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Water–Ethylene Glycol Alkyltrimethylammonium Bromide Micellar Solutions as Reaction Media: Study of Spontaneous Hydrolysis of Phenyl Chloroformate

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The spontaneous hydrolysis of phenyl chloroformate was studied in water–ethylene glycol (EG) micellar solutions of hexadecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide, and dodecyltrimethylammonium bromide, the percentage by weight of EG varying within the 0–50% range. The dependence of the observed rate constant on the surfactant concentration was investigated in all the water–EG mixtures. In addition to the kinetic measurements, conductivity, spectroscopic, and fluorescence measurements were done to obtain information about the micellar solutions used as reaction media. For the three surfactants studied, an increase in the amount of EG present in the mixture resulted in an increase in the critical micelle concentration and in an increase in the micellar ionization degree but in a decrease in the aggregation number of micelles. The polarity of the bulk–micelle interface region seems to increase somewhat by increasing the percentage by weight of EG. A simple pseudophase model was useful in rationalizing the micellar kinetic effects observed. The adjustable parameters obtained from the fittings of the experimental data show that the reaction rate in the micellar pseudophase was similar for all the water–EG cationic micellar solutions investigated. The equilibrium binding constant for the phenyl chloroformate molecules to the micellar aggregates decreases as the amount of EG in the mixture increases, this decrease being responsible for the diminution in the observed rate constant when the amount of EG present in the mixture increases.

Introduction

The self-assembly of surfactants in polar organic solvents such as formamide, *N,N*-dimethylformamide, dimethyl sulfoxide, dimethylacetamide, *N*-methylacetamide, glycerol, and ethylene glycol (EG) and in some aqueous–organic mixed solvents has been studied to investigate how the solvent characteristics influence aggregation.^{1–11} EG is of particular interest in that it has many characteristics similar to those of water. The molecule is small and can form hydrogen-bonded networks similar in nature to those in water, although differing considerably in the details of structure. Ethylene glycol also possesses a high cohesive energy and a fairly high dielectric constant.

Despite the interest shown in EG effects on the micellization process of several surfactants, to our knowledge no kinetic studies have been carried out in water–

EG micellar solutions, nor in most of the other water–cosolvent mixtures used in thermodynamic studies (with the exception of water–linear alcohols). Only one recent article about the application of the PIE model to a micellar catalyzed reaction in water–glycerol solutions was found by the authors.¹² Micelles can influence reaction rates and equilibria. In the case of bimolecular reactions, the concentration or depletion of reactants in the interfacial region have major effects on the reaction rates, these usually being called *micellar concentration effects*. Together with these, micelles also exert a *medium effect* that influences reactivity. This effect depends on the transfer of substrate from the bulk to the micelle, on the reaction mechanism, and on the properties of the interfacial region, such as local charge, polarity, and water content, and gives information about the micellar pseudophase characteristics as reaction media. For a bimolecular process, comparison of the second-order rate constants in the bulk phase and in the micellar pseudophase requires an estimation of the reagent concentrations within the micellar pseudophase as well as of the micellar reaction volume. This introduces uncertainties in the values of the second-order rate constants obtained, and the medium micellar effects are usually difficult to observe. With the idea of avoiding these uncertainties and to get information about the characteristics of the micellar pseudophases in water–EG micellar solutions, the spontaneous hydrolysis of phenyl chloroformate was studied in several cationic water–EG micellar solutions, changing the nature and concentration of the surfactant as well as the amount of EG present in the medium. This process has a well-known

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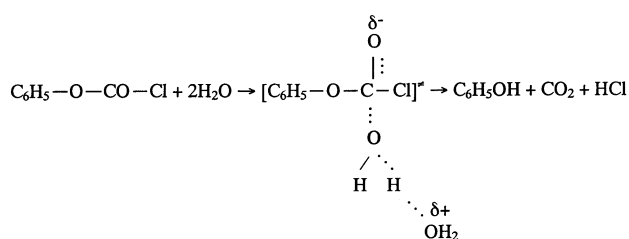
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Scheme 1



mechanism (see Scheme 1)^{13,14} and has been investigated in several aqueous micellar solutions.¹³ The surfactants were dodecyltrimethylammonium bromide, DTAB, tetradecyltrimethylammonium bromide, TTAB, and hexadecyltrimethylammonium bromide, CTAB. There is extensive information about the aqueous micellar solutions of these surfactants,¹⁵ and their study will provide information on the role of the chain length in the characteristics of the micellar pseudophases in water–EG micellar solutions.

In addition to the kinetic measurements, various experimental techniques were used to obtain thermodynamic and structural information about the water–EG micellar solutions. Critical micelle concentrations (cmc's) and micellar ionization degrees, α , were obtained from conductivity measurements. The cmc values were calculated by using various mathematical methods. The pyrene 1:3 ratio method,¹⁶ the solvent-dependent fluorescence of pyrene-3-carboxaldehyde,¹⁷ and the Reichardt's $E_T(30)$ parameter¹⁸ were used to get information about the polarity of the micellar pseudophase in the water–EG micellar solutions used as reaction media. Fluorescence quenching of pyrene by *N*-hexadecylpyridinium chloride in the water–EG micellar solutions enabled us to acquire some information about the aggregation number of the micelles in the water–EG micellar solutions.¹⁶

All the experiments were done at 298.2 K.

