alkyl nitrites between water and C₁₆E₂₀ micelles being the main reason for the observed inhibition. The kinetic results provide for a quantitative estimate of the association constants.

The observed rate constant of aqueous acid hydrolysis of alkyl nitrites increases in the presence of sodium dodecyl sulfate (SDS) micelles: first-order rate constants increase with increasing [SDS], go through maxima, and decrease at still higher concentrations of SDS. Addition of C₁₆E₂₀ to an aqueous acid solution of SDS strongly decreases the maximum for the observed rate constant, until at high [C₁₆E₂₀]:[SDS] ratio the observed rate constant decreases monotonically as the total surfactant concentration increases. Kinetic data are analysed by using the simple pseudophase ion-exchange model under the assumption that formation of mixed micelles in the binary mixed surfactant system (C₁₆E₂₀ and SDS) would occur. The properties of mixed micelles seem to be very different from those of pure surfactants. Binding constants and rate constants for the reaction in the micellar pseudophase, obtained from the kinetic analysis, are reported. Conductivity measurements were also taken.

Mixed micellar aggregates are composed of two or more different surfactants in equilibrium with the surfactant monomers. These systems are of both theoretical interest and considerable industrial importance since mixtures of surfactants often exhibit synergism in their physicochemical properties,¹ thus allowing particular applications. Non-ionic surfactants are widely used as solubilizers and emulsifiers.²

In the past two decades, interactions between ionic surfactants and neutral polymers have been investigated extensively for their importance in industrial processes and in biological systems, as well as for their fundamental interest as mimics in protein–membrane interactions.^{3–7} Most surfactants used in practical applications are mixtures.

In solutions containing mixtures of surfactants, the tendency to form aggregates differs substantially from that observed in solutions of pure surfactants. It has been reported that the effect of surface activity of a mixed surfactant system is superior to that of a single surfactant. Many papers published in recent years on the solution properties of mixed surfactant systems, offer explanations of both the structure and the properties of mixed micelles containing ionic–non-ionic or mixed ionic surfactants.⁸

Nevertheless, there appear to have been very few studies analysing the influence of mixed surfactant systems on reaction processes.⁹ Our work then is an attempt to contribute to this field.

In a previous work,¹⁰ we studied the influence of cationic and anionic micelles in the aqueous acid hydrolysis of several alkyl nitrites. Cationic micelles inhibit the reaction, and rate–surfactant profiles can be fitted quantitatively with regard to the distribution of alkyl nitrites between micellar and aqueous phases. Anionic micelles first increase and then decrease the rate of acid hydrolysis of alkyl nitrites, and rate–surfactant profiles can be fitted in terms of the pseudophase ion-exchange (PPIE) model, the reaction in the micellar pseudophase being slower than that occurring in water.

This paper shows the results of this process in two aqueous acid solutions: (i) the non-ionic surfactant C₁₆E₂₀, and (ii) a binary surfactant mixture of C₁₆E₂₀ and SDS, where SDS represents the anionic surfactant sodium dodecyl sulfate. The experimental results obtained from conductance and kinetic measurements allowed us to achieve significant information about our general system and, in particular, about the nature and structure of the mixed micelles formed. Still open for discussion are the source of interaction forces between both surfactants, the role played by the counter-ions in the complexation process, and even the structure of the mixed micelle itself.

Experimental

Materials.—Alkyl nitrites, RONO, were synthesized and purified following conventional methods.^{10,11} Surfactants of the highest available purity were supplied by Sigma or Aldrich and were used as received. D₂O (99.77%) was supplied by the Spanish Nuclear Energy Board.

In preparing the mixed surfactant solutions, the appropriate portions of a given concentration of SDS solution and C₁₆E₂₀ solution were mixed. When the experiments were carried out at a fixed ratio of [C₁₆E₂₀]/[SDS] = *r*, the desired amounts of both surfactants were weighed and dissolved in a convenient volume of water. Identical results were obtained regardless of whether the mixtures were stirred or sonicated long enough to establish their equilibrium.

Conductance.—Conductivity was measured with a radio-meter conductimeter using solutions prepared with double-distilled water purified by a millipore system. The solutions were thermostatted in the cell at 25 ± 0.1 °C for at least 15 min before measurements were initiated. The conductivity cell was equipped with a magnetic stirring device.

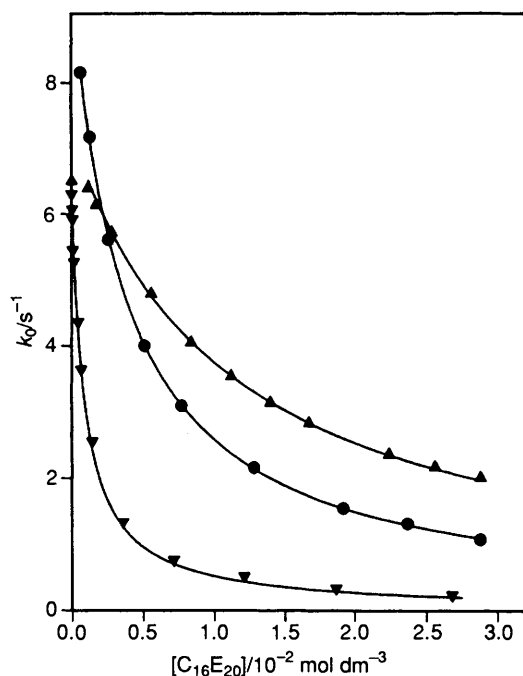


Fig. 1 Influence of $[C_{16}E_{20}]$ upon k_0 for the acid hydrolysis ($[HCl] = 1.3 \times 10^{-2} \text{ mol dm}^{-3}$) of (▲) butylnitrite, (●) cyclohexylnitrite and (▼) hexylnitrite. Solid lines fit by eqn. (1), for parameters see Table 1.

Kinetics.—Kinetics were studied using a Hi-Tech SF-61 stopped-flow apparatus. The kinetic procedure has been described elsewhere.¹⁰

The consumption of RONO was followed by recording the absorbance at 245–250 nm. The concentration of alkyl nitrite used was in the range of $(1.5\text{--}3) \times 10^{-4} \text{ mol dm}^{-3}$.

The absorbance–time data were in perfect agreement with first-order integrated equations. Subsequently, k_0 denotes the observed pseudo first-order rate constant. Each reported k_0 value is the average of at least four individual measurements with a typical variation of $\pm 2\%$ or less.

¹H NMR spectra in D₂O were recorded in a Bruker AC 200F at 200 MHz, using the HDO signal as an internal reference ($\delta = 4.60$). NMR signals were identified following ref. 12.

Results and Discussion

Reaction in Aqueous Micellar Solution of the Non-ionic Surfactant.—The influence of non-ionic surfactant concentration (varying between 0 and 0.03 mol dm^{-3}) on the acid hydrolysis of alkyl nitrites (RONO) was studied at fixed concentrations of H⁺ ($[HCl] = 1.35 \times 10^{-2} \text{ mol dm}^{-3}$) and RONO.

