of 3-hexyne/1-butyne of 2.1 was observed,[15] and if the same ratio is applicable to 2-butyne/1-butyne, a rate ratio $MeCH{=}C{=}CH_2/EtC{\equiv}CH$ of 30 can be calculated, as compared to the $CH_2{=}C{=}CH_2/MeC{\equiv}CH$ ratio of 3.8–5.7 observed here. The enhanced rate for $MeCH{=}C{=}CH_2$ indicated by this comparison seems reasonable[17] and reinforces the conclusion that hydration and CF_3CO_2H additions are comparable reactions proceeding through formation of carbocation intermediates.

Another interesting comparison can be made between the reactivity of allene and that of propene. The latter compound was studied[8a] in sulfuric acid concentrations that overlap those reported here for allene, and the rate ratio k(propene)/k(allene) in 9.12 M H_2SO_4 is only 6.5, with an interpolated rate for propene. Thus these reactions, both of which are interpreted as involving rate-limiting protonation on sp^2-hybridized carbon, proceed at rates that are rather close even though the allene reaction involves formation of a vinyl cation.[18] The rate ratio k(propene)/k(propyne) at this acidity is 37, which is surprisingly significantly larger than the reported ratio of 3.6 for k(1-hexene)/k(1-hexyne).[11] The origin of this difference is under study.

In summary, the experimental evidence is consistent with the most simple explanation, namely, that protonation of allene and propyne occurs at carbon to form the same 2-propenyl cation 1 in each case. The theoretical studies strongly favor this route, so the Ad_E2 mechanism for acid-catalyzed hydration of allene and propyne may be considered to be firmly established.

Experimental Section

Allene was obtained from PCR, Inc., propyne from Matheson of Canada Ltd., and deuterated sulfuric acid from Aldrich. These reagents were used as received. Concentrations of acid solutions were measured by titration. Kinetics were measured by bubbling the gases into the acid solution in 1-cm UV cells and then tightly capping the cells so that no gas spaces were left. The decrease in the end absorption of the substrates was monitored with time at 214 nm for allene and 205 nm for propyne. Unicam SP 1800 and Cary 14 spectrophotometers were used. Duplicate runs were made in all cases.

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Registry No. Allene, 463-49-0; propyne, 74-99-7.

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[17] The methyl group in $MeCH{=}C{=}CH_2$ would be expected to have a significant stabilizing effect on the developing vinyl cation 5 even though it is not directly substituted on the cationic carbon. When allenic methyls are on carbons where positive charge develops even larger effects are observed. Thus, the rate of protonation of $Me_2C{=}C{=}CHOAc$ at C_2 is about 100 times faster than the protonation at C_2 of $CH_2{=}CHOAc$.[3f]

[18] The rate ratio $k(EtOCH{=}CH_2)/k(EtOCH{=}C{=}CH_2)$ is only 1.5.[3g]

Kinetics of the Aminolysis of Ethyl *p*-Nitrophenyl Carbonate in the Presence of Dodecylammonium Diethylarsinate Aggregates in Chloroform. Complex Effects of Solubilized Water

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The kinetics of the aminolysis of ethyl *p*-nitrophenyl carbonate (ENPC) by dodecylamine (DA), dodecylammonium diethylarsinate (DADEA; dry aggregates and in the presence of solubilized water), and DA plus dry DADEA in chloroform were studied spectrophotometrically. Addition of 0.20 M of the surfactant enhances the rate of aminolysis by DA by a factor of 28.3 due to bifunctional catalysis by the former. In the aminolysis by 0.20 M DADEA, the rate constants were a function of the water/surfactant molar ratio R. Thus, they were insensitive to the presence of solubilized water up to $R = 0.55$, followed by a gradual decrease at higher R values. From the obtained activation parameters it could be seen that solubilized water affects both $\Delta H^\ddagger$ and $\Delta S^\ddagger$, and these showed a series of quasi-mirror-imaged maxima and minima at different R values. These results were rationalized in terms of the effects of water on the rigidity of the micelle, on the micelle–substrate interactions, and on the stabilization of the reagent and transition states.

