Micelle Formation by Sodium Dodecyl Sulfate in Water–Additive Systems

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The conductances of sodium dodecyl sulfate (SDS) have been determined in water in the presence of various additives, such as strong nitrogen organic bases (pyridine, 3- and 4-methylpyridines, and 2,6-dimethylpyridine), carboxylic acids (acetic acid, propionic acid, and butyric), and alcohols (methanol (MeOH), 1-butanol (BuOH), 2-methyl-1-propanol, 2-methyl-2-propanol, and 2-methyl-2-butanol) at 25 °C. The conductances of SDS in water in the presence of pyridine and acetic acid at temperatures between 15 and 45 °C have also been measured. From the conductivity data, the critical micellar concentration (cmc), degree of counter-ion association (α), molar conductivities at infinite dilution (Λ_0), limiting ionic molar conductivities ($\lambda_{\pm}^{\circ}$), free energy of transfer of the surfactant hydrocarbon chain from medium to the micelle ($\Delta G_{\mathrm{HP}}^{\circ}$), free energy of transfer of surface contributions ($\Delta G_{\mathrm{s}}^{\circ}$), and standard enthalpies of micellisation ($\Delta H_{\mathrm{HP}}^{\circ}$) of SDS have been computed. It has been found that the presence of strong nitrogen organic bases causes strong micelle denaturation, whereas the presence of carboxylic acids and alcohols stabilizes the micelles, with the exception of MeOH and 2-methyl-2-butanol.

The temperature effect on the micellisation of SDS in the presence of pyridine shows that the enthalpy of micellisation becomes less negative along with an increase in temperature. However, the enthalpy of transfer of a hydrocarbon group from an aqueous to a nonpolar environment in the presence of acetic acid is endothermic.

The aggregation phenomenon of amphiphilic molecules involves contributions from both repulsive and attractive interactions. Especially, in ionic surfactants, the repulsive forces originated primarily from electrostatic repulsions between the polar head groups,[1)] whereas attractive interactions have generally been attributed to hydrophobic interactions[2)] between the nonpolar tails of the surfactant monomers. However, considerable emphasis has recently also been placed in the London-dispersion interactions.[3,4)] In order to discriminate between these different kinds of interactions, the surfactant solution properties, such as critical micellar concentration (cmc), micelle shape and size, solubility, and Krafft temperature, have to be properly explored. This can be done by modifing the chemical structure of the hydrophobic group as well as that of the hydrophilic head group. However, the significant influence on the above-mentioned surfactant solution properties, especially in the case of ionic surfactants, can be observed by adding small amounts of various additives such as electrolytes[5—7)] and nonpolar[7,8)] and polar organic liquids.[9,10)]

In our earlier work,[9)] micelle formation by sodium dodecyl sulfate (SDS) in various aqueous+nonaqueous solvents was studied. It was observed that organic solvents with low relative permittivity (ε) and high hydrophobic surfaces have a strong ability to break the micelles. However, in the present study, the effect of three different categories of organic solvents viz. strong nitrogen organic bases (pyridine, 3- and 4-methylpyridines, and 2,6-dimethylpyridine), carboxylic acids (acetic acid, propionic acid, and butyric acid), and alcohols (MeOH, BuOH, 2-methyl-1-propanol, 2-methyl-2-propanol, and 2-methyl-2-butanol) was explored concerning the micellisation of SDS. Unlike previously,[9)] very small amounts of these additives were used to observe their effect on the micellisation process. It was found that even this small quantity was sufficient to cause significant changes in the micelle formation. The purpose of selecting these strong nitrogen organic bases was their extraordinary mixing behavior[11,12)] as well as their strong ability to interact with cations.[10)] The carboxylic acids were chosen in order to estimate the extent of penetration of the alkyl group in a micelle as well as their collective comparison with nitrogen bases and a wide variety of alcohols.

Experimental

Sodium dodecyl sulfate (SDS) was used after purification. Pyridine, 3- and 4-methylpyridines, and 2,6-dimethylpyridine, all 98% pure (Glaxo), methanol (MeOH), and 1-butanol (BuOH) 98%, E. Merck), were further purified by methods reported elsewhere.[13)] 2-methyl-1-propanol, 2-methyl-2-propanol, and 2-methyl-2-butanol, acetic acid, propionic acid, and butyric acid, all extra pure from E. Merck, were used as such. Conductivity water having a specific conductance of 4—8×10^{-1} S cm^{-1} was used in all of the binary mixtures.

