Proton Magnetic Resonance Study on Solubilization by Micellar Alkylammonium Propionates in Carbon Tetrachloride

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Solubilization of imidazole, methanol, 2-methyl-3-butyn-2-ol, *N*-methylimidazole, and pyrazole by micellar butylammonium propionate (BAP), hexylammonium propionate (HAP), octylammonium propionate (OAP), and dodecylammonium propionate (DAP) in carbon tetrachloride was studied using proton magnetic resonance spectroscopy. Association constants (K) for the substrate–micelle complexes were calculated from chemical shift data. The association constants depend on the substrate structure and the number of carbon atoms (X) in the alkylammonium ion. For example, in case of association with DAP, imidazole binds more strongly than *N*-methylimidazole (K = 65.3 ± 1.2, 28.8 ± 1.1 M^{-1}, respectively) and 2-methyl-3-butyn-2-ol binds more strongly than methanol (K = 51.8 ± 4.0, 39.0 ± 3.4 M^{-1}, respectively). For most of the solubilizates the association increases in going from BAP to OAP then decreases for DAP. For example, K for imidazole increases from 62.7 ± 1.8 to 105.8 ± 3.2 then decreases to 65.0 ± 1.2 M^{-1} and for *N*-methylimidazole the corresponding K values increase from 32.2 ± 0.4 to 46.3 ± 3.0 then decrease to 28.8 ± 1.2 M^{-1}, respectively.

Catalysis by micellar systems has received much attention during the past few years.[1-3] Micellar catalysis, both in water and in nonaqueous solvents, has been rationalized in terms of favorable substrate partitioning in the micellar pseudophase (or at its interface) where reactions take place. Data on the location and orientation of the substrates in the micelle and on the substrate–micelle association constants are, therefore, very important in understanding micellar catalysis. Solubilization by aqueous micelles is more studied than that by inverted micelles (surfactants in nonaqueous solvents).[3] Recently ^{1}H NMR was used to study the solubilization of a number of substrates by DAP and Aerosol-OT in several organic solvents.[4,5] Substrate–micelle association constants were found to be a function of the surfactant head group, the substrate structure, and the solvent polarity. Alkylammonium carboxylates' reversed micelles are efficient catalysts for several types of reactions.[6-10] The rate enhancement depends, among other factors, upon the alkyl chain length of the ammonium and/or the carboxylate ion of the surfactant.[8-10] In order to understand better the effects of increasing the chain length of the alkylammonium ion on the association micelle–substrate, hence on the catalysis, the solubilization of different substrates by a series of alkylammonium propionates in carbon tetrachloride was carried out using ^{1}H NMR as a probing tool.

Experimental Section

Spectroscopic grade carbon tetrachloride (Merck, Uvasol) was further dried by storing on activated Linde type 4A molecular sieve for several weeks. Imidazole (Baker) was recrystallized from benzene–acetone and dried in vacuo over P_2O_5. Methanol (Aldrich, spectroscopic grade), 2-methyl-3-butyn-2-ol (Eastman Kodak), and *N*-methylimidazole (Aldrich) were distilled from calcium hydride and the middle fraction stored on activated molecular sieve type 4A for several weeks. Pyrazole (Matheson Coleman and Bell) was recrystallized from ligroin and dried in vacuo over P_2O_5. Butyl-, hexyl-, octyl-, and dodecylamines (Aldrich) were distilled from calcium hydride. The surfactants were prepared according to the established procedure,[11] and were further purified by repeated distillation or recrystallization and their purity was established by their melting or boiling points and from the ir and ^{1}H NMR spectra.

Since solubilized water can affect the results, special care was taken to exclude moisture during sample preparations. All solid substances were weighed, then dried for 12 h in vacuo over P_2O_5 and reweighed before making up the stock solution with dry carbon tetrachloride. Owing to limited solubility of imidazole in the solvent it was dissolved in 20% v/v deuteriochloroform in carbon tetrachloride.

