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Electrical Aspects of Adsorbing Colloid Flotation. XX. NMR Studies of Lauric Acid Solubilization

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Abstract

Mixed micelles of dodecanoic acid with sodium dodecylsulfate, Triton X-100 (TX-100, an alkylphenylpolyethoxy alcohol), and dodecyltrimethylammonium chloride were studied. T_1 and nuclear Overhauser enhancement (NOE) measurements were made using dodecanoic acid C-13 labeled at the carboxyl group. Viscosity measurements were made and titration curves run of dodecanoic acid in these mixed micelles. The pK_a of dodecanoic acid increases as one goes from cationic to neutral to anionic micelles. Generally the mixed micelles are apparently small and roughly spherical; in acidic solution, however, dodecanoic acid–TX-100 micelles are large with an extended structure. NOE measurements indicate that the carboxyl group is relatively close to the protons in the micelle core, and that the carboxyl group moves out slightly into the aqueous phase on becoming ionized. The NOE of dodecanoic acid–TX-100 micelles indicates interaction between the carboxyl carbon and the protons in the ethoxy chain of TX-100.

INTRODUCTION

A recent experimental study of the use of mixed surfactant systems (sodium dodecylsulfate with alcohols or octanoic acid) in the flotation of ferric hydroxide and mixed ferric hydroxide–cupric hydroxide flocs suggests that substantial reductions in surfactant costs could be made without sacrificing separation efficiency by the use of mixed surfactants (*1*). Earlier we examined the theory of adsorption of binary surfactant mixtures on solid surfaces (*2*, *3*). Although mixed surfactant systems have not previously been used in precipitate and adsorbing colloid flotation separations, they have been employed quite extensively and profitably in ore flotation processes (*4*, *5*). All of these results encourage one to investigate further the use of mixed surfactant systems in precipitate and adsorbing colloid flotation.

The optimization of these mixed surfactant systems requires a good understanding of the interactions between the two species of surfactant in these solutions and in the hemimicellar layers they form on solid surfaces. Studies of solubilization provide an extensive source of information about interactions between amphiphilic species in solution (*6*, *7*). Quasi-elastic light scattering (*8*, *9*), NMR spectroscopy (*10–14*), and steady-state fluorescence quenching (*15*, *16*) have been used to study solubilization.

We previously reported critical micelle determinations on mixed surfactant systems using conductimetric or surface tension measurements (*1*), and on the use of viscosity measurements to get information about micellar structure in mixed micelles of Triton X-100 [TX-100, an alkylphenylpolyethoxy alcohol of approximate formula $(CH_3)_3CCH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_9OH$] and several second surfactants. Dodecanoic acid, dodecylsulfate, dodecyl amine, dodecyl phosphate, dodecyltrimethylammonium, and dodecyl alcohol were used as the second surfactants (*17*). The results indicated that if the cosurfactant is charged, fairly small mixed micelles similar in structure to those formed by TX-100 alone are formed, but that if the cosurfactant is electrically neutral or if its charge is screened by a solution of fairly high ionic strength, much larger micelles of extended structure are formed, resulting in viscosity increases by a factor of as much as 20.

In another study we reported on the use of NMR methods, particularly the measurement of relaxation times, to get information about the adsorption of dodecylbenzenesulfonate and dodecylsulfate on $Al(OD)_3$ in D_2O solution. These absorbed surfactants were found to be more constrained in their motions than are micellar surfactant ions, and motional constraints decrease as one moves away from the ionic head of the surfactant, supporting the model in which the ionic head of the surfactant is bound to a site on the floc (*18*).

The site of solubilization varies for different types of solutes. Alkanes, for instance, are mainly found in the interior of micelles, while more polar species lie close to the surface. If the solubilizate is itself an amphiphile, such as a long-chain alcohol, its polar or ionic group is located at the surface of the micelle, with its alkyl chain extended into the nonpolar phase in the interior of the micelle. For aromatic compounds it has been more difficult to assign the solubilization site; several spectroscopic approaches have been fruitful here (*13*, *19–21*). Depending on the nature of the solute and the solubilization site, solubilization can have effects on micellar size and shape, hydration, counterion binding, etc.