The precise conductances of SDS in water containing 0.5 mol% of pyridine, 3- and 4-methylpyridines, and 2,6-dimethylpyridine; 0.1 mol% of acetic acid, propionic acid, and butyric acid; and 1 mol% of MeOH, BuOH, 2-methyl-1-propanol, 2-methyl-2-propanol, and 2-methyl-2-butanol between the concentration range of (1—17000) $\times 10^{-6}$ mol dm^{-3} respectively were measured at 25 °C with an overall temperature variation of ±0.01 °C. However, it was found that the initial conductivity values of the reference solutions before the addition of a surfactant were significantly higher in acids and comparatively quite lower in alcohols with similar amounts of additives. This difficulty forced us to take different amounts of additives of different categories in order to avoid errors in the measurements. Because of this difficulty, it was only possible to study a qualitative intercomparison among the different categories of organic solvents viz. organic bases, carboxylic acids, and alcohols. However, a quantitative intracomparative effect among the different organic solvents of one category on the micellisation process of SDS in water was possible.

Apart from these measurements, the temperature effect was also studied on the micelle formation of SDS in water containing the above-mentioned amounts of pyridine and acetic acid in the 15—45 °C temperature range. The procedure for the conductance measurements was basically the same as reported earlier.[14] The accuracy of the conductance measurements was ±0.2%.

Results

The conductivity ($\varkappa$) is linearly correlated[15] to the surfactant concentration in both the pre-micellar and in the post-micellar regions, having a slope in the pre-micellar region greater than that in the post-micellar region. The intersection point between the two straight lines gives the cmc and the ratio between the slopes of the post micellar region to that in the pyre-micellar region gives the degree of counter-ion dissociation, (β), and, subsequently, the degree of counter-ion association ($\alpha = 1 - \beta$). Figure 1 shows the variation of $\varkappa$ graphically in the presence of bases. Similar plots were obtained in the presence of acids and alcohols.

The $\varkappa$ values for SDS in all of the systems in both the pre and the post micellar regions were fitted to a linear equation in order to evaluate the cmc and β,

$$\varkappa = \varkappa_0 + sC, \tag{1}$$

where $\varkappa_0$ is the conductivity at infinite dilution, s is the slope in the pre and the post-micellar regions, and C is the concentration (mol dm^{-3}) of the surfactant.

From the $\varkappa$ values, the molar conductivities (Λ) for SDS were evaluated as usual for simple electrolytes by neglecting the hydrophobic nature of the surfactants.[16,17] These values were fitted to the Onsager equation[18] in the form

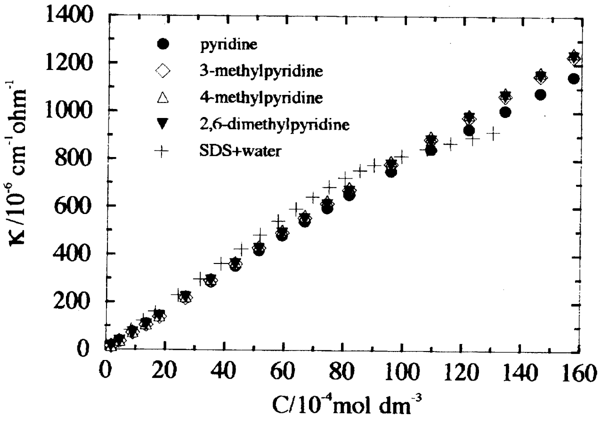

Fig. 1. $\varkappa$ vs. C of SDS in water and in the presence of different bases st 25 °C.

$$\Lambda = \Lambda_0 - (A\Lambda_0 + B)\sqrt{C} \tag{2}$$

in order to determine the limiting molar conductivities at infinite dilution (Λ_0) in the pre-micellar region, as described previously.[9,16,17]

From the Λ_0 values, the limiting ionic molar conductivities for Na$^+$ ($\lambda^\circ_{\text{Na}^+}$) and dodecyl sulfate, DS$^-$ ($\lambda^\circ_{\text{DS}^-}$) ions can be calculated using the limiting values of Na$^+$ in water, $\lambda^\circ_{\text{Na}^+}$=50.1 S cm^2 mol^{-1}, which is obtained by combining the Kunze and Fuoss[19] conductance data for NaCl in water with Longsworth's[20] transference number data. Therefore, by substracting $\lambda^\circ_{\text{Na}^+}$ from Λ_0 for SDS in water, $\lambda^\circ_{\text{DS}^-}$ can be extracted. Since keeping in consideration of the large size and large hydrophobic surface of the DS$^-$ ion, it has been assumed that the solvation of the DS$^-$ ion remains constant in water as well as in the presence of small amounts of various additives; hence, we can easily consider that the $\lambda^\circ_{\text{DS}^-}$ value remains constant, even in the presence of various additives in water.[16,17] Subsequently, such values for Na$^+$ ion in water in the presence of various additives can also be obtained.[16,17]