Experimental Section

Materials. Phenyl chloroformate was obtained from Aldrich, as was EG. All the surfactants were obtained from Fluka and used as received. HBr was from Fluka. Reichardt's dye, $E_T(30)$, pyrene, and pyrene-3-carboxaldehyde were obtained from Aldrich. The $E_T(30)$ dye was not purified, but the two pyrene compounds were purified before use by methods reported elsewhere.^{17,19}

Kinetics. Hydrolysis of phenyl chloroformate was recorded spectrophotometrically at 270 nm (appearance of phenol) with a Unicam Helios- α spectrophotometer in all the micellar media studied. The substrate was added to the reaction solutions in a

1-cm cuvette as relatively concentrated solutions in acetonitrile so that the final reaction mixtures contain 0.1 vol % in acetonitrile and the final substrate concentration was 10^{-4} mol dm⁻³. Phenyl chloroformate reacts readily with hydroxide ions. The reaction of the substrate with basic impurities was suppressed by the addition of HBr 1.5×10^{-3} mol dm⁻³ to the reaction medium. The presence of an HBr concentration within the range 10^{-2} – 10^{-3} mol dm⁻³ was found not to affect the rate constant in aqueous solution. The HBr concentration was kept constant and equal to 1.5×10^{-3} mol dm⁻³ in the kinetic measurements in all the cationic water–EG micellar solutions.

The possibility of the substrate reacting with the organic solvent (the EG was not purified) was checked by using 100% EG as the reaction medium in the absence of HBr. No change in absorbance within the range 220–400 nm was observed, and this possibility was ruled out.

The temperature for the kinetic runs was maintained at 298.2 ± 0.1 K by using a water-jacketed cell compartment. The observed rate constants were obtained from the slope of the $\ln(A_\infty - A_t)$ versus time plots, A_t and A_∞ being the absorbances at time t and at the end of the reaction, respectively. The kinetics were followed for more than five half-lives, and each experiment was repeated at least twice. Rate constants were reproducible within a precision of better than 5%.

To test our data, the observed rate constant value obtained in water, $k_w = 14.1 \times 10^{-3}$ s⁻¹, was compared with that in the literature, 13.6×10^{-3} s⁻¹.^{13d,e} Despite the experimental conditions not being the same, the agreement was good.

E_T Values. Spectra of the assay solutions containing the $E_T(30)$ dye were recorded in a Unicam Helios- α spectrophotometer at 298.2 K. These spectra were recorded against a blank consisting of an aqueous or water–EG micellar solution of a concentration identical to that of the assay solution. Five spectra were recorded for each assay solution.

The E_T values for DTAB, TTAB, and CTAB obtained were 53.7, 53.4, and 53.4, in good agreement with those in the literature.¹⁸

Conductivity Measurements. Conductivity was measured with a Crison microCM 2201 conductimeter connected to a water flow thermostat maintained at 298.2 ± 0.1 K. The conductivity cell was calibrated with KCl solutions of the appropriate concentration range.

Fluorescence Measurements. Fluorescence measurements were made by using a Hitachi F-2500 fluorescence spectrophotometer. The temperature was kept at 298.2 ± 0.1 K by a water flow thermostat connected to the cell compartment.

Solutions of pyrene (1×10^{-6} mol dm⁻³) in the different water–EG micellar media studied were prepared the same as in ref 20. In all cases, a surfactant concentration well above the cmc was used. Pyrene was excited at 334 nm, and its emissions were recorded at 373 and 384 nm, which correspond to the first and third vibrational peaks, respectively, with the use of excitation and emission slits of 10 and 5 nm, respectively. A scan speed of 240 nm/min was used. A value of I_{III}/I_I equal to 1.36 was found in CTAB micellar solutions, with [CTAB] = 0.02 M, in agreement with the literature data.²²

Solutions of pyrene-3-carboxaldehyde (10^{-5} mol dm⁻³) in the different water–EG micellar media studied were prepared in the same way that the pyrene solutions were. The surfactant concentration present in the micellar solutions was well above the cmc. Pyrene-3-carboxaldehyde was excited at 356 nm, and fluorescence spectra were recorded between 400 and 550 nm. A scan speed of 240 nm/min was used, and the excitation and emission slits were 10 nm. The fluorescence maxima shown in the spectra strongly depended on the polarity of the medium. The fluorescence maxima observed in pure EG, DTAB (0.1 M), and CTAB (0.02 M) were 454, 446, and 441 nm to be compared to 454, 446, and 440 nm.¹⁷ The agreement was good.

A study of the fluorescence quenching of pyrene by *N*-hexadecylpyridinium was carried out. The introduction of pyrene in the water–EG micellar solutions was done the same as in ref 21.

