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Effect of Acetate and Propionate Co-ions on the Micellization of Sodium Dodecyl Sulfate in Water

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Electrical conductivities of sodium dodecyl sulfate (SDS) in aqueous sodium acetate (NaAc) and sodium propionate (NaPr) solutions of different concentrations were measured at 25 °C. An anomalous behavior in the form of minima in the plots of critical micelle concentration (cmc) of SDS versus concentration of NaAc and NaPr was observed, thereby indicating the effect of acetate and propionate co-ions on micellization. The conductivity data were analyzed using a conductivity equation derived on the basis of a mixed-electrolyte model for surfactant solutions wherein ion−ion interactions were accounted for by the Debye−Hückel−Onsager equation. Such an analysis provided a method to estimate the values of cmc, counterion binding constant, and aggregation number directly from conductivity data. It was observed that ionic micelles contribute to electrical conductivity but not to ionic strength of surfactant solution. The surface potentials of SDS micelles in NaAc and NaPr solutions were computed by solving the Poisson−Boltzmann equation. The values of total free energy, electrostatic free energy, and hydrophobic free energy of micellization were estimated. The electrostatic free energy seems to control the decrease in cmc with added electrolyte concentration. On the other hand, the increase in cmc with NaAc and NaPr concentration appears to be due to the penetration of SDS micelles by the acetate and propionate co-ions.

Introduction

An earlier study[1] by us on the micellization behavior of SDS in aqueous sodium acetate and acetic acid buffer has revealed a probable dependence of cmc on the acetate co-ion concentration. The effect of co-ion on the cmc and molecular weight of the micelle was noticed by other workers[2−4] also. However, the role played by co-ion on the micellization behavior of ionic surfactants has not been properly understood.

The conductivity method is one of the widely used methods to determine cmc's of ionic surfactants. Attempts have been going on to develop a satisfactory theoretical approach to estimate from the conductivity data the three micellization parameters of ionic surfactants,viz.,cmc (c_0), counterion binding constant (b), and aggregation number (n). Out of the different approaches proposed hitherto,[5−8] the one reported recently by Shanks and Franses[8] is superior to the earlier models, as it accounts for ion−ion interactions and estimates all three micellization parameters of an ionic surfactant directly from conductivity data.

In the present work we have therefore undertaken a study on the micellization of SDS in aqueous NaAc and NaPr solutions using the conductivity method with a view (1) to ascertain the effect of acetate and propionate co-ions on the micellization of SDS, (2) to estimate directly from the conductivity data the different micellization parameters of SDS using the method of Shanks and Franses,[8] and (3) to compute the surface potentials of SDS micelles.

Experimental Section

SDS (Fluka), NaAc (AR grade, SD Fine Chemicals, India), NaPr (Sigma), and NaCl (AR grade, Qualigen, India) were used without further purification. Aqueous molal solutions of the electrolytes were prepared first, and then their conductivities were measured after each addition of a weighed amount of SDS. The electrical conductivities were measured at 25 °C and 1 kHz using the Wayne Kerr B905 automatic precision bridge and a cell of cell constant 121.11 m^{-1}, as described elsewhere.[1,9]

Theory

Conductivity of Surfactant Solution. Conductivity behavior of ionic surfactant solutions has been explained here in light of the mass-action model for monodisperse micelles and by treating the solution of a surfactant as a mixed electrolyte system. Dependence of n on surfactant concentration and polydispersity of micelles have been ignored in the present approach. Thus the electrical conductivity of a surfactant solution without the added electrolyte is due to the ionic conductivities of monomer ion, counterion, and ionic micelle. The two electrolytes forming the surfactant solution are (1) aqueous solution containing monomers and an equivalent number of counterions (aqueous phase) and (2) micellar solution containing micelles and counterions (micellar phase). Both aqueous and micellar phases are considered to be electrically neutral. In the micellar phase a neutral micelle of the form $\mathrm{M}^{n(1-\mathrm{b})-}\mathrm{A}^{+}{}_{n(1-b)}$ is considered to dissociate completely to give one mole of anionic micelle, $\mathrm{M}^{n(1-b)-}$ and $n(1-b)$ moles of counterions, A^{+}. The molar conductivity of a surfactant solution, Λ, can therefore be written as