The 60-MHz ^{1}H NMR spectra were obtained on a Varian T-60 spectrometer and the probe temperature was 36 ± 0.5 °C. All spectra were determined on freshly prepared solutions after the sample acquired the ambient probe temperature. Each spectrum was recorded at least three times. Chemical shifts, with the exception of the downfield resonances, were obtained from spectra recorded at 250 Hz sweep width and are given on the δ scale in parts per million relative to Me_4Si (δ 0 ppm). The reference Me_4Si (10% v/v in carbon tetrachloride) was contained in a sealed capillary inserted in the NMR tube. Individual measurements are accurate to ±0.5 Hz. Chemical shifts of the solubilizate protons in absence of detergent were the mean of several measurements and any experiment in which this initial reading deviates more than 0.5 Hz was discarded. Least-squares analysis of the results was carried out using a Hewlett-Packard Model 9820A programmable calculator.

Results and Discussion

The ^{1}H NMR spectra of the surfactants in carbon tetrachloride show, in order of decreasing chemical shift, a low field sharp singlet for the ammonium protons, a triplet for the methylene protons adjacent to the ammonium ion, a quartet for the CH_2 group of the propionate ion, a broad singlet for the intermediate methylene protons of the alkylammonium ion, and two triplets for the terminal methyl groups of the propionate and alkylammonium ions. The critical micelle concentration (cmc) values in carbon tetrachloride are between 2.1 and 3.1 × 10^{-2} M.[11] The inverted micelles of these surfactants are rather small aggregates in which the polar head ions are grouped around a micellar core from which the solvent is largely excluded whereas the hydrophobic tails are in contact with the solvent.[12]

For comparison purposes, most of the investigated solubilizates were those used in previous studies.[4,5] Methanol is the simplest alcohol and can bind through its OH group whereas 2-methyl-3-butyn-2-ol has two sites for bonding, viz., the OH and the acetylenic protons. The isomeric diazoles, imidazole and pyrazole have different pK_a values and each has two sites for H bonding whereas in *N*-methylimidazole one bonding site is already blocked (vide infra).

We will first examine the effect of adding solubilizates in the concentration range 0–0.05 M to 0.5 M BAP solution. Only the $^+NH_3$ protons shift appreciably as a function of solubilizates as shown in Figure 1. Since the BAP concentration is well above its cmc value, the $^+NH_3$ chemical shift variation indicates that the solubilization site of BAP is its micellar core. A similar conclusion has been reached for DAP in other solvents.[4] Table I gives the changes in the chemical shift of the ammonium protons as a function of solubilizate concentrations for BAP and DAP. The magnitude and direction of the shift depends on several factors, such as the H-bonding ability of the substrate, its self-asso-

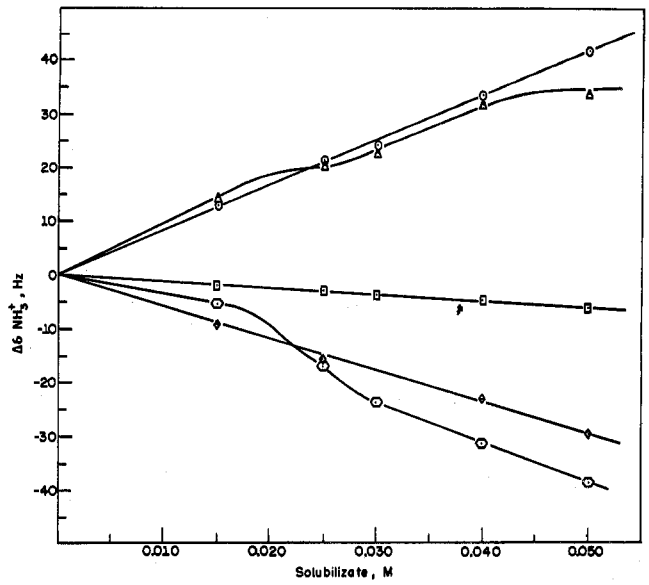


Figure 1. Effect of solubilizates on the chemical shifts of the ammonium protons of BAP: $\Delta\delta_{+NH_3}$ = chemical shift in presence of solubilizate − chemical shift in its absence; ⊙, imidazole; ⊙, methanol; ▲, 2-methyl-3-butyn-2-ol; ⊡, *N*-methylimidazole; ◈, pyrazole.