The ability of micelles to shift acid–base equilibria of a number of organic compounds has been studied (*21–24*). This has been used to study polarity and electric potential in micelles (*21*). Mukerjee et al. (*22*) showed the importance of microenvironmental polarities in affecting chemical processes from a study of dissociation constants of indicator dyes solubilized in micelles of nonionic and zwitterionic surfactants. Hinze (*24*) reviewed several such studies on the effect of solubilization on acid–base equilibria, and noted that more fundamental studies of solute–micellar systems are required before further quantitative discussion and explanation of the factors and forces involved in solubilization and equilibrium changes can be given.

Here we report an investigation of the solubilization of dodecanoic (lauric) acid in micelles of three different surfactants: sodium dodecylsulfate (SDS); Triton X-100, an alkylphenylpolyethoxy alcohol; and dodecyltrimethylammonium chloride (DTAC), by means of carbon-13 NMR. The dodecanoic acid was C-13 labeled at the carboxyl group. NMR has proven to be a useful tool in probing such interactions at the molecular level, as mentioned earlier (*18*). Use of NMR for studies of solubilization can be expected to yield information about localization, mobility, and in some cases about orientation (*13*) of the solubilized molecules. C-13 NMR has an advantage over proton NMR in that the chemical shifts for C-13 are much larger than those for protons. Also, the spin-lattice relaxation time (T_1) and nuclear Overhauser effect (NOE) give an indication of the interaction of the carboxyl carbon with the surrounding surfactant molecules or ions in the micelles.

CHEMICALS, EQUIPMENT, AND PROCEDURES

Commercial samples of SDS, TX-100, and DTAC were used without further purification. Most runs using SDS were made with Fisher lab grade SDS which contains a small amount of long-chain alcohols; a few runs made later with SDS of 99% purity from Sigma gave identical results. DTAC was obtained from Eastman Kodak, and scintillation grade TX-100 came from J. T. Baker. Deuterium oxide was obtained from Aldrich, and dodecanoic acid enriched with 90% C-13 at the carboxyl carbon was obtained from MSD Isotopes.

Dodecanoic acid (35 mM) was solubilized in 100 mM solutions of SDS, TX-100, or DTAC in D_2O. pH (or more properly, pD) adjustments were made by adding 0.1 *N* NaOD or 0.1 *N* DCl solution (Fisher NaOH or HCl in D_2O). The solutions were transferred to 5 mm NMR sample tubes and C-13 spectra were obtained on a JEOL FX-90Q spectrometer operating in the pulsed Fourier transform mode at 22.5 MHz using an internal deuterium field-frequency lock on solvent D_2O. The C-13 chemical shifts were measured with respect to acetonitrile as an internal reference. Four to eight scans yielded very good signal-to-noise ratios because of the use of C-13 enriched dodecanoic acid. Spin-lattice relaxation times were measured by the inversion recovery method (*25*) using the standard $(180°\text{-}\tau\text{-}90°\text{-}T)_n$ pulse sequence. Nuclear Overhauser enhancement was determined using gated decoupling; the ratio of the peak heights of a completely proton-noise decoupled spectrum and a gated decoupled spectrum was determined. The effect of paramagnetic impurities on the T_1 measurements was reduced by pretreating the commercial D_2O sample with Chelex-100, an ion-exchange resin. The D_2O was allowed to stand overnight in Nalgene bottles containing Chelex resin. The NMR sample tubes were also filled with D_2O and Chelex resin and allowed to stand overnight so as to minimize the leaching of paramagnetic ions from the walls of the tube during the NMR measurements.

pH titration curves were made by preparing 35 m*M* solutions of unlabeled dodecanoic acid with the required amount (about 100 m*M*) of SDS, TX-100, or DTAC. These solutions, all far above the cmc's of the surfactants, were then titrated with 100 m*M* NaOH using a Sargent-Welch model LSX pH Meter.

RESULTS AND DISCUSSION

The chemical shift values for the carboxyl carbon of dodecanoic acid in the three different micelles (SDS, DTAC, and TX-100) are given in Table 1. The deprotonation shift (Δ) varies with micellar environment. Effects of local electric fields on C-13 shifts have been suggested as causing the shift (*26, 27*). For carboxylic acids in solution, the deprotonation shift is related to the pK_a of the acid by the empirical equation (*28*)

$$\Delta = 0.77\text{p}K_a + 0.81 \tag{1}$$

This equation was developed for carboxylic acids in solution.