$$\Lambda = \Lambda_{1\mathrm{m}}P_{\mathrm{aq}} + \Lambda_{1\mathrm{mic}}P_{\mathrm{mic}} \qquad (1)$$

where $\Lambda_{1\mathrm{m}}$ is the molar conductivity of surfactant in the aqueous phase when it is in the monomer form and $\Lambda_{1\mathrm{mic}}$ is the molar conductivity of surfactant in the micellar phase when it is in the micellar form. P_{aq} and P_{mic} are the fractions of the total surfactant molecules that exist in the monomer and micellar forms, respectively. $\Lambda_{1\mathrm{mic}}$ is related to the molar conductivity

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of micelle, Λ_{nm}, by the relation, $\Lambda_{1\text{mic}} = \Lambda_{nm}/n$. The molar conductivities are related to the respective equivalent conductivities as $\Lambda_{1\text{m}} = \Lambda_{1\text{eq}}$ and $\Lambda_{nm} = \Lambda_{n\text{eq}}n(1 - b)$, where $\Lambda_{1\text{eq}}$ is the equivalent conductivity of surfactant in the monomer form and $\Lambda_{n\text{eq}}$ is the equivalent conductivity of micelle. The P terms can be evaluated as $P_{\text{aq}} = c_0/c_{\text{t}}$ and $P_{\text{mic}} = (c_{\text{t}} - c_0)/c_{\text{t}} = nc_n/c_{\text{t}}$, where c_{t} is the total concentration of the surfactant and c_n is the molar concentration of micelle. Thus eq 1 becomes

$$\Lambda = \Lambda_{1\text{eq}}c_0/c_{\text{t}} + \Lambda_{n\text{eq}}n(1 - b)c_n/c_{\text{t}} \tag{2}$$

On accounting for the effect of interionic interactions on electrical conductivity by the Debye−Hückel−Onsager equation, eq 2 becomes

$$\Lambda = [\Lambda^0{}_1 - A_1I^{1/2}/(1 + B_0a_1)]c_0/c_{\text{t}} + [\Lambda^0{}_n - A_nI^{1/2}/(1 + B_0a_n)]n(1 - b)c_n/c_{\text{t}} \tag{3}$$

This is the conductivity equation used by Shanks and Franses[8] for the estimation of micellization parameters of SDS. In eq 3 a_i's and $\Lambda^0{}_i$'s correspond to effective ionic sizes and limiting equivalent conductivities, respectively, of monomer ($i = 1$) and micelle ($i = n$). I is the ionic strength and

$$B_0 = [8\Pi N_{\text{A}}e_0{}^2/(10^3\epsilon k_{\text{B}}T)]^{1/2}I^{1/2} \tag{4}$$

$$A_i = [2.801 \times 10^6|z_+z_-|q\Lambda^0{}_i/[(\epsilon T)^{3/2}(1 + q^{1/2})]] + [41.25\ (|z_+| + |z_-|)/[\eta(\epsilon T)^{1/2}]] \tag{5}$$

$$q = [|z_+z_-|(\lambda^0{}_+ + \lambda^0{}_-)]/[(|z_+| + |z_-|)\ (|z_+|\lambda^0{}_- + |z_-|\lambda^0{}_+)] \tag{6}$$

In the above eqs 4−6, k_{B} is the Boltzmann constant, T is the absolute temperature, ϵ is the dielectric constant of water, e_0 is the elementary charge, and η is the viscosity of water. $\lambda^0{}_+$ and $\lambda^0{}_-$ are the limiting ionic equivalent conductivities of cationic and anionic species of effective charges z_+ and z_-, respectively.