In the presence of additives, the free energy of micellisation consists of SDS–SDS interactions, additive–SDS interactions and additive–additive interactions. These interactions can be divided into hydrophobic and hydrophilic contributions. In order to estimate both kinds of contributions, the thermodynamics of micelle formation, proposed by Evans and Ninham,[3] has been taken into account, which gives

$$RT \ln X_{\text{cmc}} = \Delta G^\circ_{\text{HP}} + \Delta G^\circ_{\text{s}}, \tag{3}$$

where $\Delta G^\circ_{\text{HP}}$ is the hydrophobic free energy of transfer of the surfactant hydrocarbon chain from the medium to the interior of the micelle, and $\Delta G^\circ_{\text{s}}$ corresponds to the energy associated with the surface contributions consisting of electrostatic interactions between the head groups and counter ions and all other contributions due to specific interactions. The sum of these two terms is equivalent to the total Gibbs energy per surfactant molecule ($\Delta G^\circ_{\text{M}}$=$RT$ln X_{cmc}) associates with forming micelles. In order to determine $\Delta G^\circ_{\text{s}}$, the equilibrium model of Ueno et al.[21] can be employed, which is related to the degree of counter-ion binding to the electrostatic interactions between the surfactant head groups and counter ions.[22] This model also provides a measure of the free energy of transferring the nonpolar tail from the aqueous medium to the interior of the micelle. In the present study, the following Eq. 4 can be used for the equilibrium between monomers, counter ions and monodispersed micelles:

$$(n-p)C^+ + nS^- \Leftrightarrow M^{p-}, \tag{4}$$

where C$^+$, S$^-$, and M^{p-} stand for the counter ion, surfactant monomer, and micelles, respectively. The equilibrium constant can be written in terms of the standard free energy of micelle formation per monomer as

$$\frac{\Delta G^\circ_{\text{M}}}{RT} = -(1/n)\ln C_{\text{Mp}^-} + \ln C_{\text{s}^-} + \left(1 - \frac{p}{n}\right)\ln C_{\text{c}^+}. \tag{5}$$

For typical micelles (n=50—100), the term M^{p-} is small and insensitive to large errors in determining C_{Mp^-}, and both

C_{C^+} and C_{S^-} can be replaced by the cmc in the second and third terms in Eq. 5. It becomes

$$\Delta G^{\circ}_{HP} = RT\ln X_{cmc} + RT\left(1-\frac{p}{n}\right)\ln X_{cmc}, \qquad (6)$$

where p/n is the degree of counter-ion dissociation (β). Comparing it with Eq. 3 shows that in term of the equilibrium model, ΔG°_{s} is given by

$$\Delta G^{\circ}_{s} = -\alpha RT\ln X_{cmc}. \qquad (7)$$

By using the ΔG°_{HP} and ΔG°_{s} values for SDS in each case, respective term $\Delta G^{\circ(II)}_{HP}$ and $\Delta G^{\circ(II)}_{s}$, which represent the effect of an additive on micellisation, can be calculated by means of following general Eq. 8:[9,14,23]

$$\Delta G^{\circ(II)} = \Delta G^{\circ}(\text{in aqueous additive}) - \Delta G^{\circ}(\text{in } H_2O). \qquad (8)$$

Conductivity measurements of SDS in water in the presence of pyridine and in the presence of acetic acid between 15—45 °C were also performed. From the cmc and α data, the standard enthalpies of micellisation (ΔH°_{HP}) can be obtained by assuming that α is practically constant; and inserting Eq. 6 into a Gibbs–Helmholtz equation gives the following Eq. 9:

$$\Delta H^{\circ}_{HP} = -(1+\alpha)RT^2\left(\frac{\partial \ln X_{cmc}}{\partial T}\right)_{p}. \qquad (9)$$

Since ΔH°_{HP} is not constant with respect to the temperature, the values of ΔH°_{HP} were obtained using a quadratic equation of the following form:

$$\ln X_{cmc} = a + bT + CT^2, \qquad (10)$$

and subsequently applying Eq. 9.

The computed values for cmc, α, Λ_0, $\lambda_0^{\pm}$, ΔG^{0}_{HP}, ΔG°_{s}, $\Delta G^{\circ(II)}_{HP}$, $\Delta G^{\circ(II)}_{s}$, and ΔH°_{HP}, thus obtained for SDS in water and in presence of bases, acids, alcohols and at variable temperatures, are reported in Tables 1, 2, 3, and 4, respectively. The parameters of Eq. 10 are listed in Table 5.

Discussion

Micelle Formation in Water–Base Systems. Strong nitrogen organic bases have a unique behavior in solution[10,12] due to their strong electron-donating capabilities. Table 1 shows that the presence of even 0.5 mol% of these bases in an aqueous SDS solution causes a considerable change in the micelle formation. The cmc and ΔG°_{HP} values are increased, while α and ΔG°_{s} are decreased. There is a significant change in the slopes of the κ values in the pre and post micellar regions of SDS in water+base to that of SDS in pure water. Also, the $\lambda^{\circ}_{Na^+}$ value for Na$^+$ in the presence of each base is significantly decreased (Table 1). A magnified effect of the presence of these bases on the micelle formation can be seen in Fig. 2. Here, the variation of λ versus $\sqrt{C}$ is quite interesting. For each base there is a sharp decrease in the λ values of SDS, forming a strong minimum followed by a maximum, and then a further decrease along with an increase in the concentration of SDS. However, similar trends have been observed for sodium glycodeoxycholate[17] (NaGDO), cryptate 222+NaGDO,[17] sodium deoxycholate,[24] sodium taurodeoxycholate[25] aqueous solution, and paraffin-chain salts in water and aqueous 1-propanol solutions,[26] Such trends belong neither to normal uni-univalent electrolytes nor those to classical micellar system. Recently, Sesta et al.[17] have explained the self association of bile salts on the basis of the "noncritical multimer concentration", which is a stepwise aggregation phenomenon. In the present study, the behavior of SDS in the presence of strong of nitrogen organic bases is somewhat similar to that of the above-mentioned bile salts, and can also be explained on the basis of the "noncritical multimer concentration". In Fig. 2, for the sake of a comparison, λ for NaGDO in water from Ref. 17 has also been drawn. It seems that in the first stage small aggregates with a small aggregation number are formed; these small aggregates are without counter ions, since the surfactant is considered to be entirely in the fully dissociative form. Once the ag-