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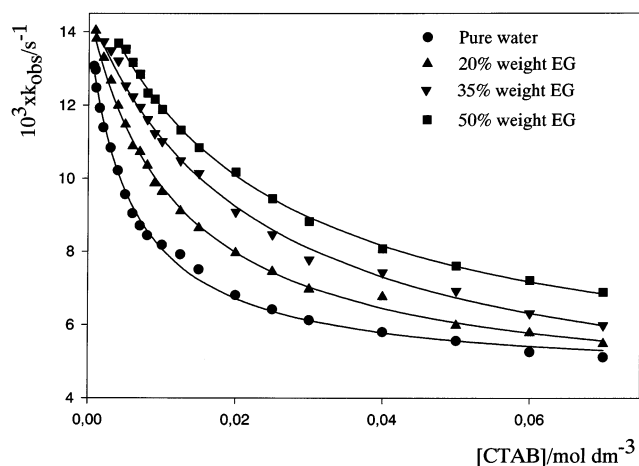


Figure 1. Dependence of the observed rate constant for the spontaneous hydrolysis of phenyl chloroformate on surfactant concentration in various water-EG CTAB micellar solutions. $T = 298.2$ K.

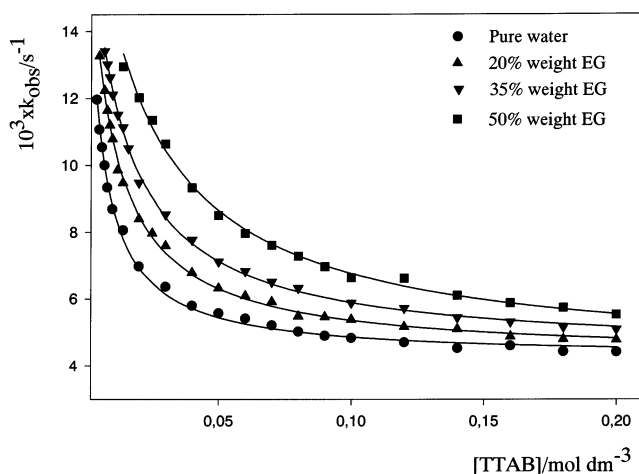


Figure 2. Dependence of the observed rate constant for the spontaneous hydrolysis of phenyl chloroformate on surfactant concentration in various water-EG TTAB micellar solutions. $T = 298.2$ K.

The probe concentration was kept low enough (2×10^{-6} mol dm^{-3}) to avoid excimer formation, and the quencher concentration was varied from 5×10^{-5} to 25×10^{-5} mol dm^{-3} . These values give [pyrene]/[micelles] and [quencher]/[micelles] ratios low enough to ensure a Poisson distribution.²³

Results

Figures 1–3 show the dependence of the observed rate constant for the spontaneous hydrolysis of phenyl chloroformate on the surfactant concentration for DTAB, TTAB, and CTAB water-EG micellar solutions in the presence of 0, 20, 35, and 50 wt % EG in the water-cosolvent mixtures. Table 4 shows the values of the observed rate constant for the reaction studied in water-EG mixtures, in the absence of surfactant. In the case of CTAB, kinetic experiments for surfactant concentrations higher than 0.08 M could not be carried out as a result of solubility problems. In all cases, an increase in the surfactant concentration decreases the observed rate constant. For a given surfactant, the reaction rate increases upon increasing the amount of EG present in the medium.

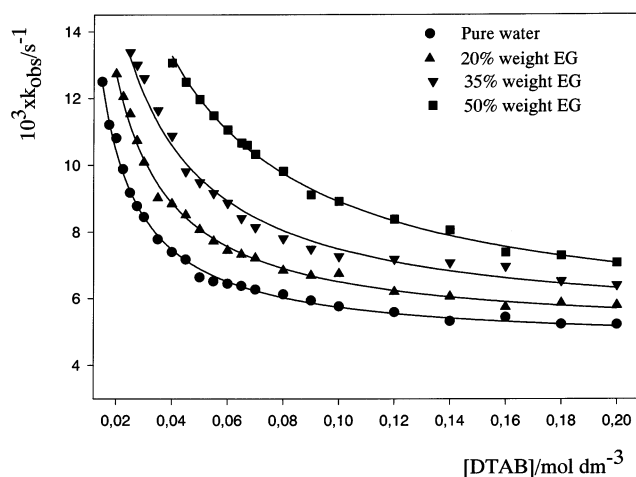


Figure 3. Dependence of the observed rate constant for the spontaneous hydrolysis of phenyl chloroformate on surfactant concentration in various water-EG DTAB micellar solutions. $T = 298.2$ K.

Table 1. cmc's and Micellar Ionization Degrees, α , of DTAB, TTAB, and CTAB in Water-EG Mixtures at 298.2 K

percent weight EG	$10^3 \times \text{cmc (mol dm}^{-3}\text{)}$		α	
	no HBr	[HBr] = 1.5×10^{-3} M	no HBr	[HBr] = 1.5×10^{-3} M
CTAB				
0	0.925	0.527	0.22	0.21
20	1.31	0.830	0.25	0.24
35	2.15	1.54	0.26	0.25
50	4.26	3.39	0.29	0.29
TTAB				
0	3.62	3.00	0.23	0.21
20	4.59	4.23	0.25	0.24
35	6.30	6.39	0.26	0.26
50	12.9	11.9	0.30	0.30
DTAB				
0	14.5	13.8	0.25	0.25
20	17.3	17.4	0.28	0.28
35	23.1	22.8	0.34	0.32
50	36.9	33.9	0.38	0.38