Surface Potential of Ionic Micelle. The surface potential of the SDS micelle was computed by using a method similar to that reported by Drummond et al.[10] According to this method also micelles are considered to be monodisperse spheres with uniformly distributed surface charge and an average aggregation number, n. The micelle concentration is presumed to be infinitely dilute. The surface potentials were computed by solving numerically the nonlinearized Poisson−Boltzmann equation in spherical symmetry, which is of the form

$$\text{d}^2y/\text{d}x^2 = (e^y - e^{-y})/2x^4 \tag{7}$$

where $y = \text{e}_0\Psi_{\text{r}}/k_{\text{B}}T$ and $x = (B_0r)^{-1}$. Ψ_{r} is the electrostatic potential at a distance r from the center of the spherical micelle. The boundary conditions used are

$$y \rightarrow 0 \quad \text{as} \quad x \rightarrow 0 \tag{8}$$

$$\text{d}y/\text{d}x = 4\Pi\rho_re_0/(\epsilon B_0k_{\text{B}}Tx^2) \quad \text{at} \quad r = r_{\text{n}} \tag{9}$$

r_n is the radius of the micelle and ρ_r is the surface charge density at a distance r from the center of the reference micelle. The micellar surface charge density was calculated from the expression

$$\rho_r(r = r_n) = e_0n(1 - b)/(4\Pi r_n{}^2) \tag{10}$$

Results and Discussion

The experimental values of the specific conductivity (κ) of SDS at 25 °C in aqueous NaAc and NaPr solutions of different concentrations are presented in Figures 1a−d as κ versus concentration of SDS plots. The cmc values were determined from the conductivity data as described earlier.[1] The values of cmc obtained thus are termed visual cmc values and are shown in Figure 2. From Figure 2 it is apparent that in NaAc solution the cmc of SDS decreases up to ca. 0.18 mol kg^{-1} of NaAc, and thereafter an unexpected increase in cmc occurs with further increase in NaAc concentration. In NaPr solution also the behavior of cmc with respect to concentration of electrolyte is similar except for the fact that the minimum in cmc occurs at ca. 0.17 mol kg^{-1} of NaPr (Figure 2). The reproducibility of this anomalous behavior of cmc of SDS in NaAc and NaPr solutions was checked by repeating the conductivity measurements. Furthermore, to ascertain the reliability of our conductivity measurements, we also measured the conductivities of solutions of SDS in NaCl solution (up to 0.5 mol kg^{-1} NaCl) since precise cmc values of SDS in NaCl solution are reported.[11−13] The values of visual cmc obtained by us for SDS in NaCl solution are found to be in good agreement with the reported values (Figures 2 and 3).[11−13]

The decrease of cmc with increasing concentration of added electrolyte is generally explained by the Corrin−Harkins relation[1,14,15] of the type

$$\ln x_{\text{cmc}} = A - b \ln x_{\text{c}} \tag{11}$$

where x_{cmc} is the cmc in mole fraction units, x_{c} is the mole fraction of counterion in solution, and A is a constant related to the free energy of micellization. Accordingly the cmc data of SDS in NaAc, NaPr, and NaCl solutions were plotted versus x_{c} as shown in Figure 3. The least-squares-fitted values of A and b are −14.97 and 0.696, −14.66 and 0.665, and −15.07 and 0.708 in NaAc (concentration range from 0 to 0.1833 mol kg^{-1}), NaPr (concentration range from 0 to 0.0923 mol kg^{-1}), and NaCl (concentration range from 0 to 0.5 mol kg^{-1}) solutions, respectively. In NaPr solution eventhough the cmc decreases with propionate concentration up to ca. 0.17 mol kg^{-1}, eq 11 is applicable only up to ca. 0.09 mol kg^{-1}. The analysis of cmc data in the above fashion using eq 11, however, does not reveal the dependence of b on counterion concentration. Moreover, eq 11 becomes applicable only when the cmc decreases with the addition of electrolyte. Therefore a more precise estimation of b as well as of aggregation number, n, has been done using eq 3.