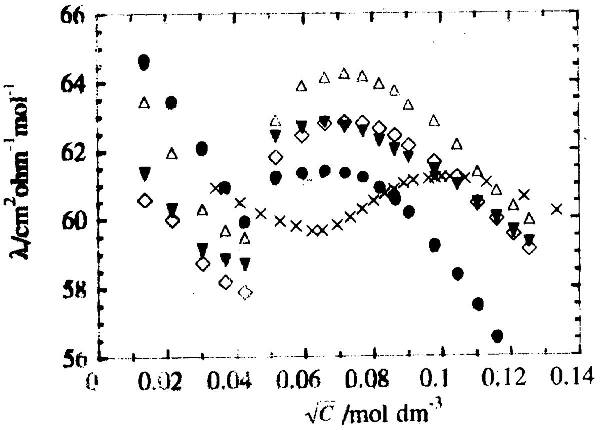

Fig. 2. λ vs. $\sqrt{C}$ of SDS in the presence of different bases at 25 °C. Symbols as for Fig. 1. (X) NaDGO from Ref. 17.

Table 1. Values of the cmc/mol dm^{-3}, α, Λ_0/cm^2 S mol^{-1}, $\lambda^{\circ}_{Na^+}$/cm^2 S mol^{-1}, $\lambda^{\circ}_{DS^-}$/cm^2 S mol^{-1}, ΔG°_{HP}/kJ mol^{-1}, ΔG°_{s}/kJ mol^{-1}, $\Delta G^{\circ(II)}_{HP}$/kJ mol^{-1}, $\Delta G^{\circ(II)}_{s}$/kJ mol^{-1}, and Slopes (s)/cm^{-1} S/mol dm^{-3} in Pre and Post Micellar Regions of SDS in Water (W) and in W+Pyridine (A), W+3-Methylpyridine (B), W+4-Methylpyridine (C) and W+2,6-Dimethylpyridine (D) at 25 °C

	Systems				
	W	A	B	C	D
cmc	0.0082	0.0094	0.0098	0.0097	0.0101
α	0.66	0.20	0.12	0.13	0.11
Λ_0	75.2	66.9	62.0	66.0	63.2
$\lambda^{\circ}_{Na^+}$	50.1	41.8	36.9	40.9	38.1
$\lambda^{\circ}_{DS^-}$	25.1	25.1	25.1	25.1	25.1
ΔG°_{HP}	−36.29	−26.04	−23.99	−24.23	−23.69
ΔG°_{s}	14.43	4.520	2.571	2.788	2.348
$\Delta G^{\circ(II)}_{HP}$	0.00	10.25	12.30	12.06	12.60
$\Delta G^{\circ(II)}_{s}$	0.000	−9.910	−11.86	−11.64	−12.08
s_{PRE}	0.092	0.079	0.082	0.084	0.082
s_{POST}	0.032	0.063	0.072	0.073	0.073

Table 2. Values of cmc/mol dm^{-3}, α, Λ_0/cm^2 S mol^{-1}, $\lambda^\circ_{\mathrm{Na^+}}$/cm^2 S mol^{-1}, $\lambda^\circ_{\mathrm{DS^-}}$/cm^2 S mol^{-1}, ΔG_{HP}/kJ mol^{-1}, $\Delta G^\circ_{\mathrm{s}}$/kJ mol^{-1}, $\Delta G^{\circ(\mathrm{II})}_{\mathrm{HP}}$/kJ mol^{-1}, $\Delta G^{\circ(\mathrm{II})}_{\mathrm{s}}$/kJ mol^{-1}, and Slopes (s)/cm^{-1} S/mol dm^{-3} of SDS in Water (W) in W+Acetic Acid (A), W+Propinoic Acid (B) and W+Butyric Acid (C) at 25 °C