Alkylammonium carboxylates and halides dissolve in nonpolar solvents to form reversed micelles whose "core" contains the surfactant head ions.[1] Reversed micelles catalyze several types of reactions, e.g., ester aminolysis and hydrolysis,[1–4] and the hydration of carbonyl compounds.[5] In all these reactions, the rate constants depend on the concentration of solubilized water. This dependence was rationalized in terms of the hydration of the surfactant head groups which changes their catalytic efficiency and alters the substrate–surfactant interactions.[1–5] Additionally, water can alter the micellar parameters (e.g., shape and aggregation number)[7] and the properties of the substrates present in the micellar core (e.g., their pK_a values).[8]

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[2] C. J. O'Connor, E. J. Fendler, and J. H. Fendler, *J. Org. Chem.*, **38**, 3371 (1973).

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Because of the interdependence of the above-mentioned factors, a clearer idea may be obtained by examining how water affects the reaction activation parameters. The few available data show that the activation parameters in the presence of solubilized water are usually different from those in bulk water,[1,2,6] and a recent publication[9] showed linear plots of $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ from which the isokinetic temperature was determined. These reports show that our understanding of the role of cosolubilized water is far from clear and demonstrate the need for more work in this area. We report here on the preparation and catalytic activity of a new type of surfactant, DADEA, which forms reversed micelles in nonpolar solvents. After an unambiguous determination of the nature of the reaction occuring between ENPC and DADEA, we studied the effects of solubilized water on the activation parameters of this reaction. The quasi-mirror-imaged dependence of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ on the water concentration was rationalized in terms of the effects of water on the rigidity of the micelle, the micelle-substrate interactions, and the relative stabilization of the reagent and transition states. The reaction with DA plus DADEA was also examined and the catalytic role of the surfactant accounted for.

Experimental Section

Melting points were not corrected. ^{1}H NMR analysis was carried out using a Varian XL-100 spectrometer, and chemical shifts are given in ppm relative to internal Me_4Si (δ 0). IR spectra were obtained with a Perkin-Elmer Model 238 spectrometer using a pair of matched CaF_2 cells whose path length was 0.2 mm.

Chloroform (Merck, Uvasol) was further dried by being stored over activated 4A molecular sieves. Dodecylamine (Aldrich) was distilled from CaH_2, and *p*-nitrophenol (Aldrich) was crystallized from benzene and dried in vacuo. Methyl-*N*-dodecylurethane was obtained from Professor J. Sunamoto[9] and diethylarsinic acid was a gift from Professor K. J. Irgolic. The acid was recrystallized from ethanol to give shiny white crystals, mp 136–137 °C (lit.[10] mp 136–137 °C). DADEA was prepared by heating, under nitrogen, equimolar amounts of diethylarsenic acid and DA at 60 °C for several hours. The solid product was dried in vacuo and analyzed: ^{1}H NMR (CCl_4) δ 0.89 (t, 3 H, CH_3 ammonium ion), 1.25–1.45 (m, 26 H, 2 CH_3 of arsinate plus $(CH_2)_{10}$ of the ammonium ion), 1.89 (q, 4 H, 2 CH_2 of arsinate) 2.66 (t, 2 H, CH_2NH_3), 6.90 (s, 3 H, $^+NH_3$). Anal. Calcd for $C_{16}H_{38}AsNO_2$: C, 54.69; H, 10.90; N, 3.98. Found: C, 54.49; H, 10.92; N, 3.99.

ENPC was prepared by slowly adding 2.8 mL (29 mmol) of ethyl chloroformate dissolved in 10 mL of dry acetonitrile to a cold (0 °C) suspension of 3.2 g (20 mmol) of sodium *p*-nitrophenoxide in 20 mL of acetonitrile. After the mixture was stirred at 0 °C for 30 min and for 2 h at room temperature, the solvent was removed and the product crystallized from benzene–acetonitrile to yield 2.56 g (65% yield) of slightly yellowish crystals, mp 66–66.5 °C (lit.[11] mp 66 °C).

Kinetic measurements were carried out spectrophotometrically by using Zeiss DMR-10 and PM6KS spectrometers equipped with thermostated cell holders, and the temperature inside the cell was controlled to ±0.05 °C. DADEA was weighed, dried in vacuo (ca. 0.1 torr) over P_2O_5 for several hours, and reweighed before the stock solution was made up. The latter was renewed daily.