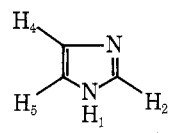
Table I. Effect of Solubilizates on the Chemical Shift of the $^+NH_3$ Group of BAP and DAP in Nonaqueous Solvents

		$\Delta\delta_{+NH_3}$, ppm[c]	
Solubilizate[a]	Solvent	DAP[b]	BAP
Imidazole	C_6H_6	−0.185	
	$CDCl_3$	−0.117	
	CH_2Cl_2	−0.170[d]	
	CCl_4		−0.640
Methanol	C_6H_6	0.112	
	$CDCl_3$	0.553	
	CH_2Cl_2	0.225[d]	
	CCl_4		0.700
2-Methyl-3-butyn-2-ol	CCl_4		0.567
N-Methylimidazole	CCl_4		−0.100
Pyrazole	C_6H_6	−0.158	
	$CDCl_3$	−0.198[d]	
	CH_2Cl_2	−0.190[d]	
	CCl_4		−0.492

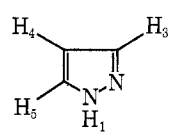
[a] Solubilizate concentration 0–0.05 M. [b] Calculated from ref 4. [c] $\Delta\delta_{+NH_3}$ = chemical shift in absence of solubilizate − chemical shift in the presence of 0.05 M. [d] Maximum solubilizate concentration 0.06 M.

ciation, as well as its local and long-range diamagnetic shielding effects. Additionally interactions between the solubilizates and the surfactant head groups will be at the expense of the ammonium carboxylate ions mutual attraction and will be reflected on the observed $^+NH_3$ chemical shift. Table I shows that for the same solubilizate the sign of the chemical shift difference is the same but the magnitude is greater for BAP than for DAP. Data for DAP in carbon tetrachloride are not available but Table I shows that its chemical shift differences are not very solvent dependent so that one expects results not far from those in benzene. The equilibrium constant for DAP micelle formation in carbon tetrachloride is some 55 times greater than that for BAP micelle.[11] This reflects stronger interactions between the $^+NH_3$ and CO_2^- groups in the former case which may manifest itself as smaller chemical shift differences. The small difference between the shifts due to methanol and 2-methyl-3-butyn-2-ol may indicate that binding in both cases is the same, i.e., via H bonding involving the OH group, and that the triple bond lies outside the micellar core. A noticable difference is observed for the solubilization of imidazole (pK_a = 6.953) and *N*-methylimidazole (pK_a = 6.95). The latter shifts the ammonium protons much less than the former. One can assume that for both solubilizates contributions to the chemical shifts from the electrostatic fields of the heteroatoms and the diamagnetic anisotropy of the nitrogen lone pair and of the aromatic π system are approximately equal. The difference can be due to the more favorable partitioning of imidazole in the polar micellar core and to the difference in the H-bonding abilities of the two substrates. Imidazole has a basic "pyridine type" nitrogen atom and a weakly acidic "pyrrole type" amino nitrogen and can act as proton acceptor and donor, i.e., it can interact with both BAP head groups whereas *N*-methylimidazole interacts only with the $^+NH_3$ group as proton acceptor.

We now turn our attention to the effect of addition of surfactants (0–0.5 M) on the chemical shifts of the solubilizate's discrete protons. Methanol shows a doublet and a quartet (J = 4.5 Hz) for the methyl and OH protons, respectively; 2-methyl-3-butyn-2-ol shows three singlets due to the two equivalent methyl groups, the OH, and the acetylenic protons. In imidazole



H(1) exchanges rapidly between the two nitrogen atoms so that H(4) and H(5) are magnetically equivalent and appear as an upfield doublet whereas H(2) appears as a lower field triplet ($J_{2\text{-}4,5}$ = 1 Hz). H(1) cannot be observed under the experimental conditions used.[13,14] *N*-Methylimidazole shows a singlet for the *N*-methyl group and three resonance lines, a lower field relatively broad one due to H(2), whereas H(4), H(5) show two triplets ($J_{2\text{-}5} = J_{4\text{-}5}$ = 1 Hz).[14] Pyrazole



shows lower field doublets for H(3), H(5) and an upfield triplet for H(4) ($J_{4\text{-}3,5}$ = 2.05 Hz).[13]