To compute the values of c_0, n, and b using eq 3, the values of r_1, r_n, a_1, a_n, A_1, A_n, $\Lambda^0{}_1$, $\Lambda^0{}_n$, $\lambda^0{}_+$, $\lambda^0{}_-$, and I are required to be determined first. r_1 was calculated from the relation[16]

$$r_1 = [(3/4\Pi)(27.4 + 26.9n_{\text{c}})]^{1/3} \tag{12}$$

where n_{c} is the number of carbon atoms per hydrocarbon chain of the surfactant used. r_1 obtained from eq 12 is in angstroms. Presuming the micelle to be spherical in shape, r_n is computed from the relation $r_n = n^{1/3}r_1$. For monomers $\Lambda^0{}_1$, $\lambda^0{}_+$ and $\lambda^0{}_-$ are experimentally determinable quantities. $\Lambda^0{}_1$ for SDS and $\lambda^0{}_+$ for Na$^+$ are taken to be 73.0×10^{-4} and 50.1×10^{-4} S m^2 mol^{-1}, respectively. $\lambda^0{}_-$ for micelle was evaluated using the Stokes−Einstein relation:

$$\lambda^0{}_-(\text{micelle}) = z_ne_0F/6\Pi\eta r_n \tag{13}$$

where F is the Faraday constant and $z_n = n(1 - b)$ is the charge on the micellar ion. Once $\lambda^0{}_-$ for the SDS micelle was computed from eq 13, $\Lambda^0{}_n$ and A_n were determined easily. a_1