The fact that Δ is smaller for dodecanoic acid in DTAC micelles than it is for dodecanoic acid in TX-100 micelles suggests a smaller pK_a, which is expected since the positively charged DTAC micelle should facilitate

TABLE 1
Deprotonation Shift of Carboxyl Carbon in Dodecanoic Acid in Surfactant Micelles

pD	SDS	DTAC	TX-100
2	176.93 ppm	176.65	175.96
11	183.22	181.43	182.35
Δ (ppm)	6.29	4.77	6.39

proton removal. Similar reasoning suggests that Δ should be larger for dodecanoic acid in SDS micelles than it is for dodecanoic acid in TX-100 micelles, but, as seen in Table 1, this is not the case, casting some doubt on the applicability of the equation to carboxylic acids in micelles.

The spin-lattice relaxation times T_1 of the carboxyl carbon of dodecanoic acid in different micellar environments are shown in Fig. 1. There are distinct minima in the T_1 values. Such minima have been observed for the T_1's of carboxyl carbons in amino acids (*29*, *30*), and were attributed to pH-dependent binding of paramagnetic impurities to the carboxyl group. The minima were found to occur at a pH near the pK_a of the acid (*31*). Our T_1 measurements obtained with samples made up with Chelex-treated D_2O are shown in Fig. 2. The T_1 values show increases in the intermediate pH region, but a minimum is still observed in each case. We take the pH at which the minimum occurs for each micellar environment as an indication of the apparent pK_a value of dodecanoic acid in the micelle. These values are shown in Table 2, along with the pK_a's calculated from the observed Δ values and Eq. (1), the literature value for the pK_a of dodecanoic acid in aqueous medium (*32*), and values obtained from titration curves. The pK_a's for dodecanoic acid from T_1 values show the expected decrease as the dodecanoic acid goes from an anionic to a nonionic to a cationic micellar environment, as the removal of the positively charged proton is facilitated by increasing the surface potential of the micelle. Cationic micelles have been found to lower the pK_a values of dyes and acid–base indicators by reducing the free-energy difference between the dye and its conjugate form (*33*), a similar effect.

This interpretation is supported by the titration curves shown in Figs. 3–5. The pK_a's calculated from these titration curves are given in Table 2, and show the expected increase in value as the micellar charge goes from positive to zero to negative.

The fact that both T_1 measurements and titration curve measurements give the same order of pK_a's, an order which is in agreement with physical intuition, indicates that the use of Eq. (1) for estimating pK_a's of

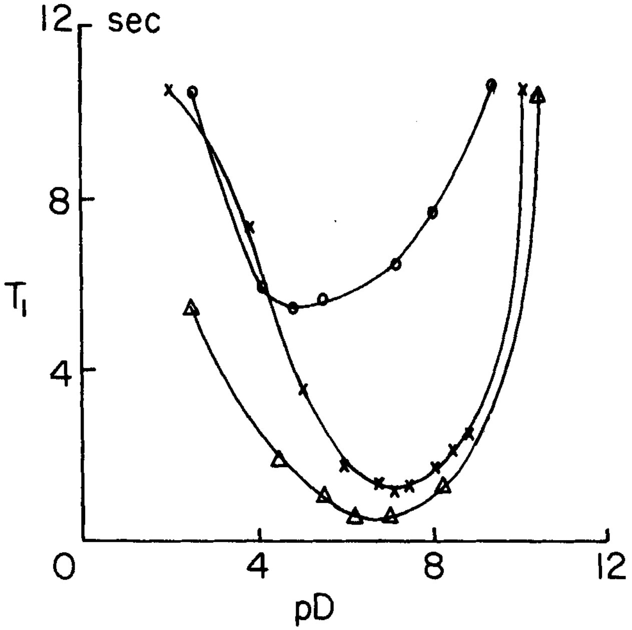

FIG. 1. T_1 of the carboxyl carbon of dodecanoic acid as a function of pD: (Δ) in TX-100 micelles, (×) in SDS micelles, (O) in DTAC micelles.

carboxylic acids in micelles is pressing this relationship beyond its range of applicability.

At acidic pH's the T_1 values are rather similar for dodecanoic acid in SDS and DTAC micelles; they are substantially lower for dodecanoic acid in TX-100 micelles. One interpretation of this is that mixed dodecanoic acid–SDS and dodecanoic acid–DTAC micelles are roughly the same size and shape, but that dodecanoic acid–TX-100 micelles are a good deal larger, tumble more slowly, and therefore yield lower T_1 values. A previous study of the viscosities of solutions of mixed micelles of TX-100 and a number of second surfactants (*17*) showed that the addition of electrically neutral cosurfactants such as dodecyl amine, dodecyl alcohol, or dodecanoic acid resulted in drastic increases in viscosity, indicating the formation of extended micellar structures in these mixed systems.