The addition of surfactants does not result in any changes in the degeneracy of the resonance lines or the coupling constants except for methanol, whose doublet collapses and quartet disappears, and for 2-methyl-3-butyn-2-ol, whose OH singlet disappears. This is the result of the fast OH proton exchange with the acidic $^+NH_3$ protons. The effects of increasing surfactants concentration on the chemical shifts of the substrate's discrete protons are shown in Figure 2. Chemical shift changes allow the calculation of binding constants K of the solubilizates (S) to the micelles (M) as given by equilibrium 1

$$M + S \overset{K}{\rightleftharpoons} MS \quad (1)$$

where MS is the micelle–substrate complex, by using eq 2[15]

$$\frac{\Delta}{M} = -\Delta K + \Delta_c K \quad (2)$$

where Δ is the difference between the observed chemical shift and that of the uncomplexed or "free" solubilizate, and Δ_c is the difference between the chemical shift of the micelle complexed and that of the uncomplexed solubili-

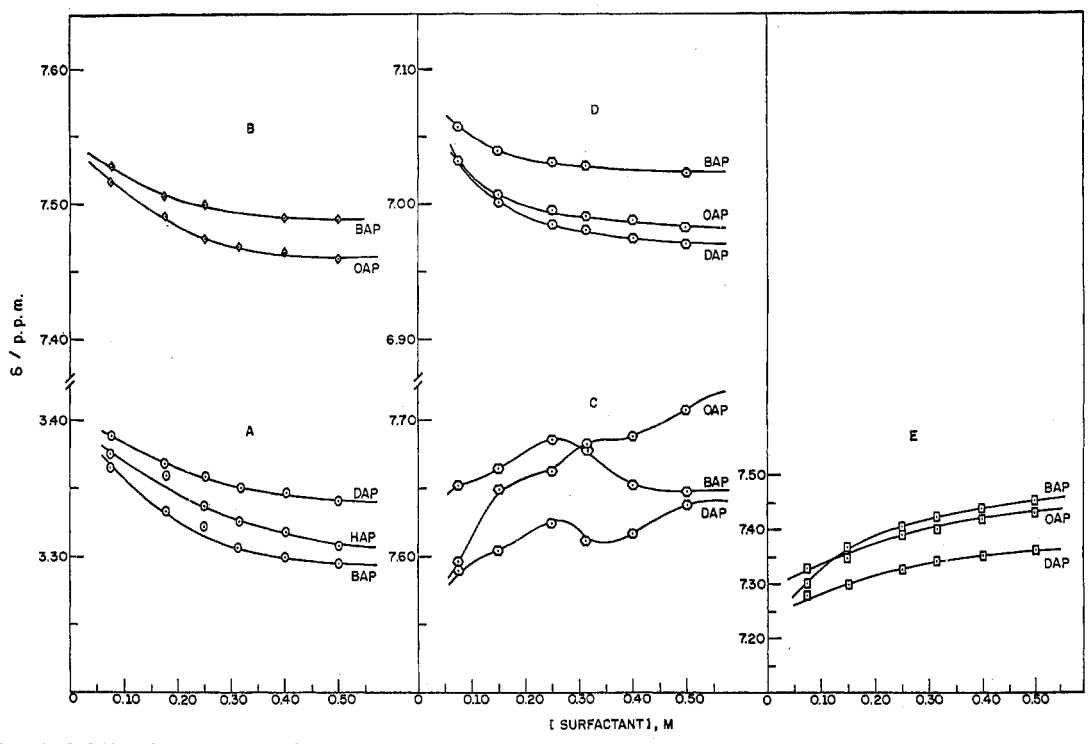


Figure 2. Chemical shift values of the solubilizate protons as a function of surfactants: A, methanol CH_3; B, pyrazole H(3,5); C, imidazole, H(2); D, imidazole H(4,5); E, *N*-methylimidazole H(2).