Kinetic experiments were carried out as given before[3] and were monitored by the appearance of the liberated *p*-nitrophenol at 311 nm. The final reagent concentrations in the reaction cuvette were 5×10^{-5} M ENPC, 0.08–0.16 M DA, and 0.024–0.20 M DADEA for the experiments in the absence of solubilized water and 0.20 M in the presence of DA or water. Observed rate constants (k_{obsd}) were obtained from the absorbance–time data by using a Burroughs 6700 computer. Good first-order rate constants were obtained in all cases and were accurate within 3%.

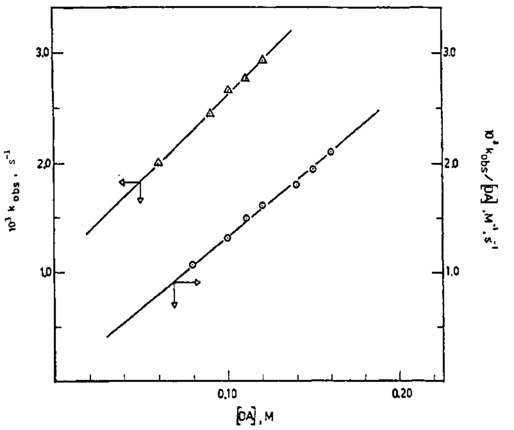

Figure 1. Plots for the aminolysis of ENPC by DA (⊙) and DA in the presence of 0.20 M DADEA (△) in chloroform at 25 °C.

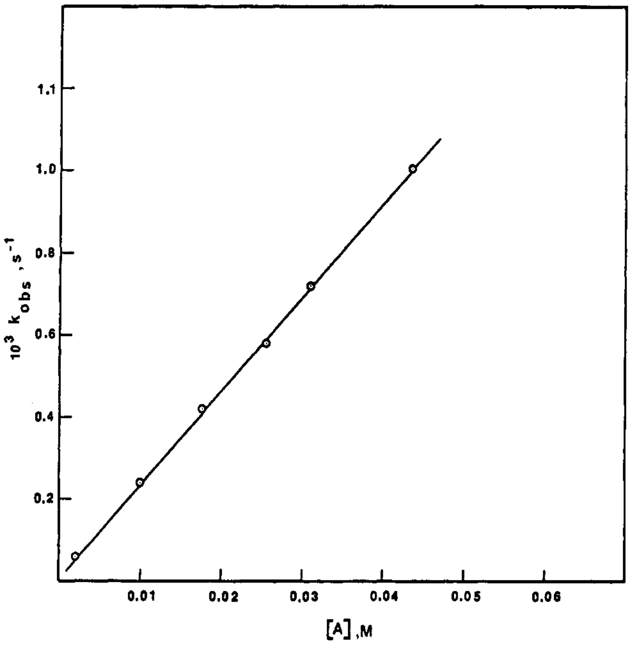

Figure 2. Plots for the aminolysis of ENPC by DADEA in chloroform at 25 °C.

Table I. Rate Constants for ENPC Aminolysis by DADEA in Chloroform at 25 °C

[DADEA], M	[DADEA] micellar/[A]	$10^3 k_{obsd}$, s^{-1}
0.024		0.007
0.028		0.03
0.034	0.002	0.06
0.066	0.010	0.24
0.096	0.0175	0.42
0.128	0.0255	0.58
0.150	0.0310	0.72
0.200	0.0435	1.03

Results

Aminolysis of ENPC by DA in chloroform obeys eq 1.

$$k_{obsd} = k_3[DA]^2 \qquad (1)$$

Thus a graph of $k_{obsd}/[DA]$ vs. [DA] is linear, with slope k_3, as shown in Figure 1. The value for k_3 was 12.6×10^{-3} $M^{-2}\ s^{-1}$. In the reaction of the carbonate ester with DADEA, the rate was very slow below 0.03 M DADEA, i.e., below the surfactant operational critical micelle concentration (cmc, vide infra). At a DADEA concentration of

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(11) A. T. Shah and K. A. Connors, *J. Pharm. Sci.*, 57, 282 (1968).