The cmc values for the different water-EG cationic micellar solutions used as reaction media in the absence as well as in the presence of $[\text{HBr}] = 1.5 \times 10^{-3}$ M are listed in Table 1. The cmc's obtained for aqueous CTAB, TTAB, and DTAB surfactant solutions are in good agreement with those in the literature.¹⁵ The micellar ionization degrees, α , of the water-EG cationic micellar solutions are also listed in Table 1. Those corresponding to the aqueous micellar solutions agree with the previous data.¹⁵ At this point, the calculation of the cmc and α values summarized in Table 1 deserves some comments. The authors, when using conductivity measurements, usually determined the cmc values from inflections in plots of conductivity, κ , against the surfactant concentration (Williams method).²⁴ The data points above and below the inflection are fitted to two equations of the form $\kappa = A[\text{surfactant}] + B$, and by solving simultaneously the two equations the point of intersection is obtained. Least-squares analysis is employed. Subsequently, the micellar ionization degree is calculated from the ratio of the slopes of the plots of κ versus [surfactant] above and below the cmc. This method allows one to calculate a reliable value for the cmc, and also for α , when conductivity shows an

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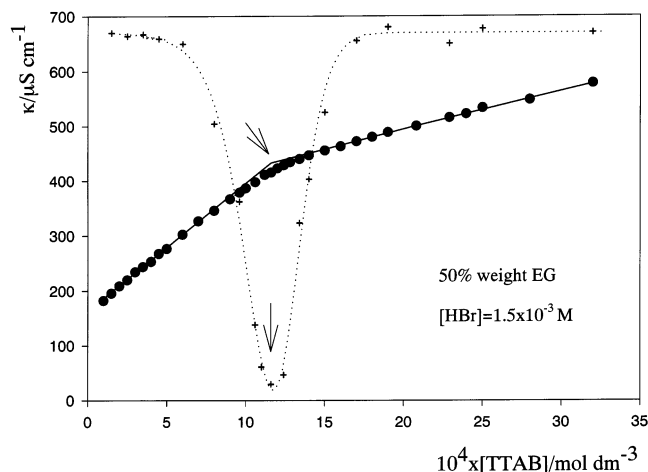


Figure 4. Specific conductivity, κ ($\mu\text{S cm}^{-1}$), of TTAB in water-EG (50 wt % EG) solutions as a function of molar surfactant concentration, in the presence of $[\text{HBr}] = 1.5 \times 10^{-3} \text{ M}$. (●) Experimental points; (+) second derivative. The arrows denote the cmc's calculated by the Williams and the Phillips methods. Gaussian is the dotted line. $T = 298.2 \text{ K}$.

abrupt change in going from the premicellar surfactant concentration range to the postmicellar surfactant concentration range. This is the case for the micellar aqueous solutions of DTAB, TTAB, and CTAB and for most of the water-EG surfactant solutions investigated. However, the addition of EG to aqueous cationic micellar solutions results in an increase in the micellar ionization degree.⁶ An increase in α supposes a less abrupt change in the conductivity and, therefore, some uncertainties in the evaluation of the cmc and of α by using the Williams method. To investigate this point, the Phillips method was considered.²⁵ Phillips defined the cmc as the concentration corresponding to the maximum change in a gradient in a solution property versus concentration ($\phi - c_t$) curve

$$(\text{d}^3\phi/\text{d}c_t^3)c_t = \text{cmc} = 0 \quad (1)$$

where

$$\phi = a[\text{S}] + b[\text{M}] \quad (2)$$

a and b being constants of proportionality and $[\text{S}]$ and $[\text{M}]$ the concentrations of the monomeric surfactant and of the micelles, respectively. The Phillips method was applied in two forms. The first, which is denoted *classical*, consists of directly fitting the second derivative of the conductivity/concentration data to a Gaussian without additional treatment of the data. The second consists of an integration by the Runge-Kutta method and a least squares Levenberg-Marquardt fitting. The application of the Runge-Kutta method to the conductivity data is described in ref 26. Figure 4 shows an example of the Phillips method application in its classical form. The crosses represent the second derivative, and the dotted line corresponds to the Gaussian. The arrows denote the cmc calculated by the Williams and Phillips methods. Figure 5 shows an example of the Phillips method application, as was proposed by Mosquera et al.²⁶ The dotted line corresponds to the Gaussian. The minimum corresponds to points of maximum variation and coincides with the cmc (denoted

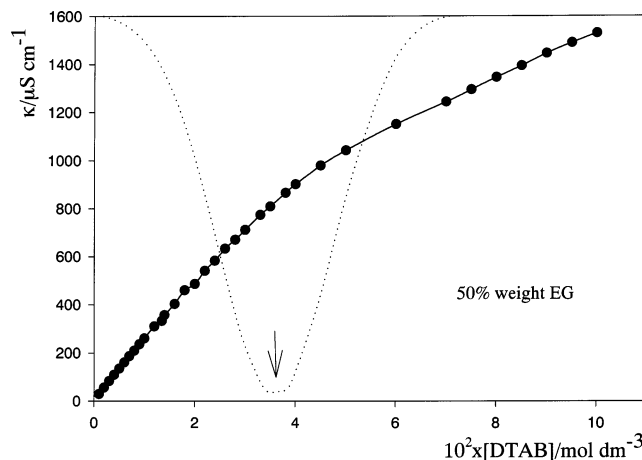


Figure 5. Specific conductivity, κ ($\mu\text{S cm}^{-1}$), of DTAB in water-EG (50 wt % EG) solutions as a function of molar surfactant concentration. (●) Experimental points. The continuous line is the fitting curve of these points. The dotted line corresponds to the Gaussian, and the arrow denotes the cmc.