The addition of surfactant decreases the observed rate constant (see Fig. 1). The kinetic data can be explained by means of the pseudophase model¹³ which treats micelles and water as separate reaction media. According to this model, profiles of k_0 vs. surfactant concentration depend on substrate charge and hydrophobicity, surfactant head group charge, and counter-ion concentration and type.

Alkyl nitrites have proved to be very hydrophobic substrates and they tend to dissolve mainly into the micellar pseudophase. On the other hand, the micellar uncharged surface of the non-ionic surfactant C₁₆E₂₀ cannot interact with H⁺ ions coulombically or specifically, and there can be no increase in the concentration of the reactive ions in the micellar interface; the concentration will be the same as for that of the bulk water pseudophase.

Accordingly, the overall reaction rate constant will be the rate

Table 1 Calculated binding constants (K_s^N) of several alkyl nitrites, RONO, to C₁₆E₂₀ micelles by fitting the experimental kinetic data obtained in its aqueous-acid hydrolysis at $[HCl] = 1.3 \times 10^{-2} \text{ mol dm}^{-3}$ and 25 °C to eqn. (1)

R-	k_w/s^{-1}	K_s^N
CH ₃ -	5.3	5.5 ± 0.3
CH ₃ CH ₂ -	7.8	12.8 ± 0.2
CH ₃ O[CH ₂] ₂ -	12.8	4.3 ± 0.2
CH ₃ CH ₂ O[CH ₂] ₂ -	11.3	6.5 ± 0.2
Br[CH ₂] ₂ -	16.5	28 ± 2
Cl[CH ₂] ₂ -	17.9	29 ± 1
CH ₃ [CH ₂] ₂ -	7.7	31.5 ± 0.5
(CH ₃) ₂ CH ₂ -	7.9	28 ± 1
CH ₃ [CH ₂] ₃ -	6.5	81.4 ± 0.5
(CH ₃) ₃ C-	13.7	62 ± 1
CH ₃ [CH ₂] ₄ -	6.7	305 ± 7
CH ₃ [CH ₂] ₅ -	6.3	1090 ± 50
C ₆ H ₅ -[CH ₂] ₂ -	10.6	393 ± 3
C ₆ H ₅ -CH-CH ₃	8.4	510 ± 8
C ₆ H ₁₁ -	9.6	284 ± 4

constant in water and will, therefore, depend on the distribution of alkyl nitrite between each pseudophase. The resulting expression for k_0 is given in eqn. (1), where k_w represents the pseudo-first-order rate constant in the absence of surfactant at experimental acidity; K_s^N is the binding constant of the alkyl nitrite to C₁₆E₂₀ micelles: $RONO_w + D_n \rightleftharpoons RONO_m$, where D_n represents micellized surfactant concentration, subscripts w and m refer to water and micellar pseudophases, and CMC represents the critical micelle concentration.

$$k_0 = k_w / \{1 + K_s^N([C_{16}E_{20}] - CMC)\} \quad (1)$$

The CMC value corresponding to this surfactant is found in the literature¹⁴ as $1.7 \times 10^{-5} \text{ mol dm}^{-3}$. As the used $[C_{16}E_{20}]$ is much greater than the CMC value, it was neglected when fitting the experimental data to eqn. (1). The theoretical fits (solid lines) of the experimental points to this equation are shown in Fig. 1. Calculated binding constants, K_s^N , for the different alkyl nitrites are listed in Table 1.

The main factor determining a higher solubility of alkyl nitrites in the micellar pseudophase than in water is a hydrophobic effect that increases with the hydrocarbon chain length of the alkyl nitrite. The variation of K_s^N with the chemical structure of the alkyl nitrite (*i.e.* with R) follows a trend similar to that found with SDS or tetradecyltrimethylammonium bromide (TTAB) micelles.¹⁰ First, the K_s^N values increase with increasing substrate hydrophobicity (*i.e.* with the length of the alkyl chain R of the alkyl nitrite). Second, the free energy of transfer, $\Delta G_{tr}^{w \rightarrow m}$, on crossing the interface, calculated as $-RT \times \ln(55.5 \times K_s^N)$,¹⁵ increases (in absolute value) linearly with the number of carbon atoms in the alkyl chain. From the slope of the line we obtained the value of $-625 \pm 30 \text{ cal mol}^{-1} *$ for the free energy of transfer per methylene group. This value is consistent with previously reported results for SDS or TTAB micelles. And third, K_s^N increases with the hydrophobic character of the micelle, that is, K_s^N increases with the length of the hydrocarbon chain of the surfactant, so that $K_s^N(C_{16}E_{20}) > K_s^N(TTAB) > K_s^N(SDS)$ conforms to a ratio of 8:4:1 in the case of R = hexyl and 2.5:1.5:1 in that of R = ethyl (see Fig. 2).

Reaction in Aqueous Solutions of C₁₆E₂₀-SDS Mixed Micelles.—(a) *Conductance measurements.* At constant SDS concentration ($0.010 \text{ mol dm}^{-3}$), specific conductivity measurements were taken of solutions of varying $[C_{16}E_{20}]$ (0–0.02 mol

* $1 \text{ cal mol}^{-1} = 4.184 \text{ J mol}^{-1}$.

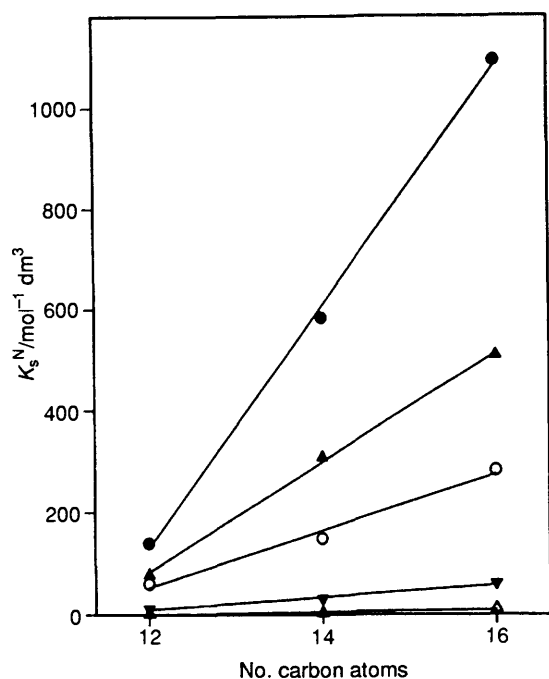


Fig. 2 Correlation between association constants of alkyl nitrites (RONO) to SDS, TTAB or $C_{16}E_{20}$ micelles and the number of C atoms of the alkyl chain of the surfactant: R = (●), hexyl; (▲), 1-phenylethyl; (○), cyclohexyl; (▼), *tert*-butyl; (△) ethyl