Table II. Observed Rate Constants and Activation Parameters for ENPC Aminolysis by DADEA in Chloroform in the Presence of Solubilized Water

$[H_2O]$, M	10^3k_{obsd}, s^{-1} 15 °C	20 °C	25 °C	30 °C	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
0.055	0.477	0.664	1.02	1.43	12.3 ± 0.1	−30.9 ± 0.5
0.11	0.478	0.650	0.950	1.31	11.2 ± 0.2	−34.6 ± 0.5
0.18	0.367	0.519	0.745	1.15	12.6 ± 0.1	−30.6 ± 0.5
0.22	0.320	0.477	0.698	1.04	13.0 ± 0.2	−29.2 ± 0.5
0.27	0.297	0.435	0.598	0.902	12.1 ± 0.2	−32.7 ± 0.7
0.33	0.251	0.364	0.508	0.721	11.6 ± 0.1	−34.8 ± 0.5
0.44	0.234	0.333	0.478	0.681	11.8 ± 0.1	−34.1 ± 0.5
0.66	0.183	0.265	0.362	0.506	11.1 ± 0.2	−37.0 ± 0.7
0.88	0.168	0.240	0.336	0.486	11.7 ± 0.2	−35.3 ± 0.8

~0.03 M, the rate increased sigmoidally, followed by a linear increase at higher surfactant concentrations. the data above the cmc fit eq 2 where [A] refers to the concentration of DADEA in the micellar form,[12] and the results are given in Table I and Figure 2. The value of k_2 was found to be 23.2×10^{-3} M^{-1} s^{-1}.

$$k_{obsd} = k_2[A] \qquad (2)$$

Addition of a fixed concentration of the surfactant (0.20 M) enhances the rate of the ENPC aminolysis by DA. In this case the reaction was first order in DA and the ester. A plot of k_{obsd} vs. (DA) was linear (Figure 1) with an intercept of 1.05×10^{-3} s^{-1}, which is in good agreement with the value of 1.03×10^{-3} s^{-1} obtained for the reaction of the ester with 0.20 M surfactant. The rate constant equation is, therefore, given by eq 3, and the value of k_3' was 357 $\times$ 10^{-3} M^{-2} s^{-1}.

$$k_{obsd} = k_3'[DA][A] \qquad (3)$$

The reaction of ENPC with 0.20 M DADEA in the presence of solubilized water was studied at different temperatures, and the results are given in Table II. Rate constants were practically independent of the water concentration up to 0.11 M, and then the rates decreased gradually as more water was introduced. The kinetic order with respect to water was obtained from the slope of the linear graphs of log k_{obsd} vs. log $[H_2O]$ at concentrations of H_2O >0.11 M and was found to be −0.5 at all temperatures. Thus, in the presence of water eq 2 becomes eq 4. Table II also shows the activation parameters at different water concentrations, and Figure 3 shows the complex, quasi-mirror-imaged variation of $\Delta H^{\ddagger}$ and $-T\Delta S^{\ddagger}$ (calculated at 15 °C) as a function of increasing the concentration of solubilized water.

$$k_{obsd} = k_2'[A]/[H_2O]^{0.5} \qquad (4)$$

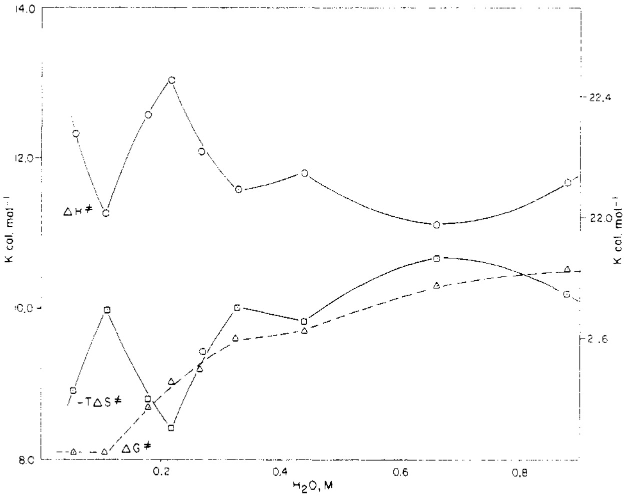

Figure 3. Effects of solubilized water on the activation parameters of the ENPC aminolysis by 0.20 M DADEA in chloroform.