Table 2. Reichardt's Parameter (E_T), I_{III}/I_I Intensity Ratio of the 1:3 Pyrene Vibronic Bands, and Wavelength of the Fluorescence Maximum of Pyrene-3-carboxaldehyde (λ_{max}) for CTAB, TTAB, and DTAB Water-EG Micellar Solutions at 298.2 K

percent weight EG	E_T (kcal mol ⁻¹)	I_{III}/I_I	λ_{max} (nm)
CTAB ^a			
0	53.4	1.36	441
20	53.3	1.35	445
35	53.4	1.36	448
50	54.0	1.39	453
TTAB ^b			
0	53.4	1.37	443
20	53.5	1.36	447
35	53.5	1.36	449
50	54.2	1.40	455
DTAB ^c			
0	53.7	1.40	454
20	53.7	1.40	455
35	53.7	1.41	457
50	54.9	1.44	462

^a [CTAB] = 0.02 M. ^b [TTAB] = 0.07 M. ^c [DTAB] = 0.1 M.

by an arrow). The cmc's obtained by using the three methods were in good agreement for all the surfactant solutions studied. This means that the use of the Williams method is appropriate in this work and gives reliability to the micellar ionization degrees listed in Table 1.

Table 2 shows the values of the Reichardt's parameter, $E_T(30)$, the intensity ratio of the vibronic bands 1:3, I_{III}/I_I , of pyrene and the maximum fluorescence wavelength of pyrene-3-carboxaldehyde for the water-EG cationic micellar solutions studied.

Discussion

Table 1 shows the cmc and micellar ionization degrees, α , of the water-EG cationic micellar solutions used as reaction media in the presence and in the absence of $[\text{HBr}] = 1.5 \times 10^{-3} \text{ mol dm}^{-3}$. In all cases, the cmc is a little smaller in the presence of than in the absence of the acid, the difference not being large because the electrolyte concentration is low. This is an expected result because the addition of an electrolyte to an ionic surfactant solution provokes a screening of the electrostatic repulsion of dissociated headgroups, which corresponds to a decrease of the electrostatic contribution to the free enthalpy of

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Table 3. Standard Free Energy of Micelle Formation, ΔG_M° , and the Effect of EG on the Free Energy of Micellization, ΔG_{EG}° , for CTAB, TTAB, and DTAB Micellar Solutions at 298.2 K^a

percent weight EG	$-\Delta G_M^\circ$ (kJ mol ⁻¹)	ΔG_{EG}° (kJ mol ⁻¹)
CTAB		
0	30.46 (33.47)	
20	28.78 (30.93)	1.68 (2.54)
35	26.48 (28.08)	3.98 (5.47)
50	23.12 (24.09)	7.34 (9.38)
TTAB		
0	24.65 (25.76)	
20	23.34 (23.83)	1.31 (2.42)
35	21.84 (21.78)	2.81 (3.92)
50	18.32 (18.66)	6.33 (7.10)
DTAB		
0	18.35 (18.57)	
20	17.29 (17.26)	1.06 (1.31)
35	15.50 (15.74)	2.85 (2.83)
50	13.24 (13.58)	5.11 (4.99)

^a The values in parentheses correspond to the surfactant solutions in the presence of [HBr] = 1.5×10^{-3} M.

micellization.²⁷ With regard to the micellar ionization degree, the presence of the low concentration of HBr used in the reaction media practically does not affect its value. The data in Table 1 can be used to obtain the Gibbs free energy of micellization, ΔG_M° , by considering eq 3:^{28,29}

$$\Delta G_M^\circ = (2 - \alpha)RT \ln \text{cmc} \quad (3)$$

where α is the micellar ionization degree. Table 3 shows the values of the standard free energy of micelle formation obtained by using eq 3. The values in parentheses are those obtained in the presence of [HBr] = 1.5×10^{-3} M. One can see from these values that the free energy of micellization becomes less spontaneous upon increasing the amount of EG present in the surfactant solutions for the three surfactants studied. It is interesting to point out that eq 3 is applicable when the aggregation number is large. Because a decrease in the aggregation number of the cationic micelles investigated as the amount of EG increases is expected,¹⁰ eq 3 may not be accurate for the higher concentrations of cosolvent used in this work, particularly in the case of DTAB.¹⁵ Therefore, some of the data listed in Table 3 have to be viewed as an approximation.