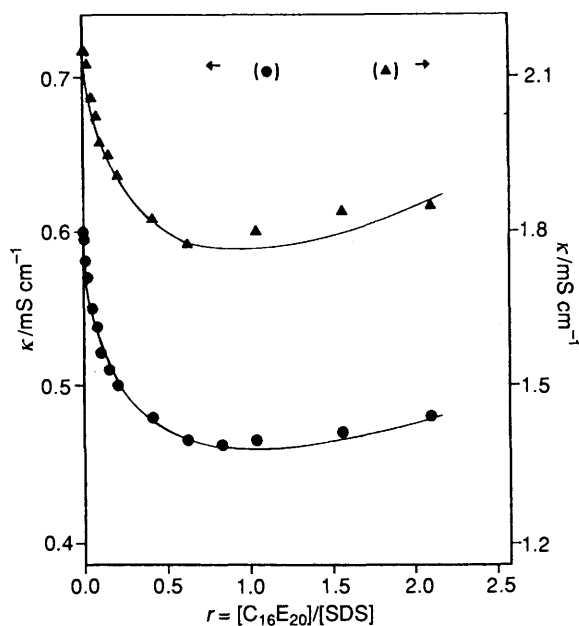


Fig. 3 Specific conductivity vs. r for (●) $[SDS] = 0.01$ and (▲) $[SDS] = 0.01$, $[HCl] = 4 \times 10^{-3} \text{ mol dm}^{-3}$

dm^{-3}). In a similar study, measurements were recorded of solutions containing a fixed $[SDS]$ and $[H^+]$ ($4 \times 10^{-3} \text{ mol dm}^{-3}$, HCl), but with variations of the non-ionic surfactant concentration. The specific conductivity variations of $C_{16}E_{20}$ -SDS solutions are plotted in Fig. 3.

Conductance decreases as r , defined as $[C_{16}E_{20}]:[SDS]$ ratio, increases; at high r values, it increases. In both experiments the number of effective carriers for conduction seems to decrease with an increasing concentration of $C_{16}E_{20}$; and one can see a greater variation of electric conductivity in the presence of H^+ ($\Delta\kappa = 390 \mu\text{S cm}^{-1}$) than in the presence of Na^+ ions alone ($\Delta\kappa = 140 \mu\text{S cm}^{-1}$).

Measurements were also made at fixed ratios of $[C_{16}E_{20}]$:

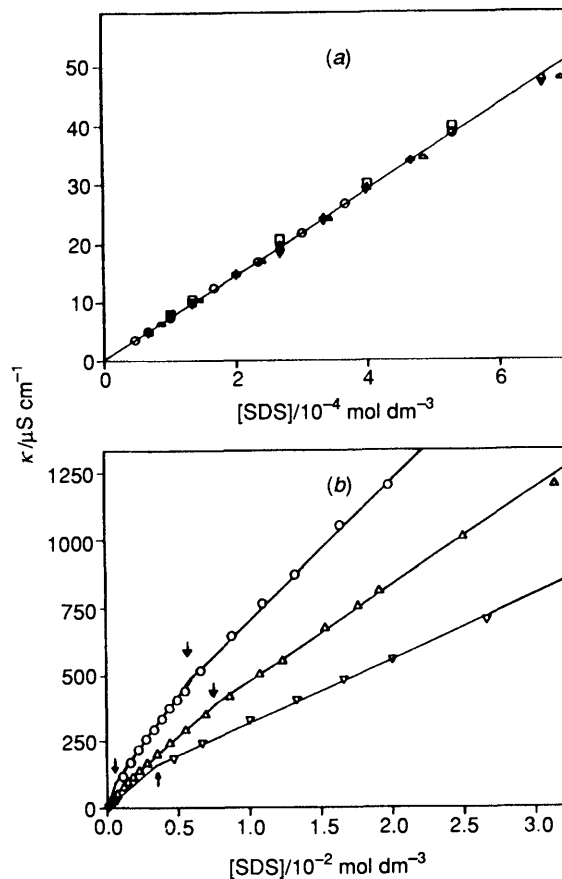


Fig. 4 Specific conductivity vs. SDS concentrations at several $[C_{16}E_{20}]/[SDS] = r$ ratios (a) below the CMC and (b) above the CMC. For parameters see Table 2. (a) $r =$ (○), 0.03; (△), 0.07; (□), 0.15; (▽), 0.30; (◇), 0.50; (○), 0.75; (●), 2. (b) (○), $r = 1$, 1.2 κ ; (△), $r = 2$; (▽), $r = 0.3$, $\kappa/1.5$.

$[SDS]$. When the total surfactant concentration is low—smaller than the critical aggregation concentration CAC —the specific conductivity of solutions is independent of $[C_{16}E_{20}]$, [see Fig. 4(a)]. This means, as expected, that the non-ionic surfactant does not contribute to electrical conductance. Therefore, this quantity is proportional to the SDS monomers' concentration.

Also, as shown in Fig. 4(b), at high r values (approximately $r > 0.7$), the κ vs. $[SDS]$ (or total surfactant concentration) plots show two inflection points, corresponding to two CAC s or CMC s of the mixing system. The second is not observed at low r values.

This experimental behaviour could be due to the formation of very large micelles in the presence of high non-ionic surfactant concentrations,¹⁶ in mixed surfactant systems, the second CMC has also been related to the formation of two kinds of micelles coexisting in the solution¹⁷ (one SDS-rich and the other $C_{16}E_{20}$ -rich), which occurs when the anionic surfactant is saturated with the non-ionic surfactant. The second possibility is more consistent with our kinetic results and viscosity measurements (at $r = 2$ the viscosity of the solution varies between $\eta = 0.866 \text{ cP}^*$ when $[\text{surfactant}]_t = 1.2 \times 10^{-3} \text{ mol dm}^{-3}$ and $\eta = 1.489 \text{ cP}^*$ when $[\text{surfactant}]_t = 0.060 \text{ mol dm}^{-3}$).

In these experiments (conductivity measurements at fixed r), the degree of ionization, α , of the micelles formed was determined from the ratio of slopes of ionic conductance above and below the first CMC . These CMC values were taken from

* $1 \text{ cP} = 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1} = 10^{-3} \text{ Pa s}$.

Table 2 Experimental parameters obtained from conductance and kinetic measurements at 25 °C

r	β	10^3 CMC^a	k_w^b	K_s^{Nc}	k_m^b	10^2 RMSD
1-Phenylethyl nitrite						
0 ^d	0.80	8.2	8.20	79	320	2.6
0.03	0.65	7.1	8.20	47	294	3.9
0.07	0.58	5.5	8.20	45	218	4.9
0.15	0.55	4.1	8.20	45	119	4.6
0.30	0.49	3.2	8.20	43	71	2.5
0.50	0.46	2.6	7.50 ^f	41	48	1.5
0.75	0.40	2.2	7.20 ^f	33 ± 1	—	—
1.0	0.33 (0.36) ^e	1.6	6.56 ^f	30 ± 1	—	—
2.0	0.28	0.99	6.4 ^f	150 ± 20	—	—
∞	—	0.02	8.20	510 ± 8	—	—
Hexyl nitrite						
0 ^d	0.80	8.2	5.8	140	136	3.2
0.07	0.58	5.5	5.8	66	110	4.8
0.15	0.55	4.1	5.8	79	66	2.0
0.30	0.49	3.2	5.8	72	38	4.5
∞	—	0.02	5.9	1094 ± 54	—	—

^a CMC values determined for binary mixed surfactant solutions from conductivity measurements; the CMC values used to fit the kinetic data are *ca.* fourfold smaller. ^b In s⁻¹ and [HCl] = 1.27 × 10⁻² mol dm⁻³. ^c In dm³ mol⁻¹. ^d Ref. 10. ^e Ref. 23. ^f Extrapolated values at [surfactant] = 0.