	Systems			
	W	A	B	C
cmc	0.0082	0.0071	0.0069	0.0063
α	0.66	0.72	0.66	0.60
Λ_0	75.2	73.1	71.0	67.2
$\lambda^\circ_{\mathrm{Na^+}}$	50.1	48.0	45.9	42.1
$\lambda^\circ_{\mathrm{DS^-}}$	25.1	25.1	25.1	25.1
$\Delta G^\circ_{\mathrm{HP}}$	−36.29	−37.77	−37.00	−36.03
$\Delta G^\circ_{\mathrm{s}}$	14.43	15.55	14.71	13.51
$\Delta G^{\circ(\mathrm{II})}_{\mathrm{HP}}$	0.000	−1.480	−0.710	0.260
$\Delta G^{\circ(\mathrm{II})}_{s}$	0.000	1.120	0.280	−0.920
s_{PRE}	0.092	0.092	0.088	0.078
s_{POST}	0.032	0.026	0.030	0.031

gregation number attains a critical value, some counter ions must be bound; this tendency is enhanced with increasing the aggregation number up to a well-defined micelle. This is represented by the maximum in the Λ value in Fig. 2. However, as the concentration of SDS is increased further, the conductance starts to decrease. This trend is attributed to an evaluation of higher aggregates, leading to a decrease in the surface-charge density, resulting in an overall decrease in the molar conductance.

From a thermodynamic point of view, the decrease in $\Delta G^\circ_{\mathrm{s}}$ can be ascribed to the energy associated with the non-availability of Na$^+$ counter ions for electrostatic interactions with the head groups on the surface of the micelle, due to strong complexation with the base molecules. The removal of this from the micellar interface enhances the surface potential by increasing the electrostatic repulsions between the head groups, which consequently destabilizes the micelles; thus, $\Delta G^\circ_{\mathrm{HP}}$ becomes less negative. It can also be said that a stronger base could have subsequently stronger energetic effects, could be reflected from the variation of $\Delta G^{\circ(\mathrm{II})}_{\mathrm{HP}}$ and $\Delta G^{\circ(\mathrm{II})}_{\mathrm{s}}$ (Table 1).

Table 3. Values of cmc/mol dm^{-3}, α, Λ_0/cm^2 S mol^{-1}, $\lambda^\circ_{\mathrm{Na^+}}$/cm^2 S mol^{-1}, $\lambda^\circ_{\mathrm{DS^-}}$/cm^2 S mol^{-1}, $\Delta G^\circ_{\mathrm{HP}}$/kJ mol^{-1}, $\Delta G^\circ_{\mathrm{s}}$/kJ mol^{-1}, $\Delta G^{\circ(\mathrm{II})}_{\mathrm{HP}}$/kJ mol^{-1}, $\Delta G^{\circ(\mathrm{II})}_{\mathrm{s}}$/kJ mol^{-1}, and Slopes (s)/cm^{-1} S/mol dm^{-3} of SDS in Water (W), in W+MeOH (A), W+BuOH (B), W+2-Methyl-1-propanol (C), W+2-Methyl-2-propanol (D), W+2-Methyl-2-butanol (E) at 25 °C

	Systems					
	W	A	B	C	D	E
cmc	0.0082	0.0085	0.0065	0.0068	0.0058	0.0084
α	0.66	0.61	0.20	0.22	0.33	0.27
Λ_0	75.2	74.0	71.0	68.3	62.0	68.7
$\lambda^\circ_{\mathrm{Na^+}}$	50.1	48.9	45.9	43.2	36.9	43.6
$\lambda^\circ_{\mathrm{DS^-}}$	25.1	25.1	25.1	25.1	25.1	25.1
$\Delta G^\circ_{\mathrm{HP}}$	−36.29	−35.06	−26.93	−27.24	−30.22	−27.69
$\Delta G^\circ_{\mathrm{s}}$	14.43	13.28	4.488	4.912	7.498	5.887
$\Delta G^{\circ(\mathrm{II})}_{\mathrm{HP}}$	0.000	1.230	9.360	9.050	6.070	8.600
$\Delta G^{\circ(\mathrm{II})}_{\mathrm{s}}$	0.000	−1.150	−9.942	−9.518	−6.932	−8.543
s_{PRE}	0.092	0.094	0.093	0.087	0.080	0.087
s_{POST}	0.032	0.036	0.074	0.068	0.053	0.064

Comparing the micellisation of NaGDO[17] in the presence of a small amount of cryptate 222 with that of SDS in presence of nitrogen bases, it can be said that both additives have a strong affinity for Na$^+$ counter ions in their respective surfactant solution. This is due to the fact that the lone pairs of both the cryptate 222 cavity and that of the nitro-

Table 4. Value of cmc/mol dm^{-3}, α, Λ_0/cm^2 S mol^{-1}, $\Delta G^\circ_{\mathrm{HP}}$/kJ mol^{-1}, $\Delta G^\circ_{\mathrm{s}}$/kJ mol^{-1}, $\Delta G^\circ_{\mathrm{M}}$/kJ mol^{-1}, and $\Delta H^\circ_{\mathrm{HP}}$/kJ mol^{-1}, of SDS in Water in Presence of Pyridine Acetic Acid at Various Temperatures