Discussion

The dependence of the rate constant on the square of the amine concentration (eq 1) has been observed for ester aminolysis in different solvents[3,15] and can be taken to indicate either general-base-catalyzed amine attack or an (kinetically indistinguishable) attack by amine dimers. ^1H NMR and IR data showed, however, no detectable amine autoassociation in the range used in this work.[16] The second amine molecule acts, therefore, as a general base for the one attacking the carbonate ester. The reaction involved is shown in eq 5, and the reaction products were identified, right from the start of the reaction, by using TLC (solvent water–dioxane, 2:8 v/v).

$$EtOC(O)OC_6H_4NO_2 + 2C_{12}H_{25}NH_2 \rightarrow EtOC(O)NHC_{12}H_{25} + C_{12}H_{25}NH_2 + HOC_6H_5NO_2 \qquad (5)$$

According to Sunamoto et al.,[9] the reaction between methyl *p*-nitrophenyl carbonate and dodecylammonium propionate reversed micelles in benzene, in the presence of solubilized water, is ester hydrolysis. This conclusion is in conflict with our previous data which showed that in the reaction of *p*-nitrophenyl acetate under the same conditions only aminolysis occurs.[3] It was necessary to check, therefore, if aminolysis and hydrolysis occur as competing pathways in the reaction of ENPC with DADEA containing solubilized water. Equations 6 and 7 show the products expected if the reaction was ester aminolysis or hydrolysis, respectively. The fact that we detected ethyl-*N*-dodecylurethane by TLC right from the start of the reaction rules out the possibility that only hydrolysis took place. The following IR results show clearly that, as

$$EtOC(O)OC_6H_4NO_2 + (Et)_2AsO_2^-H_3N^+C_{12}H_{25} + H_2O \rightarrow EtOC(O)NHC_{12}H_{25} + HOC_6H_4NO_2 + (Et)_2AsO_2H + H_2O \qquad (6)$$

$$EtOC(O)OC_6H_4NO_2 + H_2O + DADEA \rightarrow EtOH + CO_2 + HOC_6H_4NO_2 + DADEA \qquad (7)$$

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[12] The variation of the chemical shifts of the discrete protons of DADEA as a function of its concentration in chloroform-*d* follows closely that of dodecylammonium carboxylates.[13] Plots of the chemical shifts of the NH_3^+, CH_2-N^+H_3, and $CH_2AsO_2^-$ protons vs. (DADEA) show distinct breaks at 0.026 M. This concentration was taken as the operational critical micelle concentration. Treatment of the data according to the known procedure[13] yields an average aggregation number (*N*) of 4. The value of *A* can be calculated from[13] A = ([DADEA] − cmc)/*N*. We also found a linear correlation between the values of cmc and the solvent polarity parameter E_T[14] in benzene-d_6, carbon tetrachloride, chloroform-*d*, and dichloromethane. Details of the aggregation behavior of this surfactant will be published elsewhere.

[13] O. A. El Seoud, E. J. Fendler, J. H. Fendler, and R. T. Medary, *J. Phys. Chem.*, 77, 1876 (1973).

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[15] F. M. Menger, *J. Am. Chem. Soc.*, **88**, 3081 (1966); D. Oakenfull, *J. Chem. Soc., Perkin Trans. 2*, 1006 (1973).

[16] V. F. Bystrov and V. P. Lezina, *Opt. Spektrosk.*, **16**, 340 (1964); C. S. Springer, Jr., and D. W. Meek, *J. Phys. Chem.*, **70**, 481 (1966); F. H. Lohman and W. E. Nortman, Jr., *Anal. Chem.* **35**, 707 (1963); J. E. Sinsheimer and M. M. Keuhnelian, *ibid.*, **46**, 89 (1974).