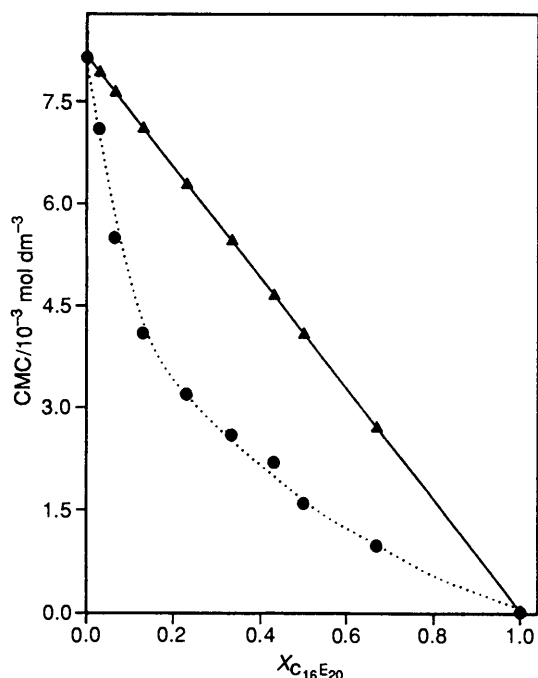


Fig. 5 Variation of the experimental CMC of C₁₆E₂₀-SDS mixtures with the mol fraction of C₁₆E₂₀ (●) in the amphiphile mixture (dotted line), and for a perfectly ideal mixture (▲) calculated from an equation analogous to Raoult's law (see ref. 19)

the intersection of the tangents drawn before and after the first break in the conductivity *vs.* concentration plot. The results are reported in Table 2. As one can see, on increasing the ratio of non-ionic surfactant in the mixed surfactant system, *i.e.* on increasing r , both the degree of the fractional charge neutralized $\beta(1 - \alpha)$ of the mixed micelles and the CMC decrease.

As the head group of C₁₆E₂₀ is larger than that of SDS, the radius of the mixed micelle with the electrical double layer increases with an increasing concentration of C₁₆E₂₀. Thus, the surface charge density of counter-ions would decrease with an increasing concentration of C₁₆E₂₀. Consequently, the degree of ionic dissociation, α , of the mixed micelle increases with the proportion of non-ionic surfactant in the mixed micelle. The variation of α with the mole fraction of C₁₆E₂₀ follows the normal trend.¹⁸ On the other hand, ideal mixing

does not take place in the present binary surfactant system, as is to be expected¹⁹ because of the different head groups of the amphiphiles used. Negative deviations from ideality are observed; *i.e.* CMC values are lower (see Fig. 5) than those predicted for perfectly ideal mixing, indicating that the average repulsive force in the mixed micelle is lower than in micelles formed by pure components. Nonetheless, our system does not show synergism: the mixing CMC is never smaller than that of either individual components, at least in the range of compositions studied.

In studying the conductivity of C₁₆E₂₀-SDS solutions the following inferences emerged. In aqueous solutions of two surfactants the observed alterations in physical properties can be associated with the formation of mixed micelles, which contain both surfactant components in equilibrium with the monomeric type in the aqueous phase. The observed decrease in conductance as r increases (see Fig. 3) could be attributed to a complex formation between the Na⁺ ions and the ether oxygens of the polyoxyethylene chain, probably in a way similar to that found between crown and acyclic polyethers.²⁰ The greater conductance decrease observed in the presence of H⁺ indicates that this ion also interacts with the polyoxyethylene chain, probably by protonating the ether oxygens, giving it a positive charge that strengthens its interaction with the anionic surfactant. Several studies on the influence of cations in the binding of non-ionic surfactants to SDS show that the cation plays a role in the phenomenon of binding.²¹ The results of these studies suggest that the simultaneous (electrostatic) affinity of the cations for the micelle and the (coordination) association with the polyoxyethylene surfactant energetically contribute to the binding force between C₁₆E₂₀ and SDS micelles.

Therefore, during the formation of mixed micelles a solubilization process between both surfactants may take place. Theoretical equations based on the 'regular solution theory' have been proposed²² in order to calculate the extension of the miscibility between the surfactants. Likewise, Abe *et al.*,²³ found a value of -6.18 for the molecular interaction parameter corresponding to a 1:1 mixture of the surfactants used in the present work. A high negative value of this parameter indicates high miscibility. The mixed micelles may become stabilized primarily through the contact with hydrocarbon chains of both surfactants; the SDS polar head groups are located in the ethylene oxide region of the non-ionic surfactant in a 'hydrophilic region' (second, third ethylene oxide of the non-ionic surfactant).²⁴

Table 3 Proton chemical shifts of SDS and C₁₆E₂₀ in D₂O at 25 °C^a

Proton	SDS ^b	C ₁₆ E ₂₀ ^c	SDS + C ₁₆ E ₂₀ ^d
H ₁	3.845 (0.024)	3.469 (0.036)	3.815–3.477 (0.072)
H ₂	1.501 (0.036)	—	1.480 (0.039)—
H ₃	1.468 (0.036)	—	1.450 (0.030)—
H _{4–11 or 3–15}	1.124 (0.039)	1.103 (0.018)	1.128 (0.028)
E ₂₀	—	3.508 (0.007)	3.515 (0.019)
H _{1,2 or 16}	0.708 (0.030)	0.703 (0.014)	0.690–0.724 (0.015)

^a The values in parentheses correspond to differences, $\Delta\delta$, of the proton NMR chemical shifts of the H signals of the title surfactants in the absence and in the presence of 1-phenylethyl nitrite. ^b 0.15 mol dm⁻³ in SDS. ^c 0.030 mol dm⁻³ in C₁₆E₂₀. ^d Mixture of SDS + C₁₆E₂₀ at $r = 0.30$ and $[\text{surfactant}]_t = 0.15 \text{ mol dm}^{-3}$.