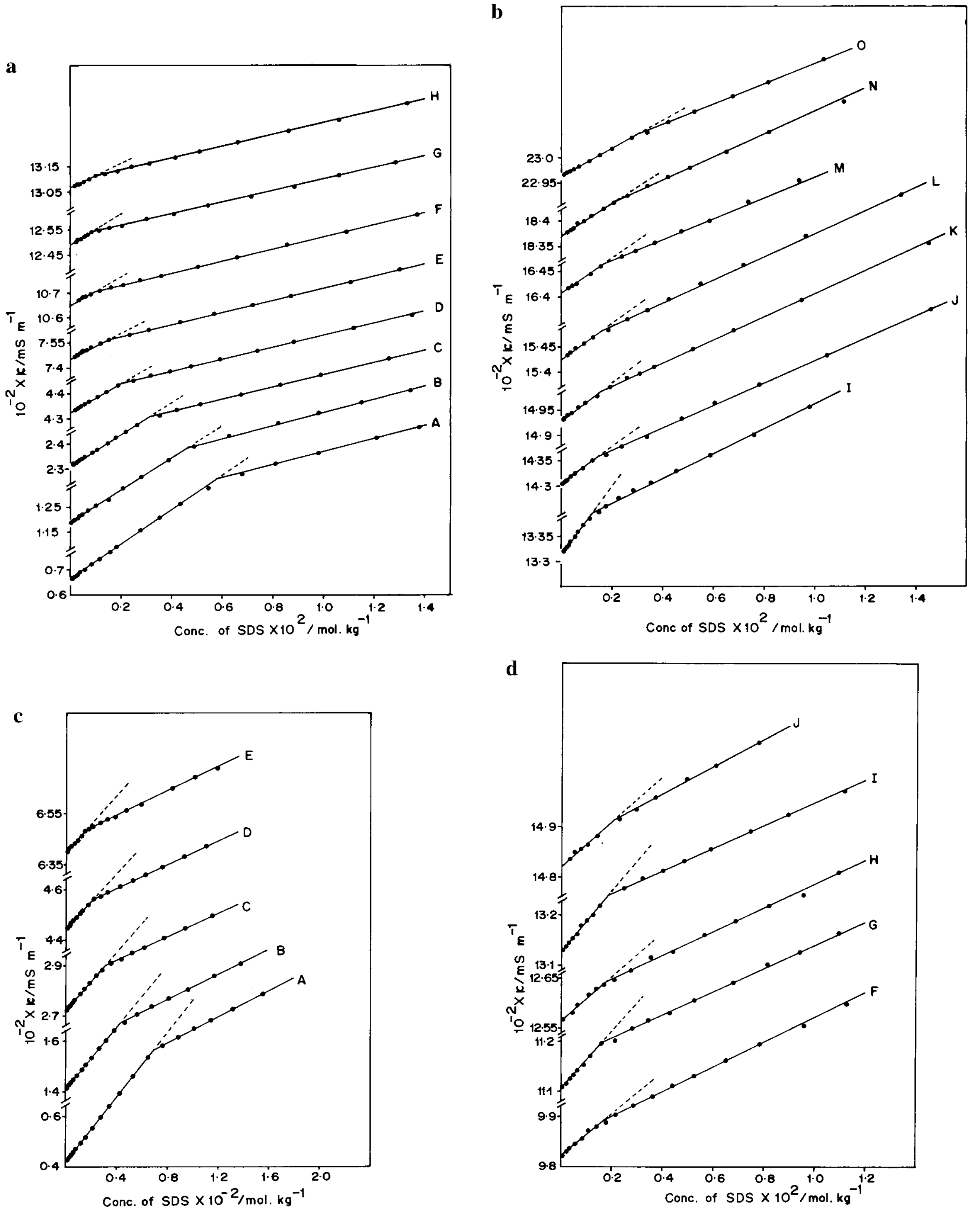

Figure 1. (a) Plots of specific conductivity of SDS in sodium acetate solutions of different concentrations at 25 °C versus concentration. Concentrations (mol kg^{-1}) of sodium acetate solution: A = 0.0071, B = 0.0135, C = 0.0275, D = 0.0548, E = 0.1014, F = 0.1522, G = 0.1833, H = 0.1934. (b) Plots of specific conductivity of SDS in sodium acetate solution of different concentrations at 25 °C versus concentration. Concentrations (mol kg^{-1}) of sodium acetate solution: I = 0.2005, J = 0.2154, K = 0.2271, L = 0.2364, M = 0.2539, N = 0.2918, O = 0.3858. (c) Plots of specific conductivity of SDS in sodium propionate solutions of different concentrations at 25 °C versus concentration. Concentrations (mol kg^{-1}) of sodium propionate solution: A = 0.0049, B = 0.0175, C = 0.0356, D = 0.0612, E = 0.0923. (d) Plots of specific conductivity of SDS in sodium propionate solutions of different concentrations at 25 °C versus concentration. Concentrations (mol kg^{-1}) of sodium propionate solution: F = 0.1512, G = 0.1749, H = 0.2029, I = 0.2139, J = 0.2486.

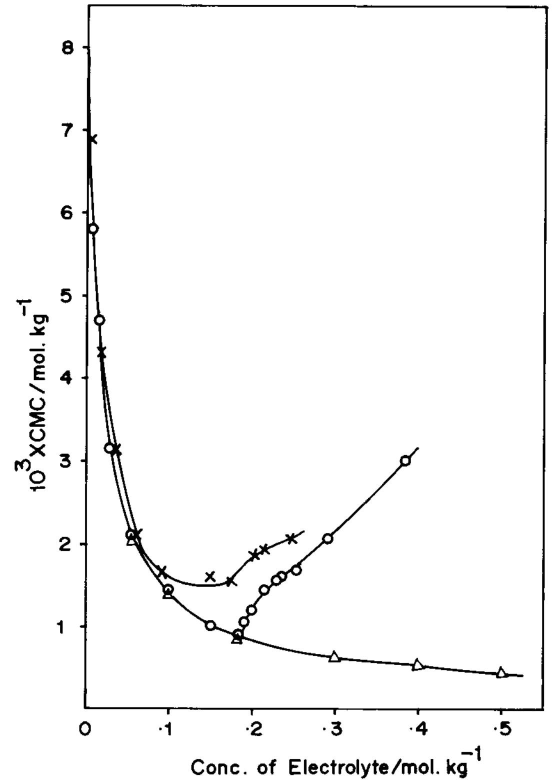

Figure 2. Variation of cmc of SDS with concentration in sodium acetate (○), sodium propionate (×), and sodium chloride (△) solutions at 25 °C.