Before discussing the aggregation behavior of CTAB, TTAB, and DTAB in water–EG mixtures, the authors tried to obtain some information about the dependence of the aggregation number of the cationic micellar aggregates on the amount of EG present in the mixture. The quenching of pyrene by hexadecylpyridinium chloride (CpyC; the Turro and Yekta method)³⁰ was used in CTAB micellar solutions in the presence of 0 and 50 wt % EG in [CTAB] = 0.02 M. Following the work of Schryver,³¹ the correction factor for the CpyC that remains in water was considered, and the aggregation numbers obtained were 51 and 37, respectively. The value of N_{agg} obtained in water is small.¹⁵ An explanation for this low value was given in ref 31 by considering that the quenching process with CpyC is not very effective. For such a bulky quencher

in large CTAB micelles, the diffusion toward an excited probe molecule is too slow to ensure complete quenching in all micelles containing both an excited probe and a quencher molecule. There is another point that can also be responsible for the nonadequacy of the quenching method used to obtain N_{agg} in the cationic micellar solutions studied. As indicated by Grätzel and Thomas,³² the CTAB micelles contain a large fraction of adsorbed bromide ions that quenched the pyrene excited state. Nonetheless, despite the method rendering aggregation numbers too low, it is clear that N_{agg} decreases by increasing the amount of EG in the mixture, according to the theoretical estimations of Nagarajan and Wang.¹⁰ Some quenching experiments done with TTAB and DTAB water–EG micellar solutions also showed that N_{agg} decreases by increasing the amount of EG present in the mixture.

To explain the dependence of the cmc, α , and N_{agg} on the amount of EG present in the mixture, three solvent-dependent contributions to the free energy of micellization can be considered:¹⁰ (i) the surfactant tail transfer free energy, (ii) the aggregate–core solvent interfacial free energy, and (iii) the headgroup interaction free energy on the composition of the mixed solvents. The large magnitude of the cmc originates mainly from the small magnitude of the tail transfer free energy from EG compared to that from water. In respect to the decrease in the aggregation number, it can be rationalized as being due to the low EG–hydrocarbon interfacial tension compared with the water–hydrocarbon interfacial tension. The dielectric constant of EG is smaller than that of water (37.7 compared to 78.39 at 298.2 K),³³ for 50 wt % EG the dielectric constant has decreased from 78.39 in pure water to 65.75 at 298.2 K.³³ However, the ionic interactions at the micelle surface decrease rather than increase in water–EG mixtures because of the higher monomer concentration (because of the larger cmc's), which gives rise to higher ionic strengths. Nonetheless, despite the larger ionic strengths and weaker ionic headgroup repulsions (and, therefore, higher micellar ionization degrees) the equilibrium aggregation numbers are small because of the dominating influence of the interfacial energy contribution. To calculate the effect of EG on the micelle aggregation process, eq 4 can be used:^{9c}

$$\Delta G_M^\circ = \Delta G_{M(\text{EG-water})}^\circ - \Delta G_{M(\text{water})}^\circ \quad (4)$$

the values of ΔG_{EG}° are listed in Table 3 for the three surfactants studied. The values in parentheses are those obtained in the presence of [HBr] = 1.5×10^{-3} M. One can see from Table 3 that the presence of EG in the bulk phase affects the aggregation process more the longer the hydrocarbon chain of the surfactant is. This is a reasonable result if variations in the surfactant tail transfer free energy are the main factor controlling the cmc. Table 3 also shows that the presence of HBr strengthens the effect of EG on the micellization in CTAB and TTAB (although the effect is major in TTAB), not affecting the ΔG_{EG}° values in DTAB. This could be due to the fact that the relative increase in the ionic concentration in the bulk provoked by the presence of [HBr] = 1.5×10^{-3} M follows the trend CTAB > TTAB > DTAB. Nonetheless, taking the assumptions involved in eq 3 and, thus, in eq 4 into account, the data in Table 3 have to be viewed as approximate.

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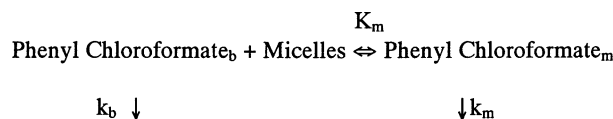
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To obtain some information about the polarity of the micellar surface region of the different aggregates in water–EG mixtures, the Reichardt E_T parameter was used. The results obtained are listed in Table 2. This table shows that CTAB and TTAB micellar surfaces have similar polarities, the DTAB micellar surface being somewhat more polar, as was found before.¹⁸ On the other hand, on the basis of the E_T values, the polarities of the micellar surfaces of the three cationic micelles studied are similar for 0, 20, and 35 wt % EG in the mixture, 50% EG being more polar. To check if these results could be due to some impurities of the commercial EG used, the E_T parameter was obtained for the water–EG mixtures in the absence of surfactants, when possible. The E_T value for pure water is 63.1 kcal mol⁻¹ and for pure EG is 56.3 at 298.2 K.³⁴ We obtained the values of 60.5 and 59.8 for the Reichardt parameter in 35 and 50% EG in water at 298.2 K. Therefore, the trend shown in Table 2 is not due to any impurity of the solvent used. The E_T parameter gives information about the polarity of the surroundings of the $E_T(30)$ molecules in the micellar solutions. NMR studies in various water micellar solutions have shown that $E_T(30)$ molecules are predominantly solubilized in the micellar surface region.¹⁸ If the addition of EG to the medium results in the $E_T(30)$ molecules moving further away from the micellar core, in the penetration of solvent molecules in the palisade layer, or both, their direct environment will be more polar and the E_T value will be higher. The authors decided to investigate the polarity of the micellar surface by using two other methods: the intensity ratio of the 1:3 vibronic bands of pyrene¹⁶ and the fluorescence maximum of pyrene-3-carboxaldehyde.¹⁷ The results obtained are summarized in Table 2.