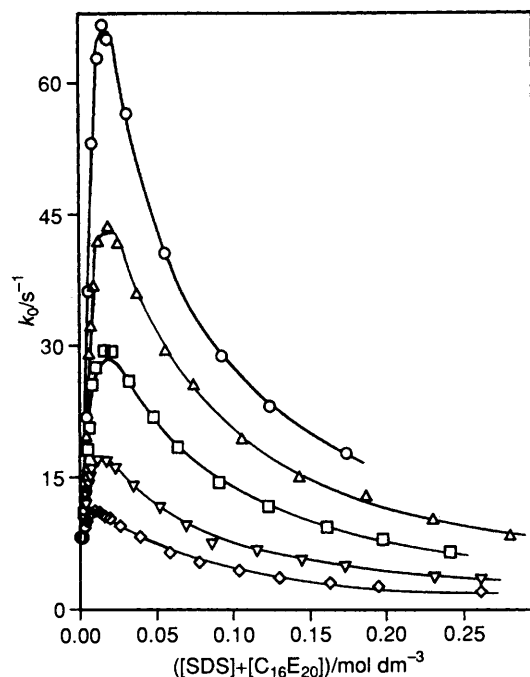


Fig. 6 Variation of the pseudo first-order rate constants for the acid hydrolysis ($[\text{HCl}] = 1.27 \times 10^{-2} \text{ mol dm}^{-3}$) of 1-phenylethyl nitrite as a function of total surfactant concentration and of $r = [\text{C}_{16}\text{E}_{20}]/[\text{SDS}]$. Full lines were drawn fitting eqn. (3) to the experimental points by a simulation program. For parameters see Table 2. $r = (\circ)$, 0; (Δ), 0.03; (\square), 0.07; (∇), 0.15; (\diamond), 0.30.

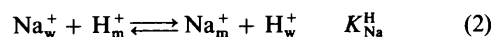
Site-specific environmental information should be available by ¹H NMR chemical shifts in simple micelles and micellar mixtures. The presence of C₁₆E₂₀ produces a substantial downfield shift in the SDS response, suggesting a more polar environment for the SDS monomers in the mixed micelle.²⁵ Table 3 reports the values obtained.

(b) *Kinetic measurements.* The dependence of the total surfactant concentration ($[\text{SDS}] + [\text{C}_{16}\text{E}_{20}]$) on the pseudo first-order rate constant, k_0 , for the acid denitrosation of 1-phenylethyl and hexyl nitrite by $1.27 \times 10^{-2} \text{ mol dm}^{-3}$ hydrochloric acid was studied in a series of experiments at fixed $r = [\text{C}_{16}\text{E}_{20}]/[\text{SDS}]$. Fig. 6 shows typical results.

The observed rate constant increases as the total surfactant concentration increases, goes through maxima, and decreases at still higher concentrations of surfactant. This is the behaviour found at low r values; but when r is higher than approximately 0.6, the measured pseudo first-order rate constant decreases monotonically as the total surfactant concentration increases.

The experiments carried out at $r = 0.03, 0.07, 0.15, 0.30$ and 0.50 show the normal behaviour²⁶ for micellar-catalysed bimolecular processes of counter-ions with hydrophobic

substrates and are explained by the simple PPIE model developed by Romsted.²⁷ The concentration of H⁺ at the micellar surface of SDS–C₁₆E₂₀ micelles depends on competition with the inert counter-ion, Na⁺, and this competition can be treated quantitatively by the ion-exchange equilibrium put forward in eqn. (2).



The pseudo-first-order rate constant for disappearance of alkyl nitrite, therefore, will follow eqn. (3), where k_2 is the second-order rate constant in the aqueous phase; where k_m , in s⁻¹, is the rate constant in the micellar phase; and where K_s^{N} represents the equilibrium constant for the association of the alkyl nitrite to mixed micelles. The concentration of H⁺ bound to the micelle ($[\text{H}_m^+]$) can be calculated from the ion-exchange equilibrium (2) as described in the literature.²⁸ The term D_n represents surfactant in micellar form, so that $[D_n] = [D] - \text{CMC}$, where $[D]$ is the bulk concentration of surfactant. (All concentrations are relative to the total volume of the solution.)

$$k_0 = \frac{k_2[\text{H}^+]_{\text{tot}} + (k_m K_s^{\text{N}} - k_2)[\text{H}_m^+]}{1 + K_s^{\text{N}}[D_n]} \quad (3)$$

Experimental kinetic data can be adapted to this model by simulation techniques.²⁹ The experimental data were fitted to the model to estimate the 'best' values of K_s^{N} , K_{Na}^{H} , and k_m by using constant values of CMC and the molar fraction of neutralized charge, β , (see Table 2) determined from the experimental α values. We found that values of K_{Na}^{H} in the range 0.7–0.8 all fit to experimental points very well, yielding quite similar values for the optimized parameters. We thus chose a value of 0.75 for K_{Na}^{H} in every case. Moreover, this was the value found in other studies of acid catalysed reactions in SDS micelles.^{10,30}

Table 2 shows the calculated parameters that best explain the experimental results. The root-mean-square deviation (RMSD) of the experimental points from the model is also given. As can be seen, it is always below 5%. Fig. 6 shows the theoretical fits for the experimental points.

The binding constants for the mixed micelles produced in the mixed micellar system of SDS–C₁₆E₂₀ are smaller than the corresponding association constants of the pure surfactant micelles. Since these association constants are a measure of the hydrophobicity of the substrate and of the micropolarity of the binding site in the micelle, these results could indicate a more open and water-penetrated structure in the mixed micelles. The addition of C₁₆E₂₀ seems to enhance the porosity of the SDS micelles. Accordingly, from 5.2 to 10.5 water molecules per ethylene oxide unit are trapped in the polyoxyethylene oxide chain when forming the mixed micelle.³¹ Another possible occurrence would be the formation of microdomains, a process found in aqueous solutions of pure polyethoxylated surfactants C_mE_n.³² Nevertheless, drawing from the fact that K_s^{N} was lower than the corresponding value for pure SDS or pure C₁₆E₂₀ (that is, K_s^{N} is not an intermediate value between them) we might conclude that our system is composed of mixed micelles, whose properties are different from those of pure components.

If the mixed micelle interface were more open and more hydrated, one would expect that k_m , the rate constant in the micellar pseudophase, would increase with r ; however, this rate constant decreases as r increases (see Table 2). While considering that k_m , in s⁻¹, represents the bimolecular reaction constant in the micellar pseudophase divided by the molar reaction volume of the Stern layer ($k_m = k_2^{\text{m}}/\bar{V}$) we might attribute the decrease in k_m to an increase of \bar{V} . With an increase in the ratio of non-ionic surfactant in the mixed micelle, the hydrodynamic radius of the mixed micelle should increase. This

Table 4 Kinetic and equilibrium parameters for the acid denitrosation of 1-phenylethyl nitrite at 25 °C in H₂O and D₂O in the presence of SDS-C₁₆E₂₀ micelles at $r = [C_{16}E_{20}]/[SDS] = 0.30$ and 1.27×10^{-2} mol dm⁻³ hydrochloric acid