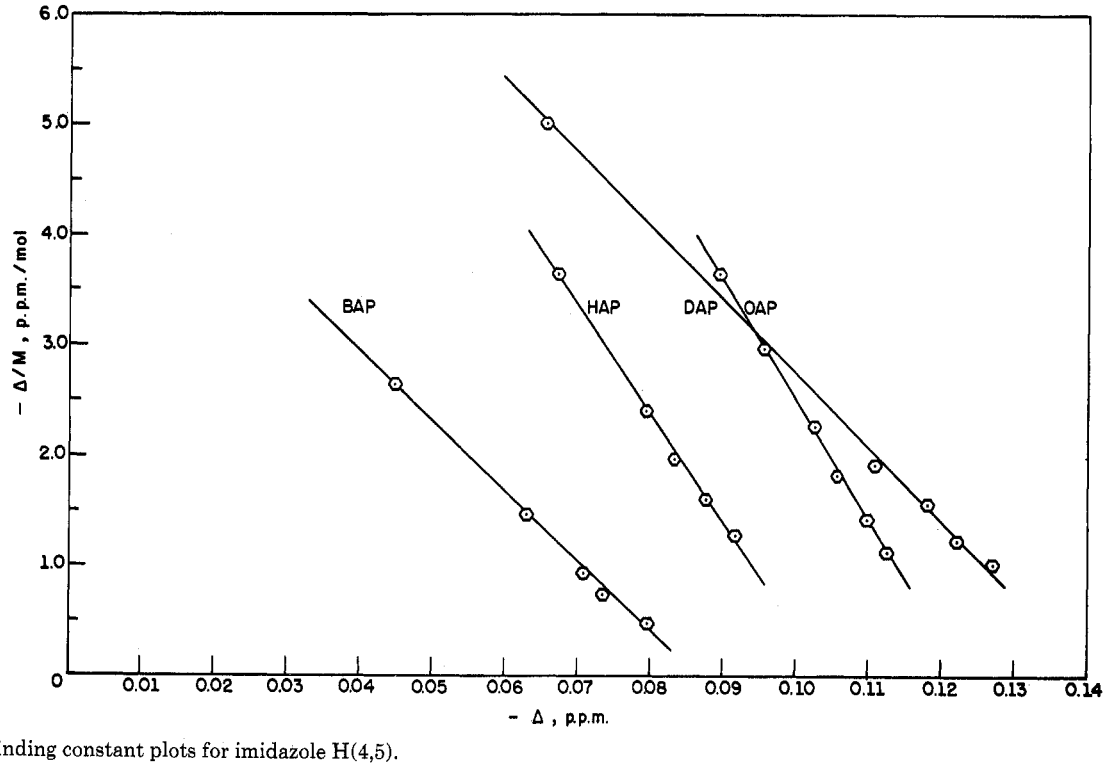


Figure 3. Binding constant plots for imidazole H(4,5).

zate. Chemical shifts of the "free" solubilizates were those measured in absence of the surfactants since chemical shifts for the protons followed were practically concentration independent over the concentration range 0.02–0.075 M.[4,5] M is the micellar concentration calculated from eq 3[4]

$$(\mathrm{M}) = \frac{C_D - \mathrm{cmc}}{N} \qquad (3)$$

where C_D is the total detergent concentration and N is the aggregation number taken from ref 11.[16] Plots of Δ/M against Δ yield good straight lines whose slope is equal to $-K$ and intercept equal to $K\Delta_c$. A typical binding constant plot is shown in Figure 3 and the results are given in Table II and Figure 4. We were not able to compute the association constant values for imidazole H(2) because its chemical shift did not change systematically as a function of surfactant concentration (Figure 2). Typically the correlation coefficient was 0.99; however, K values for which the coefficient was less than 0.95, e.g., some of the values of *N*-methylimidazole and the values for the CH_3 group of 2-methyl-3-butyn-2-ol, are not reported in the table.

Association constants determined by following different

Table II. Association of Solubilizates with Alkylammonium Propionates in Carbon Tetrachloride