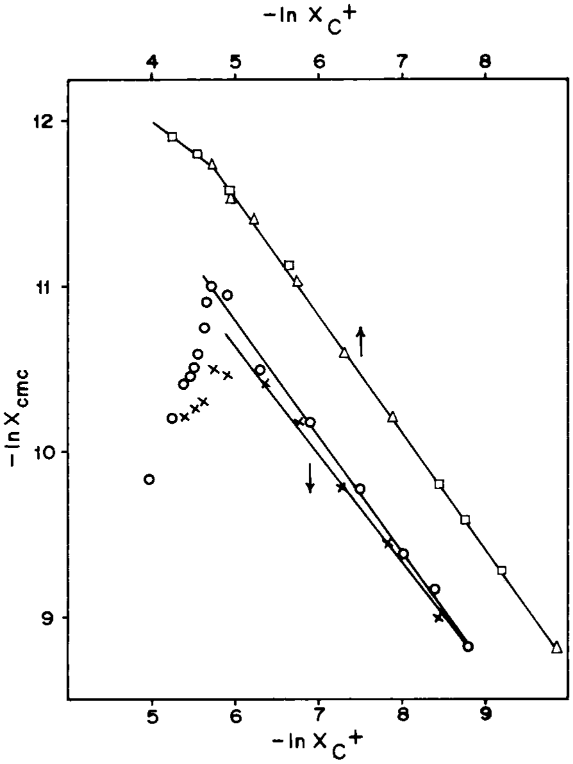

Figure 3. Plot of ln x_{cmc} of SDS in sodium acetate, sodium propionate, and sodium chloride solutions of different concentrations at 25 °C versus ln x_{c^+}.

TABLE 1: Models Used for the Evaluation of Ionic Strength

model	expression for I^a	
1	$I = c_t$	$c_t < c_0$
	$I = c_0$	$c_t > c_0$
2	$I = c_t$	$c_t < c_0$
	$I = c_0 + 0.5n(1 - b)c_n$	$c_t > c_0$
3	$I = c_t$	$c_t < c_0$
	$I = c_0 + 0.5n(1 - b)^2c_n$	$c_t > c_0$
4	$I = c_t$	$c_t < c_0$
	$I = c_0 + 0.5n(1 - b)c_n[1 + n(1 - b)]$	$c_t > c_0$

[a] The above expressions are used in the absence of added electrolyte. In the presence of added electrolyte, the fixed concentration of the electrolyte (1:1) is added to the above expressions to get the value of I.

and a_n were determined by adding the Stokes ionic radius of the counterion to r_1 and r_n, respectively.

The most important parameter required for data fitting is the ionic strength, I. Different earlier studies[8,17–19] have indicated that highly charged micelles do not contribute to the ionic strength. We first tested four models for I as suggested by Shanks and Franses[8] by analyzing the measured conductivity data of SDS in water at 25 °C using eq 3 and the four different expressions for I which are given in Table 1. For fitting the conductivity data to eq 3 an iterative least-squares method was used. The computer program was developed on the basis of the Newton−Raphson method and the iteration procedure was similar to that used by Kay[20] in electrolytic solutions. Conductivity data of SDS in water in two different concentration regions, viz., 2.4 × 10^{-3} to 246.2 × 10^{-3} mol kg^{-1} and 2.4 × 10^{-3} to 97.2 × 10^{-3} mol kg^{-1}, were least-squares fitted separately to eq 3 using the four models for I given in Table 1. It was noticed that model 1 for I fits the conductivity data to eq 3 better than the other three models when the concentration range of SDS covered in the data fitting is larger. When a narrow range of concentrations was used for data fitting, it was observed that models 1, 2, and 3 for I fit the data to eq 3 almost equally well. The above observations are in accordance with the inferences made by Shanks and Franses.[8] The best-fit values of the micellization parameters of SDS in water are $c_0 = (8.4 \pm 0.1) \times 10^{-3}$ mol kg^{-1}, $b = 0.71 \pm 0.01$, and $n = 54 \pm 10$. The visual cmc value of SDS was found to be 8.2 ×10^{-3} mol kg^{-1}. These values of c_0, b, and n are in good agreement with the values reported by Shanks and Franses.[8] Model 4 for I provided unreasonable values for n, envisaging the inapplicability of this model, which in turn indicates that micelles contribute to the conductivity but not to the effective ionic strength as reported by others.[8,17–19]