Solvent	H ₂ O	D ₂ O
k_w/s^{-1}	8.2	9.7
k_m/s^{-1}	71 ± 1	90 ± 2
$K_s^m/dm^3 mol^{-1}$	43 ± 2	48 ± 3
K_{Na}	0.75	0.75
β	0.49	0.49
CMC/mol dm ⁻³	5×10^{-4}	3×10^{-4}
10 ² RMSD	2.5	4.8

Table 5 Effect of temperature on the rate of acid denitrosation of 1-phenylethyl nitrite in C₁₆E₂₀-SDS mixed micelles in water^a

T/°C	10 ³ CMC	$k_2/mol^{-1} dm^3 s^{-1}$	$k_2^m/mol^{-1} dm^3 s^{-1b}$	K_s^m
20	0.8	450	30	49 ± 2
25	0.85	660	45	44 ± 2
30	1.0	1060	71	39 ± 1
35	1.5	1590	110	37 ± 2

Activation parameters

In water: $\Delta H_w^\ddagger = 61.2$ kJ mol⁻¹. In micelles: $\Delta H_m^\ddagger = 62.5$ kJ mol⁻¹
 $\Delta S_w^\ddagger = 14.7$ J mol⁻¹ K $\Delta S_m^\ddagger = -3.4$ J mol⁻¹ K

^a [HCl] = 1.27×10^{-2} mol dm⁻³; $r = [C_{16}E_{20}]/[SDS] = 0.15$; $K_{Na}^H = 0.75$ and $\beta = 0.55$. ^b $k_2^m = \bar{V} \times k_m$ with $\bar{V} = 0.38$ mol⁻¹ dm³.

hypothesis requires alkyl nitrites to reside in the Stern layer. From ¹H NMR measurements the mean location of 1-phenylethyl nitrite in the mixed micelles were evaluated from the ring current effects of the phenyl ring. (Aromatic rings shift micelle H signals to an extent that depends on the distance of the ring from the H atom concerned.)³³ As one may note from the data in Table 3, the ¹H NMR spectrum of the protons of the -CH₂- group of the surfactant next to the first oxyethylene unit, in C₁₆E₂₀ micelles, or next to the sulfate group, in SDS micelles, show the greatest changes in chemical shifts on introduction of 1-phenylethyl nitrite into the surfactant-D₂O system.

If we suppose that k_2^m is constant (*i.e.*, that the micropolarity of the reaction site will be the same when r increases), the molar reaction volume of the micellar interface must increase from 0.14 dm³ mol⁻¹ in pure SDS¹³ to 0.63 dm³ mol⁻¹ when $r = 0.30$, according to the results of Table 2. And if one assumes that the increase in the micellar volume on increasing r is fundamentally due to an increase in the volume of the micellar interface, these results agree well with the values determined for the hydrodynamic radius of pure micelles of SDS, $R_H = 24.7$,³⁴ 36 ³⁵ and 21 ³⁶ Å (the last being the most consistent value with the molar volume of SDS micelles at 25 °C), and of mixed micelles of C₁₆E₂₀-SDS, in which case $R_H = 55.1$ Å²³ for a 1:1 mixture of both surfactants or $R_H = 46$ Å (estimated value for C₁₆E₂₀ micelles from data of Corti *et al.*)³⁷ According to the model of mixed micelles, the interface obviously undergoes a greater change in its properties than does the micellar core. (The agreement of the results is only in the sense that the size of C₁₆E₂₀-SDS mixed micelles increases as compared to those of pure SDS or C₁₆E₂₀-micelles.)

On the other hand, the rate constant decrease in the mixed micelles could be attributed to a decrease of the dielectric constant in the micelle as r increases. Nevertheless, having the picture of a mixed micelle in mind, the dielectric constant of the micellar interface should vary between the value of pure SDS and that corresponding to pure C₁₆E₂₀, which are almost the same. The observed rate constant for our reaction system

strongly depends on the polarity of the reaction medium³⁸ (*i.e.*, $k_0 = 0.62$ s⁻¹ when $\epsilon = 44$ and $k_0 = 0.12$ s⁻¹ when $\epsilon = 27$ —determined from dioxane-water mixtures). Perhaps both effects could contribute to the decrease of k_m .

Solvent Isotope Effect.—At $r = 0.30$, the SDS + C₁₆E₂₀ concentration dependence on k_0 for the acid denitrosation of 1-phenylethyl nitrite by 0.0127 mol dm⁻³ hydrochloric acid in D₂O is of the typical form predicted by the PPIE model. Table 4 lists the corresponding data for the reaction in D₂O and H₂O.

The solvent isotope effect found for the reaction in water, $k_{H^+}^{H_2O}/k_{D^+}^{D_2O} = 0.85$, conforms with previously reported values³⁸ and implies that no protonated intermediate is formed prior to the rate-determining step of the reaction. The low value of the solvent isotope effect when the reagent is H₃O⁺ is understandable in terms of the fractionation factor theory,³⁹ in which the low value (0.69) of the fractionation factor of the protons in the hydronium ion is determinant.

The corresponding isotope effect in the micellar pseudophase is nearly equal to that discussed above: $k_{H^+}^{H_2O}/k_{D^+}^{D_2O} = 0.79$. This supports strongly the hypothesis that the effective protonating species in the micellar pseudophase is L₃O⁺, as we have recently demonstrated.^{30a}

The fact that the values of K_s and K_{Na}^H in D₂O and in H₂O are similar suggests that the micelle structure in D₂O and in water are the same, which is to say that the intermicellar interactions and head group repulsions are very similar in the two media.³⁴

Effect of Temperature.—The influence of temperature was studied at $r = 0.15$ in the range 20–35 °C. The dependence of the reaction rate on SDS + C₁₆E₂₀ concentrations was also interpreted in terms of the PPIE model.

Table 5 lists the results of fitting eqn. (3) to the experimental data using $\beta = 0.55$ and $K_{Na}^H = 0.75$. We have assumed that the system's ion-exchange constant, as well as β , are not altered by the difference in temperature, as has been determined by Kaler *et al.*³⁴

The reported CMC values were determined kinetically as the lowest surfactant concentration producing an effect on the reaction rate. The substrate micelle association constant decreases slightly as the temperature increases. The kinetic constants, k_2 or k_2^m (determined from k_m taking \bar{V} , the molar reaction volume in the micelle, as 0.38 dm³ mol⁻¹), increase nearly fourfold with the rise in temperature.

The activation parameters for the reaction in water and in SDS micelles are also reported in Table 5. The reaction is slower in SDS micelles than in water, mainly owing to the difference in entropy. The corresponding activation enthalpies are very similar. This means that the interaction with the surfactant has the same effect on the stability of the reagents as on that of the transition state. These results are evidence that the reaction takes place in a highly hydrated region in the micelle.

The positive value found for the entropy in the aqueous pseudophase agrees perfectly with our previous results,³⁸ in which we have considered that there was no complete bonding of the electrophile reagent (H₃O⁺) to the substrate before the leaving group departs. On the contrary, in the transition state, negative charge is developed on the O atom and proton transfer has reached a fairly advanced stage.