T/K	cmc	α	Λ_0	$\Delta G^\circ_{\mathrm{HP}}$	$\Delta G^\circ_{\mathrm{s}}$	$\Delta G^\circ_{\mathrm{M}}$	$\Delta H^\circ_{\mathrm{HP}}$
			SDS–water–pyridine				
288.15	0.0084	0.20	55.3	−25.29	4.215	−29.50	−28.78
293.15	0.0090	0.20	60.2	−25.63	4.361	−29.99	−28.19
298.15	0.0094	0.21	66.9	−26.05	4.520	−30.57	−27.49
303.15	0.0096	0.22	74.3	−26.52	4.694	−31.22	−26.68
308.15	0.0098	0.22	82.7	−27.01	4.871	−31.88	−25.75
318.15	0.0099	0.23	106.8	−28.08	5.252	−33.34	−23.54
			SDS–water–acetic acid				
288.15	0.0073	0.71	61.5	−36.61	15.20	−51.81	22.99
293.15	0.0071	0.72	65.8	−37.58	15.73	−53.31	19.02
298.15	0.0070	0.72	73.3	−38.28	16.02	−54.31	14.59
303.15	0.0071	0.71	85.7	−38.64	16.04	−54.68	9.773
308.15	0.0073	0.69	103.0	−38.69	15.80	−54.49	4.643
313.15	0.0078	0.67	111.7	−38.57	15.47	−54.04	−0.708
318.15	0.0083	0.64	118.7	−38.21	14.91	−53.12	−6.238

Table 5. Parameters of Eq. 10 and Correlation Factor (R) for SDS–Water–Pyridine (I) and SDS–Water Acetic Acid(II)

	a	b(K)	c(K^2)	R
(I)	33	0.15	−0.0002	0.996
(II)	28	−0.25	−0.0004	0.997

gen bases undergo strong electrostatic interactions with a cation like Na^+. However, the induction of cryptate 222 in an aqueous NaGDO solution helps concerning the stability of the primary micelles of NaGDO, whereas that of strong nitrogen bases in aqueous SDS destabilizes the micelles of SDS. This is due to the presence of cryptate-GDO$^-$ and the absence of base-DS$^-$ hydrophobic interactions, which may be responsible for changing the abrupt aggregation of SDS into a stepwise aggregation in the presence of pyridine. This makes the surfactant a weak surfactant, like bile salts.

Micelle Formation in Water–Acid Systems. The additive effect of carboxylic acid seems to be opposite on the micellisation of SDS to that of the previously observed bases. The cmc is significantly decreased whereas the change in the energetic effects is not very significant with the addition of small amount of each acid in an aqueous SDS solution (Table 2). These results can be explained on the bases of the hydrophobic hydration[27,28] of additive molecules. The hydrophobic hydrated part of the alkyl chain of carboxylic acids directly participates in the micelle formation by inserting its hydrophobic end into the interior of the micelle. An increase in the alkyl chain length increases the hydrophobic character,[29] resulting in a further decrease in the cmc (Table 2). It is to be noted that the slopes for $\varkappa$ in the presence of acids before cmc are somewhat lower than those in pure water (Table 2). This indicates that the additive molecules are incorporated with the surfactant molecules, which subsequently results in a decrease in the $\lambda^{\circ}_{Na^+}$ value. A decrease in the slopes above the cmc also indicates the participation of additive molecules in micelles formation, which is probably responsible for the somewhat higher negative value for ΔG°_{HP}; also, the increase in the $\Delta G^{\circ(II)}_{S}$ value upon addition of acetic acid and propionic acid can be explained as being due to the partitioning of acids into the micelle.

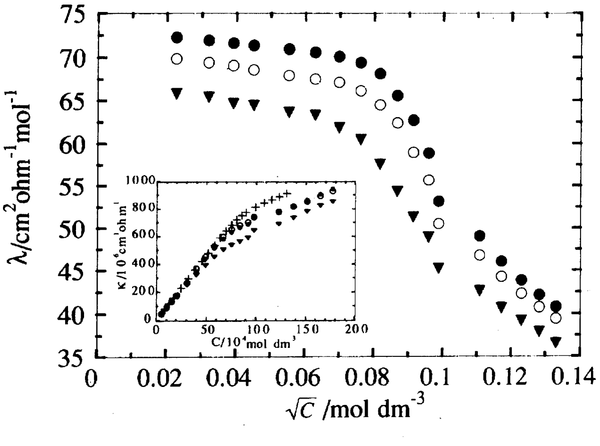

Fig. 3. λ vs. $\sqrt{C}$ of SDS in water and in the presence of acetoc acid (●), propionic acid (○), and butyric acid (▼) at 25 °C. Inset: $\varkappa$ vs. C.

Figure 3 shows that there is a predominant break in each λ versus $\sqrt{C}$ plot of SDS in water in the presence of different carboxylic acids after a cmc of around 0.01 mol dm^{-3}. Although it is known that SDS has a post-micellar transition[30] at around 0.25 mol dm^{-3}, in the present case, it is very difficult to ascribe it as a post-micellar transition. It seems to be a characteristic feature of present carboxylic acids; it is thus desirable to determine the shape and size of the micelle by means of light-scattering measurements.