We therefore made viscosity measurements on several mixed surfactant solutions over a range of pH's. [The procedure used was described earlier (*17*).] The results are given in Table 3. Solutions of dodecanoic acid and TX-100 at low pH's exhibit viscosities roughly 10 times larger

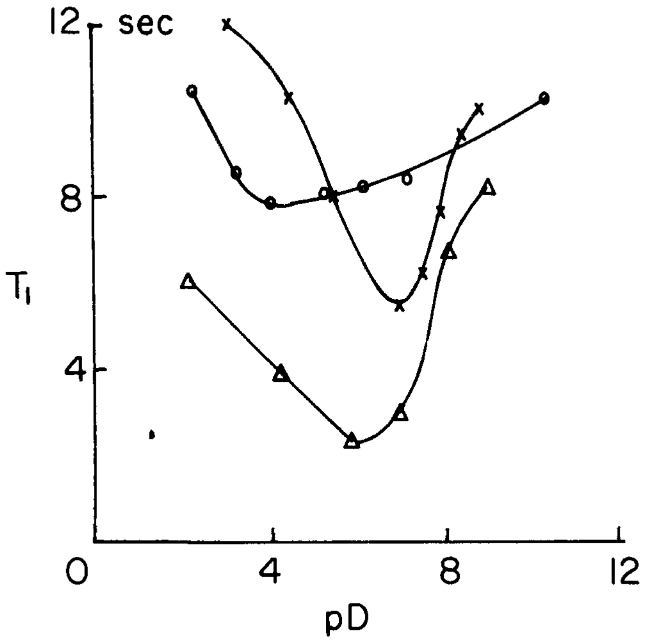

FIG. 2. T_1 of the carboxyl carbon of dodecanoic acid as a function of pD in samples treated with Chelex: (Δ) in TX-100 micelles, (X) in SDS micelles, (O) in DTAC micelles.

than those of the other mixed micelle systems and by dodecanoate ion–TX-100 solutions at pH 10.5, in agreement with the suggestion that the relatively low T_1 values of the dodecanoic acid–TX-100 solutions at low pH are due to a change in the micellar structure.

The nuclear Overhauser enhancement (NOE) values for these systems are given in Table 4. In all three mixed micelle systems the NOE values are rather large, presumably due to the proximity of the dodecanoic acid carboxyl carbon to a large number of protons in the alkyl chains of the

TABLE 2

pK_a Values of Dodecanoic Acid in Surfactant Micelles

	SDS	DTAC	TX-100
Calculated from Eq. (1)	7.12	5.1	7.25
From T_1 minimum	6.9	4.3	6.0
From titration curves	7.1	5.0	6.8
Free acid in aqueous solution (*32*)	5.3		

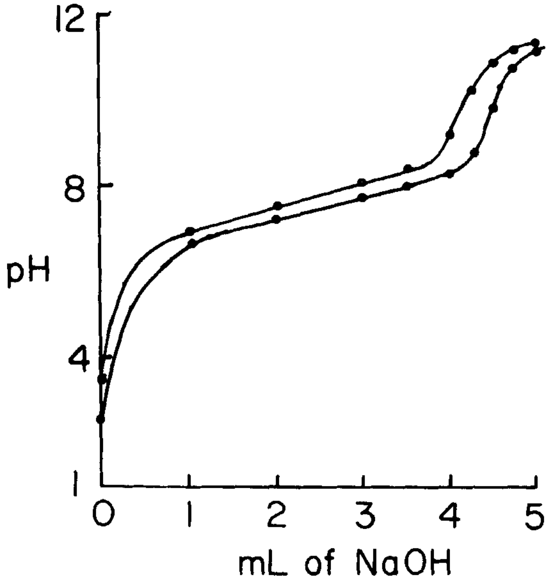

FIG. 3. pH titration curves of dodecanoic acid in SDS micelles. Mean pK_a = 7.12.