The kinetic data obtained in the experiments carried out at $r > 0.75$ cannot be explained by the PPIE model; k_0 *vs.* surfactant profiles can be fitted quantitatively to an eqn. of type (1), predicted by the pseudophase model, providing that there is distribution of the alkyl nitrite between micellar and aqueous phases and that the reaction take place only in the aqueous phase. In this equation the term k_w should correspond to the value of the pseudo first-order constant determined in the absence of surfactant.

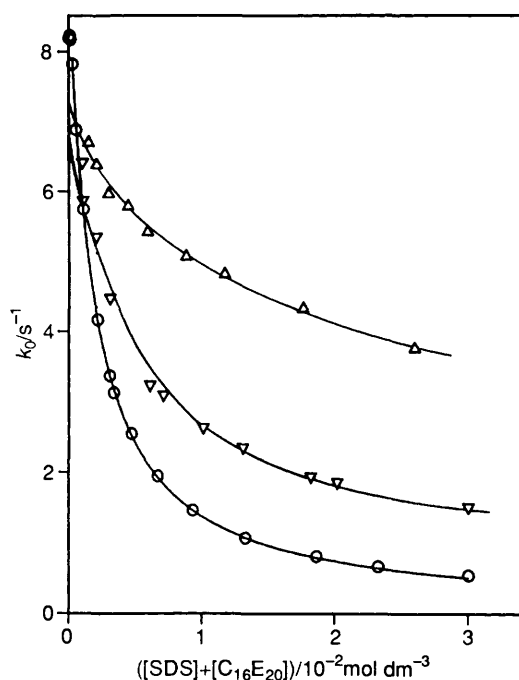


Fig. 7 Pseudo first-order rate constant for the acid hydrolysis of 1-phenylethyl nitrite as a function of increasing (○) $[C_{16}E_{20}]$ and $[SDS] + [C_{16}E_{20}]$ at (△) $r = 1$ and (▽) $r = 2$

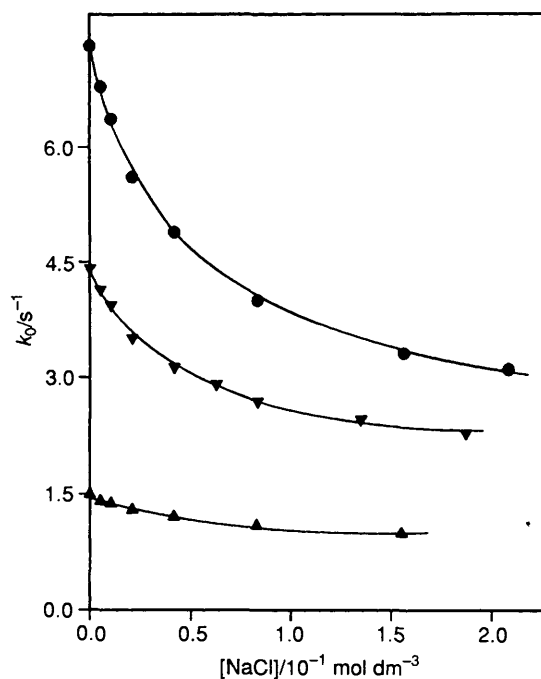


Fig. 8 Influence of $[NaCl]$ upon the pseudo first-order rate constant for the acid hydrolysis ($[HCl] = 1.27 \times 10^{-2} \text{ mol dm}^{-3}$) of 1-phenylethyl nitrite at (●) $[surfactant] = 0.017$, $[SDS] = 0.011$; (▽) $[surfactant]_i = 0.018$, $[SDS] = 0.009$ and (▲) $[surfactant]_i = 0.032$, $[SDS] = 0.010$, all concentrations in mol dm^{-3}

Table 2 lists the values of k_w derived by extrapolating the experimental data to $[surfactant] = 0$ (see Fig. 7) and used in eqn. of type (1) to fit the experimental points. As is shown, these values are lower than the corresponding values determined in pure water or than the values extrapolated to $[surfactant] = 0$ from the experiments carried out in the presence of $C_{16}E_{20}$ only.

The kinetic behaviour can be explained if we suppose that the micelles are nearly completely ionized, $\alpha \rightarrow 1$. The conduct-

ivity measurements show a high degree of micellar ionization. In fact, the influence of $[NaCl]$ (see Fig. 8) shows that at $r > 0.75$, k_0 remains practically independent of $[Na^+]$. This fact supports the conclusion of nearly total micellar ionization, and this is why there is no reaction in the micellar phase.

The most likely to exist in these experimental conditions are not only mixed micelles of $SDS + C_{16}E_{20}$, but also pure $C_{16}E_{20}$ micelles. Thus the determined value for K_s^N is a combination of both values corresponding to mixed micelles and to pure $C_{16}E_{20}$ micelles, whose proportions depend on the percentage of pure non-ionic surfactant micelles produced when saturating the SDS micelles with $C_{16}E_{20}$ monomers. Nevertheless, it is difficult to explain the obtained results quantitatively.

Conclusions

Our results substantiate the formation of mixed micelles between $C_{16}E_{20}$ and SDS surfactants. The results may imply a more open and water-penetrated structure for the mixed micelles, the properties of which—highly ionized, more hydrophilic and with a more voluminous interface—seem to be completely different from those corresponding to pure surfactants. The above mentioned characteristics ensure that the important catalytic effect observed in the acid hydrolysis of alkyl nitrites in the presence of SDS micelles may be completely suppressed by the addition of a certain quantity of a non-ionic surfactant, probably because of the combination of three effects operating in the same direction: (i) the $[H^+]$ is reduced from the micellar region as α increases, (ii) the increase of the molar reaction volume, which produces a dilution of both reactants in the micellar region and (iii) a probable change in the apparent dielectric constant of the reaction site in the micelle.

Acknowledgements

Financial support from *Xunta de Galicia* (Project XUGA 10302A93) is gratefully acknowledged. We also thank the referees for their valuable suggestions and comments.