Micelle Formation in Water–Alcohol Systems. In recent years,[31—33] aqueous mixtures of alcohol and surfactants have been extensively studied by means of different experimental techniques in order to understand the interactions and structures of micelle. The role of alcohol in micelle formation is expected to depend upon several factors. It is possible that alcohol molecules may modify the water structure when present in small concentration. At higher concentrations, some other effects, such as alteration in the relative permittivity of the solvent or the partitioning of alcohol molecules between bulk and the micellar phase, may become more important. In the present study, the solubalisation of alcohols in aqueous amphiphilic solutions can be explained on the basis of disruption of the water structure upon the addition of a small amount of alcohol and the formation of new hydrogen bonds between the alcohol and water molecules, leading to the formation of cavity[7] around the added alcohol molecules. This causes an ordering of the water molecules, or an enhancement of the structure, which subsequently helps to increase the hydrophobic effects.[7,26] Thus, the cmc is reduced in the presence of BuOH, 2-methyl-1-propanol, and 2-methyl-2-propanol. The variation in the $\Delta G^{\circ(II)}_{HP}$ values (Table 3) for these alcohols also support favorable hydrophobic interactions due the structure producing effects, instead of the partitioning of alcohol molecules between the bulk and micelles. However, MeOH is already known for destabilizing micelles,[34] whereas such an effect of 2-methyl-2-butanol can be due to a steric hinderance,[7] which restricts the degree of association of the surfactant monomers. The structure-making effects of alcohols are also expected to appreciably decrease the conductivity of SDS (Table 3). The presence of BuOH, 2-methyl-1-propanol, and 2-methyl-2-propanol do not show any systematic order, though the additive effect of 2-methyl-2-propanol seems to be stronger compared to other alcohols in lowering the cmc of SDS.

Intercomparison between Bases, Carboxylic Acids, and Alcohols on Micelle Formation of SDS. On the basis of the above results, a qualitative intercomparison among three different categories of organic solvents can be made. We have previously found[9] that the micelle formation of SDS mainly depends upon the hydrophilic and hydrophobic nature of the additives (organic solvents). The presence of a long or short, straight or branched, rigid or flexible chain in additive molecules determines the hydrophobic behavior,[35] whereas a cationic, anionic or nonionic head group influences the hydrophilic nature of the additive.[36,37] Hydrophilic entities such as electrolytes[5)] in micellar solutions, also alter the micellar structure significantly, which subsequently leads to micellar transitions, due to the strong electrostatic interactions. In the present study, the nature of organic nitrogen bases was entirely hydrophilic due to their strong electron-donating capabilities, whereas that of carboxylic acids and alcohols were found to be hydrophobic (Tables 2 and 3). It is also interesting to note that the slopes in the pre-micellar region of the conductivity of SDS in the presence of bases and acids (Tables 1 and 2) are decreased, directly related to the electrical mobility of the surfactant molecules. Because of this, $\lambda^{\circ}_{\mathrm{Na}^+}$ is decreased due to surfactant-additive interactions. On the other hand, in the post-micellar region, the slopes are overall increased in the presence of bases and alcohols, they are while decreased in the presence of acids. This indicates, perhaps, that only acids or surfactant-acids complexes can be incorporated into the micelles, because of which the free energy of transfer of the hydrocarbon tail ($\Delta G^{\circ}_{\mathrm{HP}}$) from the medium to the micelle becomes more negative, especially in the cases of acetic acid and propionic acid (Table 2). On the other hand, the energy associated with the surface contribution due to the electrostatic interactions between the head groups and the counter ions($\Delta G^{\circ}_{\mathrm{S}}$) has been significantly lowered in the presence of bases compared to acids and alcohols, which could be due to the strong complexation of the base molecules with the Na^+ counter ions. From the above results, it can be concluded that the presence of bases in an aqueous SDS solution results in a considerable destabilization of micelles, whereas that of acids and alcohols stabilize the micelle by one or another factor.