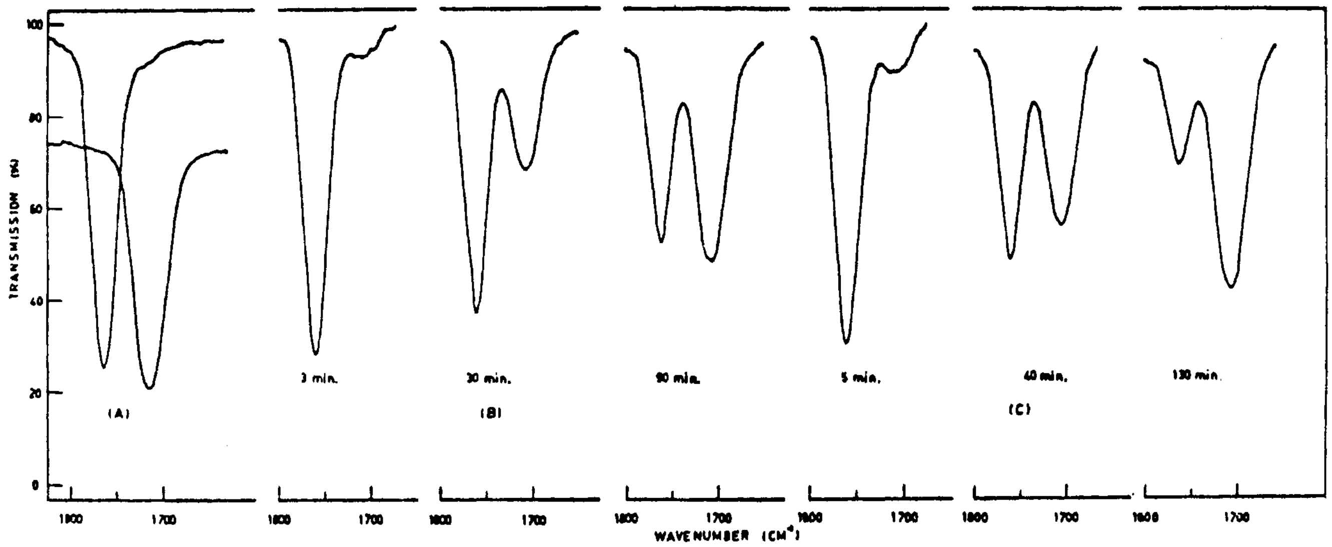


Figure 4. IR spectra in chloroform showing (A) methyl-*N*-dodecylurethane and ENPC both 0.05 M, (B) aminolysis of 0.05 M ENPC by 0.10 M DA, and (C) reaction between 0.5 M ENPC and 0.10 M DADEA in the presence of 0.20 M solubilized water.

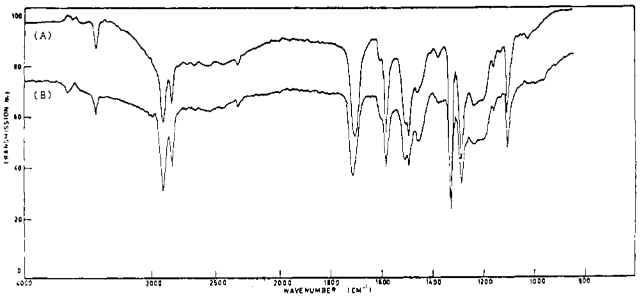
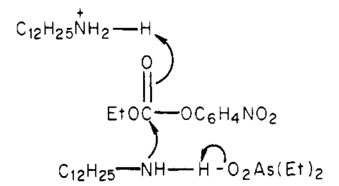


Figure 5. IR spectra in chloroform: (A) 0.05 M ENPC + 0.10 M DADEA + 0.20 M H_2O; (B) 0.10 M DADEA + 0.05 M *p*-nitrophenol + 0.05 M methyl-*N*-dodecylurethane + 0.20 M H_2O.

in the case of *p*-nitrophenyl acetate,[3] only aminolysis occurs. The spectra of a solution containing 0.10 M DA and 0.05 M ENPC in chloroform showed that the ester carbonyl band ($\nu_{CO} = 1762$ cm^{-1}) disappeared and another band at 1712 cm^{-1} appeared (Figure 4A). The absorption frequency of the last band is equal to that of the CO group of methyl-*N*-dodecylurethane in the same solvent (Figure 4B). A chloroform solution containing 0.05 M ENPC, 0.20 M water, and 0.10 M DADEA showed the same behavior as in the amine–ENPC reaction; i.e., the ester CO peak disappeared, and the urethane CO peak appeared (Figure 4C). After several hours the carbonate ester CO peak disappeared completely, and the spectrum was similar to that of a mixture of 0.05 M *p*-nitrophenol, 0.05 M methyl-*N*-dodecylurethane, and 0.2 M water solubilized in 0.10 M DADEA in chloroform (Figure 5). From the peak areas of the pure ester and urethane (Figure 4A) and those of the reaction of ENPC with DADEA in the presence of solubilized water (Figure 4C) we found that the concentration of the reacted ester and that of the produced urethane were equal within 4%.[17] These results clearly show that the reaction between ENPC and the surfactant in the presence of solubilized water is the same as the one between the ester and DA, i.e., ester aminolysis. The quantitative experiment showed that hydrolysis is negligible indeed.[18]

Scheme I



Equation 6 involves the attack of a molecule of the amine (derived from DADEA, pK_a in water of 11.6)[20] on an ester whose leaving group is *p*-nitrophenol (pK_a in water of 7.1)[20] so that the slow step probably involves the amine attack to form a tetrahedral intermediate.[19,21,22]

Rate constants below the surfactant cmc indicate a negligible reaction between the ester and the DADEA monomers. Thus, increasing the surfactant concentration from a value slightly below the cmc (0.024 M) to a value slightly above the cmc (0.034 M) induced a ninefold decrease in $t_{1/2}$. The sigmoidal increase in the cmc region may be due to incorporation of the ester in the rapidly increasing number of micellar aggregates.