References

- 1 M. J. Rosen, *Surfactants and Interfacial Phenomena*, Wiley, 2nd edn., 1989, p. 393; D. N. Rubingh, in *Solution Chemistry of Surfactants*, ed. K. L. Mittal, Plenum Press, New York, 1979, vol. 1, p. 337; P. M. Holland and D. N. Rubingh, in *Cationic Surfactants*, ed. D. N. Rubingh and P. M. Holland, Marcel Dekker, New York, 1991, p. 141.
- 2 R. A. Mackay, in *Nonionic Surfactants. Physical Chemistry*, ed. M. J. Schick, Marcel Dekker, New York, 1987, p. 297; M. J. Schick, in *Nonionic Surfactants. Physical Chemistry*, ed. M. J. Schick, Marcel Dekker, New York, 1987, p. 757.
- 3 M. N. Jones, *J. Colloid Interface Sci.*, 1967, **23**, 36.
- 4 J. Francois, J. Dayantis and J. Sabbadin, *Eur. Polym. J.*, 1985, **21**, 165.
- 5 E. Ruckenstein, G. Huber and H. Hoffmann, *Langmuir*, 1987, **3**, 382.
- 6 J. C. Brackman and J. B. F. N. Engberts, *Chem. Soc. Rev.*, 1993, **85**; *Langmuir*, 1991, **7**, 2097; *J. Colloid Interface Sci.*, 1989, **132**, 250.
- 7 J. Xia, P. Dubin and Y. Kim, *J. Phys. Chem.*, 1992, **96**, 6805.
- 8 *Mixed Surfactant Systems*, eds. P. M. Holland and D. N. Rubingh, Am. Chem. Soc., Washington, DC, 1992.
- 9 C. A. Bunton, S. Wright, P. M. Holland and F. Nome, *Langmuir*, 1993, **9**, 177; S. Wright, C. A. Bunton and P. M. Holland, in ref. 8, ch. 13; D. N. Rubingh and M. Bauer, in ref. 8, ch. 12.
- 10 L. García-Río, E. Iglesias, J. R. Leis and M. E. Peña, *Langmuir*, 1993, **9**, 1263.
- 11 W. A. Noyes, *Organic Syntheses, Collect.*, Wiley, New York, 1933, vol. II.
- 12 A. A. Ribeiro and E. A. Dennis, in *Nonionic Surfactants. Physical Chemistry*, ed. M. J. Schick, Marcel Dekker, New York, 1987, vol. 23, pp. 971–1009; Z. Gao, R. E. Wasylshen and J. C. T. Kwak, *J. Phys. Chem.*, 1991, **95**, 462.
- 13 C. A. Bunton, F. Nome, F. H. Quina and L. S. Romsted, *Acc. Chem. Res.*, 1991, **24**, 357 and refs. therein.

- 14 M. Abe, H. Uchiyama, T. Yamaguchi, T. Suzuki and K. Ogino, *Langmuir*, 1992, **8**, 2147.
- 15 C. A. Bunton and L. Sepúlveda, *J. Phys. Chem.*, 1979, **83**, 680.
- 16 C. Tanford, in *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*, Krieger Publ. Co., Florida, 2nd edn., 1991, p. 79; U. Henriksson, M. Jonströmer, U. Olsson, O. Söderman and G. Klose, *J. Phys. Chem.*, 1991, **95**, 3815.
- 17 K. Ogino, N. Tsubaki and M. Abe, *J. Colloid Interface Sci.*, 1985, **107**, 509.
- 18 D. G. Hall and T. J. Price, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 1193.
- 19 C. Tanford, in *The Hydrophobic Effect: Formation of Micelles and Biological Membrane*, Krieger Publ. Co., Florida, 2nd edn., 1991, p. 90.
- 20 P. Firman, E. M. Eyring and S. Petrucci, *J. Phys. Chem.*, 1991, **95**, 9500; D. Balasubramanian and B. Chandani, *J. Chem. Ed.*, 1983, **60**, 77.
- 21 R. Sartori, L. Sepúlveda, F. Quina, E. Lissi and E. Abuin, *Macromolecules*, 1990, **23**, 3878; C. Maltesh and P. Somasundaran, *Langmuir*, 1992, **8**, 1926; P. L. Dubin, J. H. Gruber, J. Xia and H. Zhang, *J. Colloid Interface Sci.*, 1992, **148**, 35.
- 22 P. M. Hall and D. N. Rubingh, *J. Phys. Chem.*, 1983, **87**, 1984 and ref. 1.
- 23 K. Ogino, T. Kakihara, H. Uchiyama and M. Abe, *J. Am. Oil Chem. Soc.*, 1988, **65**, 405; K. Ogino and M. Abe, in ref. 8, ch. 8.
- 24 P. Baglioni, L. Dei, L. Kevan and E. Rivara-Minten, in ref. 8, ch. 10.
- 25 R. E. Stark, R. W. Storrs and M. L. Kasakevich, *J. Phys. Chem.*, 1985, **89**, 272.
- 26 J. H. Fendler, *Membrane Mimetic Chemistry*, Wiley-Interscience, New York, 1982; C. A. Bunton and G. Savelli, *Adv. Phys. Org. Chem.*, 1986, **22**, 213.
- 27 L. S. Romsted, in *Surfactants in Solution*, ed. B. Lindman and K. L. Mittal, Plenum Press, New York, 1984, vol. 2, p. 1015; L. S. Romsted, *J. Phys. Chem.*, 1985, **89**, 5107, 5113; F. Quina and H. Chaimovich, *J. Phys. Chem.*, 1979, **83**, 1844; ref. 13.
- 28 S. Vera and E. Rodenas, *Tetrahedron*, 1986, **42**, 143; C. Bravo, P. Hervés, J. R. Leis and M. E. Peña, *J. Phys. Chem.*, 1990, **94**, 8816.
- 29 C. Bravo, Ph.D. Thesis, University of Santiago de Compostela, Spain, 1991.
- 30 (a) L. García-Río J. R. Leis, M. E. Peña and E. Iglesias, *J. Phys. Chem.*, 1992, **96**, 7820; (b) E. Pérez-Benito and E. Rodenas, *J. Colloid Interface Sci.*, 1990, **139**, 87.
- 31 K. Ogino, H. Uchiyama and M. Abe, *Colloid Polym. Sci.*, 1987, **265**, 52.
- 32 E. Alami, N. Kamenka, A. Raharimihamina and R. Zana, *J. Colloid Interface Sci.*, 1993, **158**, 342.
- 33 J. C. Eriksson and C. Gillberg, *Acta Chem. Scand.*, 1966, **20**, 2019; A. L. Maçanita, F. P. Costa, S. M. B. Costa, E. C. Melo and H. Santos, *J. Phys. Chem.*, 1989, **93**, 336.
- 34 N. J. Chang and E. W. Kaler, *J. Phys. Chem.*, 1985, **89**, 2996.
- 35 N. Funassaki, *Adv. Colloid Interface Sci.*, 1993, **43**, 87.
- 36 P. Mukerjee, in *Solution Chemistry of Surfactants*, ed. K. L. Mital, Plenum Press, New York, 1979, vol. 1, p. 153.
- 37 M. Zulauf, K. Weckström, J. B. Hayter, V. Degiorgio and M. Corti, *J. Phys. Chem.*, 1985, **89**, 3411; L. J. Magid, in *Nonionic Surfactants. Physical Chemistry*, ed. M. J. Schick, Marcel Dekker, New York, vol. 23, p. 677.
- 38 L. García-Río, E. Iglesias, J. R. Leis, M. E. Peña and D. L. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1673.
- 39 R. P. Bell, *The Proton in Chemistry*, Chapman and Hall, London, 1973; L. Melander and W. H. Saunders, *Reaction Rates of Isotopic Molecules*, Wiley, New York, 1980.

Paper 3/07407B

Received 16th December 1993

Accepted 9th May 1994