Effect of Temperature on Micelle Formation in the Presence of Pyridine and Acetic Acid. The temperature effect on the micellisation of SDS in water, in the presence of pyridine and acetic acid of the above-mentioned amounts, was determined. Figure 4 depicts the variation in the cmc of SDS in the presence of both additives at various temperatures. The cmc in the presence of pyridine increases nonlinearly with an increases in the temperature, which becomes quite gradual after 25 °C. However, in the presence of acetic acid, it gradually decreases then, after 35 °C it increases significantly. However, the variation of α in the presence of pyridine with respect to the temperature is not very significant in comparison to that in the presence of acetic acid (Table 4) conductivity of surfactant solutions is generally increased along with increase in the temperature[38)] (Table 4). A perusal Table 4 shows that the enthalpy of micellisation in the presence of pyridine becomes less negative along with an increase in the temperature. Generally, the enthalpy becomes more negative[4,8)] with a rise in temperature when cmc is increasing and α is decreasing. This discrepancy in the present study might be due to the almost insignificant change in the α values with respect to the temperature. Gunnarsson et al.[39)] have stated that the electrical contributions related to the micellar surfaces may be the controlling factor in the trend of the $\Delta H^{\circ}_{\mathrm{HP}}$ values. Therefore, such a variation of $\Delta H^{\circ}_{\mathrm{HP}}$ with respect to the temperature can be attributed to almost constant $\Delta G^{\circ}_{\mathrm{S}}$ values (Table 4), which, on the other hand, help to increase the hydrophobic interactions, due to which $\Delta G^{\circ}_{\mathrm{HP}}$ becomes less negative (Table 4). The variation in cmc of SDS in the presence of acetic acid with respect to the temperature is somewhat similar to that of many ionic surfactants.[4,35,40,41)] The temperature effect in the presence of acetic acid seems to be opposite to that in the presence of pyridine. The change in $\Delta G^{\circ}_{\mathrm{HP}}$ with respect to the temperature (Fig. 5) is a second-order polynomial; also the decrease in the free energy above

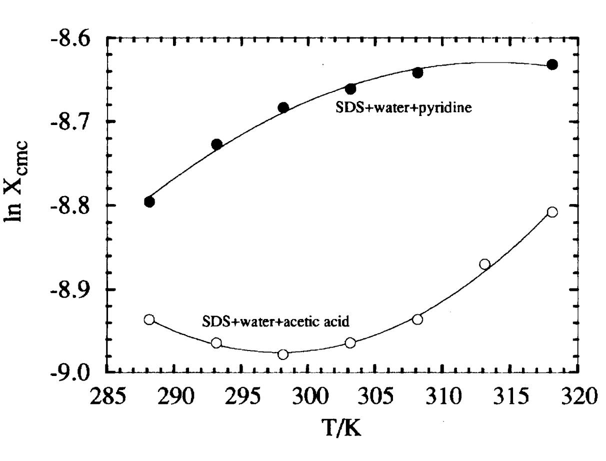

Fig. 4. $\ln X_{\mathrm{cmc}}$ vs. absorlute temperature (T).

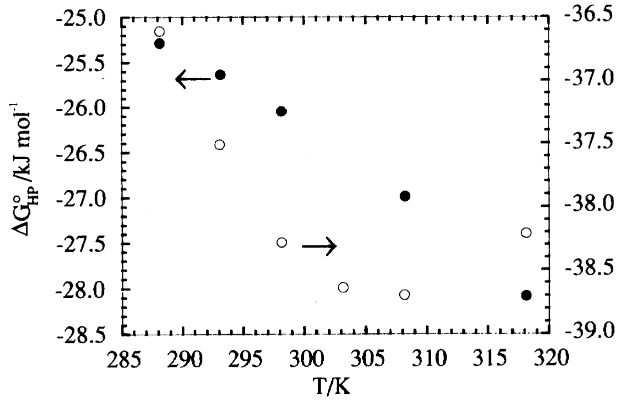

Fig. 5. $\Delta G^{\circ}_{\mathrm{HP}}$ vs. T for SDS+water+pyridine(●) and SDS+water+acetic acid (○) at different temperatures.

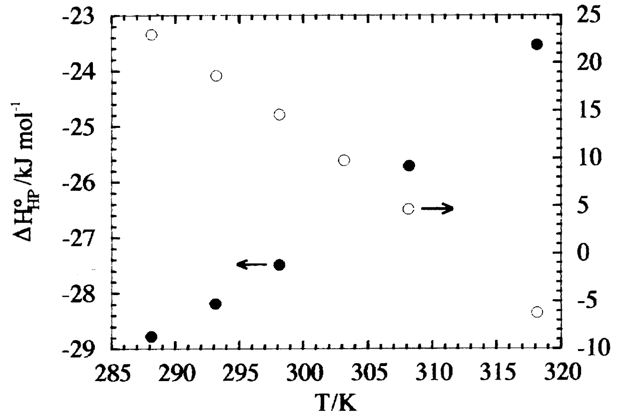

Fig. 6. $\Delta H^{\circ}_{\mathrm{Hp}}$ vs. T for SDS+water+pyridine(●) and SDS+water+acetic acid (○) at different temperatures.

and below 35 °C reflects an increasing solubility of the hydrocarbon, which stabilizes the surfactant monomers and is responsible for the minimum in cmc versus the temperature for many surfactants.[4,35,40,41] Similar conclusions were drawn by Shinoda.[42] However, $\Delta H^{\circ}_{\mathrm{Hp}}$ (Fig. 6) has a positive contribution, which decreases along with an increase in temperature; then, after 35 °C it becomes negative. This is due to the fact that the transfer of a hydrocarbon group from an aqueous to a nonpolar environment is generally endothermic.[4,35,40,41]

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