Registry no.	Solubilizate	Proton used	K,[a] M^{-1} BAP	HAP	OAP	DAP	Δ_c,[b] ppm
288-32-4	Imidazole[c]	H(4,5)	62.7 ± 1.8	97.0 ± 2.9	105.8 ± 3.2	65.3 ± 1.2	8.7, 10.5 12.4, 14.2
67-56-1	Methanol	CH_3	26.1 ± 1.6	30.2 ± 1	37.7 ± 0.9	39.5 ± 3.4	9.2, 16.3 10.0, 14.7
115-19-5	2-Methyl-3-butyn-2-ol	-C≡CH	33.8 ± 4			51.8 ± 4	4.2, 6.9
616-47-7	*N*-Methylimidazole	H(2)	32.2 ± 0.4	46 ± 0.8	46.3 ± 3	28.8 ± 1.2	30.3, 37.1 28.4, 20.0
		H(4)	48.7 ± 3.6		44.9 ± 5	37.3 ± 5	7.5, 5.8 2.7
		CH_3	45.4 ± 2.9				7.7
288-13-1	Pyrazole	H(3,5)	76 ± 4	74.6 ± 0.7	49.7 ± 0.6	62.6 ± 5	10.4, 10.6 11.2, 13.4
		H(4)	49 ± 5	88.1 ± 2.4	101.4 ± 3.2	94.9 ± 4	8.1, 8.0 6.9, 8.4

[a] Temperature 36 ± 0.5 °C. [b] Δ_c for BAP, HAP, OAP, and DAP, respectively. Values for imidazole, methanol, 2-methyl-3-butyn-2-ol, and pyrazole should be multiplied by −0.01 and that for *N*-methylimidazole by 0.01. [c] Solvent $CDCl_3$–CCl_4 (20:80 v/v).

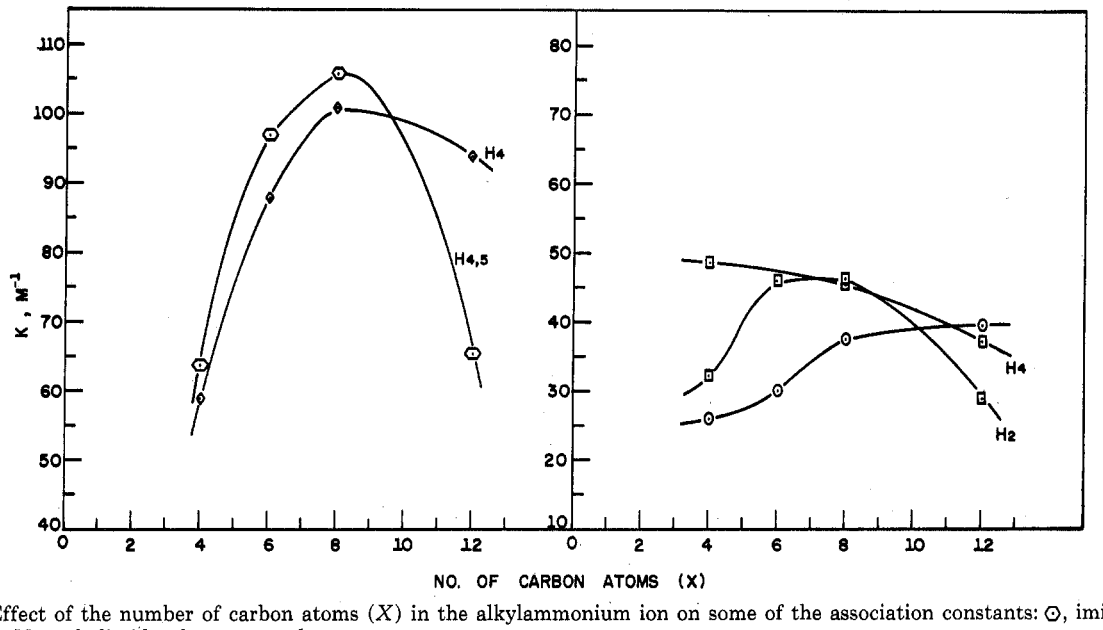


Figure 4. Effect of the number of carbon atoms (X) in the alkylammonium ion on some of the association constants: ⊙, imidazole; ⊙, methanol; ⊡, *N*-methylimidazole; ◈, pyrazole.