The vibrational band intensities of pyrene monomer are solvent-dependent. They show a strong dependence on the solvent environment, both the solvent dipole moment and dielectric constant being important in this effect. The relative intensities of the third and first vibronic peaks of the pyrene fluorescence spectra are directly related to the apparent dielectric constant where the probe is housed. The I_{III}/I_I values shown in Table 2 for the aqueous cationic micellar solutions indicate that pyrene is located close to the micellar surface in all the micellar solutions studied.³⁵ One can see that the ratio follows the trend CTAB \approx TTAB < DTAB. With regard to the effect of the EG presence in the solutions, Table 2 shows that the polarities of the pyrene surroundings are similar for 0, 20, and 35% EG, increasing slightly in the case of 50% EG for the three surfactants studied. The results agree with those obtained by using the Reichardt parameter.

Excitation of dilute solutions of pyrene-3-carboxaldehyde (with light of wavelength 360 nm) leads to a blue-violet fluorescence. The fluorescence is due to the monomeric, excited singlet state and displays a strong solvent dependence.¹⁸ The fluorescence maximum shows a red shift with increased solvent polarity. For several pure solvents and solvent mixtures, a linear relationship between the fluorescence maximum and the bulk dielectric constant has been found. NMR and UV spectral studies have shown that pyrene-3-carboxaldehyde molecules are solubilized in micelles with their hydrophobic (aromatic) moiety in the micellar core and with the hydrophilic group protruding into or anchored at the micellar surface or

Scheme 2



Products

double layer.³⁶ The values of λ_{\max} in Table 2 provide a direct measure of the polarity of the micelle–bulk interface region. Therefore, one can see that for aqueous micellar solutions the polarity of the micelle–water interface region follows the trend CTAB < TTAB < DTAB, although the CTAB and TTAB interfaces are more similar than that of DTAB. With regard to the effect of the addition of EG to the mixture, the interface region becomes more polar when the amount of EG present in the mixture increases, although the greater change is from 35 to 50 wt % EG for the three surfactants investigated. The three methods used show that when the EG percentage by weight increases from 0 to 50%, the bulk–micelle interface region becomes more polar. The observed changes in λ_{\max} , E_T , and I_{III}/I_I could be related to the decrease in the aggregation number of the aggregates when the amount of EG present in the mixture increases. A decrease in N_{agg} would suppose a less-packed micelle, thus making the penetration of solvent molecules and water, as well as EG, in the palisade layer easier and resulting in a more polar environment of the polarity probes.

Now that information about the micellar solutions used as reaction media has been obtained, the kinetic data will be considered. Figures 1–3 show the dependence of the observed rate constant for the spontaneous hydrolysis of phenyl chloroformate on the surfactant concentration for water–EG mixtures in the presence of 0, 20, 35, and 50 wt % EG, the surfactants being CTAB, TTAB, and DTAB. In all cases, the hydrolysis is retarded by the presence of micelles. This is understandable in that deacylations are inhibited by decreases in the solvent polarity and water content, and these are less in micellar interfacial regions than they are in water. However, this inhibition is not large, indicating that the reaction occurs in a relatively *wet* region; that is, the hydrolysis takes place in the bulk–micelle interface region. For CTAB, TTAB, and DTAB, an increase in the amount of EG present in the mixture results in an increase in the observed rate constant.

In the presence of micelles, the reaction occurs as shown in Scheme 2, where k_b and k_m refer to pseudo-first-order rate constants in the bulk (that is, in the water–EG mixtures) and micellar pseudophases, respectively. K_m is the equilibrium binding constant of the phenyl chloroformate molecules to the micelles present in the reaction medium, and it is written in terms of the molarity of micellized surfactant. In a previous work,^{13f} the fractional charge at the reaction center in the hydrolysis of phenyl chloroformate was estimated using the Eyring equation to analyze the micellar rate effects in cationic and anionic micellar solutions.³⁷ An apparent fractional charge in the transition state equal to -0.25 was estimated. Despite the simplifications involved in the model used, this was taken as indicative of a negative fractional charge developing at the reaction center, in agreement with the mechanism proposed in Scheme 1. That is, the mechanism in aqueous micellar solutions was the same as that in

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Table 4. Influence of the Amount of EG on the Spontaneous Hydrolysis of Phenyl Chloroformate in Water–EG Mixtures at 298.2 K ([HBr] = 1.5×10^{-3} M)

percent weight EG	0	20	35	50
$10^3 \times k_{\text{obs}}$ (s ⁻¹)	14.1	13.8	13.9	13.8

Table 5. Equilibrium Binding Constants and Pseudo-First-Order Rate Constants for the Hydrolysis of Phenyl Chloroformate in Various Water–EG Alkyltrimethylammonium Bromide Micellar Solutions Obtained from the Fittings of the Kinetic Data by Using Eq 5 at 298.2 K

percent weight EG	K_m (mol ⁻¹ dm ³)	$10^3 \times k_m$ (s ⁻¹)
CTAB		
0	104	4.4
20	77	4.0
35	41	3.9
50	39	4.1
TTAB		
0	100	4.2
20	80	4.2
35	56	4.4
50	30	4.1
DTAB		
0	76	4.6
20	55	4.9
35	34	5.0
50	20	4.9

water. Some experiments have shown that, in the presence of 50 wt % EG, the spontaneous hydrolysis of phenyl chloroformate is substantially slower in anionic than in cationic water–EG micellar solutions (as was found in aqueous micellar solutions); this indicates that a negative fractional charge in the transition state is developed in water–EG mixtures. On this basis, it is reasonable to assume that the reaction occurs through a mechanism in water–EG the same as that in water micellar solutions. Following Scheme 2, the observed rate constant can be written as³⁸

$$k_{\text{obs}} = \frac{k_b + k_m K_m [\text{surfactant}_m]}{1 + K_m [\text{surfactant}_m]} \quad (5)$$