Aminolysis of ENPC by DA in the presence of the surfactant is 28.3 times faster than in its absence. This can be explained on the basis of Scheme I, which in this case will lead to an uncharged tetrahedral intermediate and a more stabilized incipient transition state. This bifunc-

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[17] No difference was noticed if the ester used was methyl or ethyl *p*-nitrophenyl carbonate. This experiment was carried out in duplicate by using the absorbance mode of operation. Eight points covering 130 min were used for calculating the reactant and product concentrations. Methyl-*N*-dodecylurethane was stable in the presence of 0.20 M water solubilized in 0.10 M DADEA in chloroform.

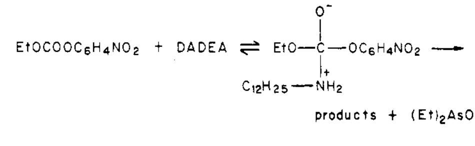
[18] This is similar to the reaction of these carbonates with amines in water where only aminolysis occurs, probably because of the much higher reactivity of amines relative to water.[19]

[19] M. J. Gressner and W. P. Jencks, *J. Am. Chem. Soc.*, **99**, 6963, 6970 (1977).

[20] R. C. Weast, Ed., "Handbook of Chemistry and Physics", 56th ed., CRC Press, Cleveland, OH, 1976.

[21] Provided that the difference between the pK_a values of these species does not change much in going from bulk water to the micelle-solubilized water.

[22] The reaction between the carbonate ester and the surfactant can be represented by a mechanism similar to that suggested for ester aminolysis in aprotic solvents,[23] as shown below:



$$EtOCOOC_6H_4NO_2 + DADEA \rightleftharpoons EtO\text{—}\underset{C_{12}H_{25}\text{—}\overset{+}{N}H_2}{\overset{O^-}{C}}\text{—}OC_6H_4NO_2 \longrightarrow \text{products} + (Et)_2AsO_2H$$

[23] F. M. Menger and J. H. Smith, *J. Am. Chem. Soc.*, **94**, 3824 (1972); F. M. Menger and A. C. Vitale, *ibid.*, **95**, 4931 (1973).

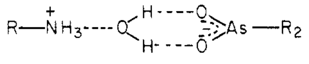
tional catalysis by the surfactant has been used to explain the catalysis of the mutarotation of tetramethylglucose by dodecylammonium propionate micelles in hexane.[1] It was also invoked to explain the catalytic effect of alkylammonium salt reversed micelles on ester aminolysis and hydrolysis.[1-4] Additional evidence for the importance of the concerted proton transfer was inferred from the very low catalytic activity of quaternary ammonium salts (which cannot transfer protons).[4,24]

One of the main objectives of this work is to shed some light on the role of water in reversed micellar catalysis by examining its effects on the rate constants and on the activation parameters. The inverse dependence on the water concentration has been observed in several micelle-catalyzed reactions and is generally attributed to the head group hydration.[4,9,28,29] Our ^{1}H NMR data on the solubilization of D_2O in 0.30 M DADEA in $CDCl_3$ show the site of D_2O solubilization in the micelle and the decrease in the micelle–water interactions at higher water/surfactant molar ratio (R). Thus, the location of this D_2O in the micellar interior can be inferred from the fact that only the groups at the "core" or close to it ($^+NH_3$, $CH_2N^+H_3$, $CH_2AsO_2^-$) showed appreciable chemical shift variations as a function of solubilizing D_2O. The chemical shift $\delta_{^+NH_3}$ decreased from 7.90 ppm for the dry micelle to 5.41 ppm at $R = 4.5$. However, 73% of this decrease was observed up to $R = 1.2$ ($\delta_{^+NH_3}$ 6.08). This is also in agreement with the idea that, depending on R, water inside reversed micelles can be present in one or more hydration spheres.[30]