protons in the same solubilizate agree well as shown for pyrazole H(3,5), H(4) and for *N*-methylimidazole H(2), H(4) and the methyl group. Any discussion of K values has to take into account the autoassociation of the solubilizates, the possible effect of the surfactant on this self-association, the distribution coefficient of the substrate between the micellar and bulk phases, and the pK_a values of the alkylamines. The association of imidazole is due to intermolecular H bonding.[17] In carbon tetrachloride at 18 °C the dimerization constant is 234 ± 5 M^{-1} and the subsequent stepwise association constant is 760 ± 20 M^{-1}. Methanol exists as monomers, dimers with either cyclic or open structures, trimers, tetramers, and higher polymers.[18] At 21 °C the equilibrium constant for monomer ⇌ tetramer is 28.4 M^{-3},[19] at 40 °C the association constant for monomer ⇌ dimer is 17.9, for dimer ⇌ trimer is 30.1, and for trimer ⇌ tetramer is 44.4. [20] *N*-Methylimidazole does not self-associate in carbon tetrachloride[21] whereas 2-methyl-3-butyn-2-ol forms cyclic and open dimers with the latter dominating.[22] Pyrazole is intermolecularly H bonded to form cyclic dimers and trimers.[23,24] At 18 °C the equilibrium constant for dimerization is 47.5 M^{-1} and that for trimerization is 7540 M^{-2}.[24] It is recalled here that exchange between aggregated species is fast on the NMR time scale so that only average spectra and hence average K values are obtained.

Comparison of these data with the equilibrium data of Table II gives an idea about the extent of micelle–substrate association in relation to its self-association. For simplicity we assume that only monomers and open-ended polymers can H bond and that the bigger the aggregate the weaker its binding to the micelle. One has to take into consideration also the possible effect of the surfactant on the distribution of the substrate aggregates especially in the case of methanol and imidazole where several aggregates are formed. Association constants for methanol–surfactants are comparable with its autoassociation values. It seems that owing to its relatively smaller size methanol can penetrate and bind itself strongly to the micelle. On the other hand, the imidazole–surfactants association constants are well below the values for its autoassociation which may be the result of the weaker binding of the micelles with imidazole linear oligomers (vide supra). *N*-Methylimidazole does not self-associate and interacts with the surfactant via H bonding to the ammonium group. Its distribution between the micellar and bulk phases may show little variation from BAP to DAP and consequently its K values do

not change appreciably as a function of (X). Owing to similar pK_a values of imidazole and N-methylimidazole one can assume that the difference between their K values reflects the part due to H bonding between imidazole H(1) and the surfactant carboxylate group.

The effect of increasing the number of carbon atoms (X) in the alkylammonium ion on the observed K values is a modest one when compared with the corresponding case for aqueous micelles[25,26] where hydrophobic interactions are operative. The variation of K as a function of increasing (X) is not easy to rationalize because of the complexity of the variables involved (vide supra), but one can attempt to explain the trend of variation. Two factors can be considered, viz., the tightness of the micelle and the steric effects of the surfactant alkyl groups. The possibility of steric interactions between the solubilizates and the hydrophobic tails increases as (X) increases. This makes the penetration of the substrate into the micelle more difficult and its K falls off as (X) increases.[27] On the other hand, the equilibrium constant and the pK_a of the amines (both indicate micelle tightness)[9] change in a different way,[28,29] so that their contribution to K does not parallel that due to the steric effects. The delicate balance of these forces seems to favor association with OAP for most of the solubilizates (see Table II). Complete understanding of the factors affecting solubilization by these surfactants and by reversed micelles in general has to wait for the separation and quantitative estimation of the above-mentioned variables and for more data on the effects of solubilization on the micellar structure.[3]

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Registry No.—BAP, 17081-35-5; HAP, 39107-99-8; OAP, 39108-00-4; DAP, 17448-65-6.

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Base-Catalyzed β-Elimination Reactions. VI. Elimination from *tert*-Butyl 3-(Para-substituted phenoxy)- and 3-(Para-substituted benzoyloxy)thiolpropionates in 45% (Weight/Weight) Dioxane–Water[1]

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Triethylamine catalyzed and hydroxide ion catalyzed β-elimination reactions of the title compounds are second order overall. The Elcb mechanism with thiol ester carbanion formation rate determining is postulated on the basis of the insensitivity of the second-order rate constants to leaving group tendencies (small ρ's) and the linear relationship between log k_{OH} for thiol esters of this study and log k_{OH} for analogously substituted β-oxy-2-butanones for which the Elcb mechanism likely operates.

The probability that enzyme-catalyzed dehydration of β-hydroxythiol esters proceeds via a carbanion mechanism[2,3] prompted us to examine nonenzymic, base-catalyzed elimination reactions of *tert*-butyl β-oxythiol esters