In this equation, $[\text{surfactant}_m] = [\text{surfactant}_{\text{total}}] - \text{cmc}$. The solid lines in Figures 1–3 were obtained from the fittings of the kinetic data by using eq 5. The cmc and k_b values considered in the fittings were those listed in Table 1 (in the presence of HBr) and Table 4, respectively. One can see that the agreement between the experimental and the theoretical kinetic data was good for the three surfactants investigated. Values for the two adjustable parameters obtained, k_m and K_m , are listed in Table 5 and agree with the literature data.^{13e} Before discussing the values listed in Table 5, it is worth noting that recently,³⁹ various authors have stressed the problem concerning the possible lack of meaning of the kinetic constants estimated from the fittings of the kinetic data. In this regard, the use of k_b and cmc experimental data has reduced as much as possible the number of adjustable parameters, and the values listed in Table 5 are those that render the best fittings. Unfortunately, the equilibrium binding constants

cannot be determined experimentally because of hydrolysis, and this results in more uncertain k_m values. Taking this into account, small changes in k_m and K_m will be considered meaningless.

The K_m values estimated are low in all the water–EG micellar solutions studied. Low equilibrium binding constants were also found by El Seoud et al.^{14b} for the substrate 4-nitrophenyl chloroformate in various micellar solutions and are typical of organic solutes with a phenoxy group.⁴⁰ The K_m values found for phenyl chloroformate decrease upon increasing the amount of EG present in the mixture, K_m seeming a little smaller for DTAB with respect to CTAB and TTAB. This diminution can be explained by considering that an increase in the percentage by weight of EG provokes changes in the characteristics of the bulk phase of the micellar solutions, which improves the solubilization of phenyl chloroformate within it with respect to its solubilization in the cationic micelles. A decrease in the dielectric constant, in the Reichardt parameter, E_T , in the Gutman donor number, DN, or in the π^* polarity index³³ would result in the water–EG mixtures being a better solvent for the organic substrate the higher the percentage by weight of EG is. Besides, the data in Table 2 show that the bulk–micelle interface region (where the phenyl chloroformate molecules are expected to be located)^{13e} seems to become more polar when the amount of EG in the mixture increases, making the affinity of the organic substrate molecules for the micellar aggregates weaker. On this basis, a diminution in K_m is expected going from water to water–EG 50%, as is found.

The k_m values are not much affected by the presence of EG in any of the micellar solutions studied, the values being similar for CTAB, TTAB, and DTAB. As was mentioned above, an increase in the amount of EG in the mixture diminishes the polarity of the bulk phase of the micellar solution. However, Table 2 shows that a parallel diminution in the polarity of the micellar interfacial region does not occur, this being higher in the presence of 50% EG than in its absence. Nonetheless, because the changes in the polarity showed in Table 2 are not large and the reaction under study is not particularly sensitive to changes in the polarity of the medium, no substantial changes in the rate of the spontaneous hydrolysis investigated were expected. Brinchi et al.^{13e} found for the reaction under study that the rate constant in the micellar pseudophase followed the trend CTACI > CTAOMs > CTABr, OMs being mesylate. This sequence was explained by considering that the cationic character and the water content of the micellar interfacial region follow the same trend. In the case of the surfactants studied, CTAB and TTAB have similar micellar ionization degrees and DTAB micelles seem a little more ionized (Table 1 and ref 15). However, no large differences were found and, therefore, no substantial changes in k_m were expected, as found.

In conclusion, the increase in the percentage by weight of EG from 0 to 50% in CTAB, TTAB, and DTAB water–EG micellar solutions results in a less spontaneous micellization process, an increase of the aggregation number, and an increase in the micellar ionization degree. However, all these structural changes are not accompanied by large changes in the polarity of the bulk–micelle interfacial region, characterized by spectroscopic and fluorescence probes. This is shown through the kinetic micellar effects observed on the spontaneous hydrolysis

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of phenyl chloroformate in the same water–EG cationic micellar solutions. Whereas the equilibrium binding constant for the organic substrate decreases by increasing the amount of EG in the mixtures (the water–EG mixture is a better solvent for organic compounds than water), the rate constant in the micellar pseudophase is not practically affected by the presence of EG in the bulk phase of the micellar reaction medium. In fact, the increase in the observed rate constant found in the water–EG micellar solutions upon increasing the percent by weight of EG was due to the diminution of K_m . That is, when the amount of EG present in the mixture increases, the percentage of the reaction occurring in water increases. The agreement between the kinetic theoretical and experimental data showed that, at least for the reaction studied, the simple

pseudophase model used is adequate to rationalize kinetic micellar effects in water–EG cationic micellar solutions.

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