The variation of $\Delta H^{\ddagger}$ and $T\Delta S^{\ddagger}$ shown in Figure 3 has never been reported and is different from that observed by Sunamoto et al.,[9] who reported a gradual increase in $\Delta H^{\ddagger}$ and in $\Delta S^{\ddagger}$ as R was increased from 0.25 to 4.46. Figure 3 shows that at a water concentration range between 0.055 and 0.11 M ($R = 0.27$–0.55), $\Delta G^{\ddagger}$ is constant due to a decrease in $\Delta H^{\ddagger}$ and a similar decrease in $T\Delta S^{\ddagger}$ ($\Delta\Delta H^{\ddagger} = 1070$ cal and $T\Delta\Delta S^{\ddagger} = 1068$ cal). At higher R values $\Delta G^{\ddagger}$, however, increased gradually.

The complex behavior shown in Figure 3, specially the inflection points at water concentrations of 0.11 and 0.22 M, respectively, will now be explained. In doing this, one has to consider the possible effects of the solubilized water on the rigidity of the micelle,[30,31] on the relative stabilization of the reactants and transition state, and on the substrate–micelle interactions.[3,4] At a water concentration <0.11 M there will be one water molecule per two or three surfactant molecules. The simultaneous bonding of water to several head ions may disturb the electrostatic attraction between the AsO_2^- and the H_3N^+ groups, which may lead to a less rigid micelle. On the other hand, any transition-state stabilization by solvation should be small because at this R value water is highly immobilized in the solvation shells.[30,31] Thus there will be an increase in the degrees of freedom of the reagents, and $\Delta S^{\ddagger}$ decreases. The decrease in $\Delta H^{\ddagger}$ is probably due to a stronger solvation of the cationic head group,[30-32] liberating the arsinate group to participate as a general-base catalyst.

At a water concentration range of 0.11–0.22 M ($R = 0.55$–1.11) both activation parameters increase. The increase in entropy can be the result of an increase in the micellar rigidity due to increased bonding of the head ions via the water molecules. Using several techniques to investigate the interactions of solubilized water with cationic, anionic, and zwitterionic reversed micelles, Sunamoto et al. clearly showed a high degree of micellar rigidity at a water/surfactant molar ratio of 1.[31] At $R = 1$, the surfactant–water complex can be depicted as shown in I,[33] and in this species, the interaction between the head groups via the water molecule is probably most efficient. Thus it appears that the variation in $\Delta S^{\ddagger}$ is largely due to the effects of water on the reactants. If species I is assumed to contribute significantly, then the increase in $\Delta H^{\ddagger}$ can be taken to indicate stabilization of the reactants which is not reflected in the transition state. When $R = 1.11$–1.66, both $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ decrease. As shown before[30,32] and from our ^{1}H NMR data, the solubilized water is probably already present in a secondary solvation shell where it can autoassociate, thereby interacting less with the surfactant. At this stage stabilization of the transition state by solvation probably becomes more important. As expected, this entails a decrease in $\Delta S^{\ddagger}$ (transition state with less degrees of freedom) and in $\Delta H^{\ddagger}$ (transition state stabilized by solvation; water can participate as a proton-transfer agent). At higher R values, the activation parameters variation is much less pronounced.



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The above results show that water in these restricted media can alter the rate constants by significantly affecting the activation parameters in a way not easily envisaged. Clearly, more work is needed in this area before a general, quantitative treatment of the effects of solubilized water on micellar catalysis can be reached.

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Registry No. ENPC, 6132-45-2; DA, 124-22-1; DADEA, 77257-16-0; methyl-*N*-dodecylurethane, 66769-57-1; *p*-nitrophenol, 100-02-7; diethylarsenic acid, 4964-27-6.

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[24] A referee has kindly drawn our attention to another mechanism which has recently been suggested to explain the aminolysis of *p*-nitrophenyl acetate by dodecylammonium propionate reversed micelles in benzene.[25] In this mechanism, the intermediate formation of acetic propionic anhydride is assumed to occur via nucleophilic attack on the ester by the surfactant propionate group. This type of mechanism has been considered unlikely,[26] especially since the RCO_2^- anion can hardly be assumed to be a "bare" species (hence a good nucleophile) when hydrogen-bond donors are present in solution.[26,27] More importantly, it was not possible to detect the presence of this mixed anhydride.[25] At the moment, we feel that more work is needed in order to test this mechanism.

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