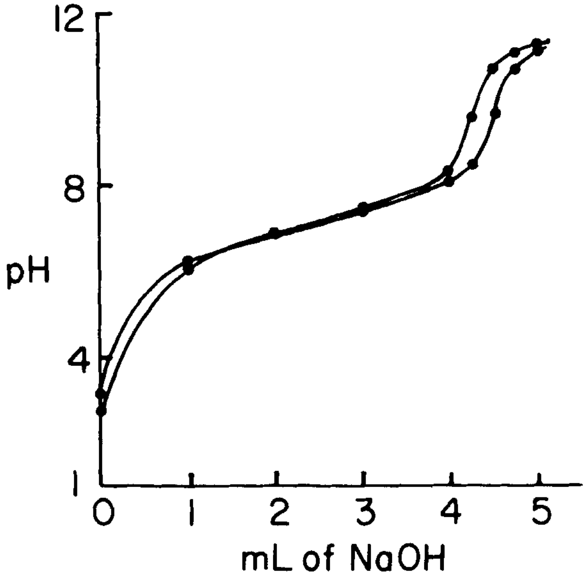

FIG. 4. pH titration curves of dodecanoic acid in TX-100 micelles. Mean pK_a = 6.80.

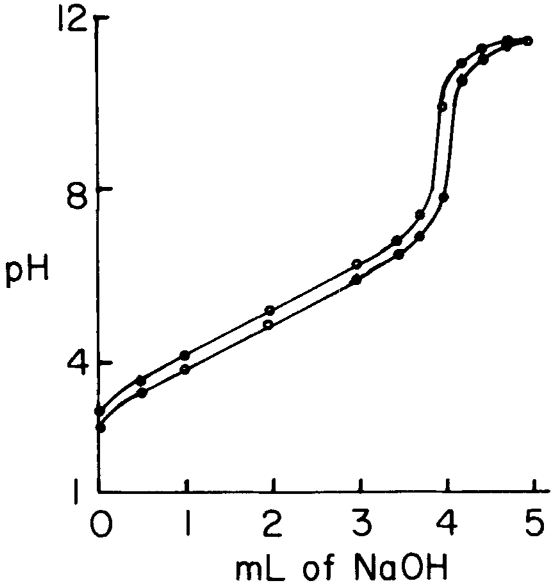

FIG. 5. pH titration curves of dodecanoic acid in DTAC micelles. Mean pK_a = 4.99.

surfactant species in the micelle. The largest NOE values are found for dodecanoic acid in TX-100 micelles at acidic or neutral pH's. In these micelles the hydrophilic portion of the structure, consisting of D_2O and the ethoxy chains of the TX-100 molecules, contains a rather high concentration of protons which can contribute to the effect. In the micelles of the other surfactants, the hydrophilic shell contains no protons to contribute to the NOE. The decrease in NOE with increasing pH may be due to increased solubility in D_2O of dodecanoate as

TABLE 3

Viscosities of Dodecanoic Acid-Second Surfactant Solutions at Different pH's

Sample	pH	η (cP)
SDS + dodecanoic acid	2.5	1.76
	10.5	1.6
TX-100 + dodecanoic acid	2.5	19.2
	10.5	1.7
DTAC + dodecanoic acid	2.5	1.5
	10.5	1.6

TABLE 4
Nuclear Overhauser Enhancement of Carboxyl Carbon in Solubilized Dodecanoic Acid

	Solubilizing surfactant		
pD	DTAC	SDS	TX-100
2.5	0.87	0.93	1.36
7.0	0.81	0.89	1.02
10.0	0.77	0.71	0.84

compared to dodecanoic acid; it may also be due to a movement of the dodecanoate ions in the micelle so that the carboxylate ionic head projects further into the aqueous phase than does the electrically neutral carboxyl group which is present at the lower pH's.

CONCLUSIONS

Titration curves and C-13 T_1 measurements indicate that the pK_a of dodecanoic acid solubilized in micelles increases as one goes from cationic to neutral to anionic solubilizing surfactants. C-13 T_1 measurements and viscosity measurements indicate that mixed micelles of dodecanoate with SDS, TX-100, and DTAC are fairly small and globular; mixed micelles of dodecanoic acid with SDS and DTAC are also small and globular, while mixed micelles of dodecanoic acid with TX-100 are quite extended structures. The nuclear Overhauser enhancement data indicate that the carboxyl carbon of dodecanoic acid/dodecanoate is relatively close to the protons in the micelle, but that this carbon is somewhat further out of the micelle in alkaline solution than in acid. The NOE data also indicate interaction of the carboxyl carbon with the protons in the ethoxy chains of TX-100–dodecanoic acid mixed micelles.

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