In view of the above observation all the subsequent least-squares fits of conductivity data of SDS in NaAc and NaPr solutions to eq 3 were therefore done using only model 1 for I. In fact, in model 1 the additional contribution to I due to NaAc and NaPr was included during data fitting. All the data fittings were done by varying the values of b and n, while the value of c_0 was fixed as that of the visual cmc. The results of such data fittings are given in Tables 2 and 3. The variations in the computed values of b and n with electrolyte concentration are shown in Figure 4. In view of the error limits in n, the changes observed in n with electrolyte concentration are not significant below ca. 0.25 mol kg^{-1} of NaAc or NaPr. In other electrolytes such as sodium halides or NaSCN n is reported[11−13] to increase with electrolyte concentration. In NaAc solution only above ~0.25 mol kg^{-1} does n seem to increase with electrolyte concentration. However, the values of n derived from conductivity data are reported[8] to be invariably lower than the aggregation number obtained from light scattering and other methods. The counterion binding constant, on the other hand, exhibits a decreasing trend with increasing concentration of NaAc or NaPr up to ca. 0.18 mol kg^{-1}, and thereafter b increases

TABLE 2: Values of the Micellization Parameters of SDS in Aqueous NaAc Solutions at 25 °C

conc of NaAc (mol kg^{-1})	$10^3 \times$ (cmc ± 0.1) (mol kg^{-1})	b	n	std dev in κ (S m^{-1})
0.0071	5.8	0.70 ± 0.01	58 ± 5	0.0011
0.0135	4.7	0.73 ± 0.01	59 ± 5	0.0003
0.0275	3.1	0.70 ± 0.01	63 ± 5	0.0004
0.0548	2.1	0.68 ± 0.01	65 ± 10	0.0003
0.1014	1.6	0.63 ± 0.01	67 ± 10	0.0003
0.1522	1.0	0.54 ± 0.04	65 ± 15	0.0009
0.1833	0.9	0.49 ± 0.04	65 ± 10	0.0004
0.1934	1.0	0.50 ± 0.05	64 ± 10	0.0003
0.2005	1.2	0.50 ± 0.05	64 ± 10	0.0015
0.2154	1.4	0.51 ± 0.05	70 ± 10	0.0013
0.2271	1.5	0.52 ± 0.04	64 ± 5	0.0011
0.2364	1.6	0.53 ± 0.05	67 ± 5	0.0015
0.2539	1.7	0.57 ± 0.08	87 ± 20	0.0015
0.2918	2.1	0.59 ± 0.08	85 ± 20	0.0020
0.3858	3.0	0.62 ± 0.08	140 ± 50	0.0036

TABLE 3: Values of the Micellization Parameters of SDS in Aqueous NaPr Solutions at 25 °C

conc of NaPr (mol kg^{-1})	$10^3 \times$ (cmc ± 0.1) (mol kg^{-1})	b	n	std dev in κ (S m^{-1})
0.0049	6.9	0.74 ± 0.01	54 ± 10	0.0010
0.0175	4.3	0.72 ± 0.01	56 ± 10	0.0008
0.0356	3.1	0.72 ± 0.01	59 ± 10	0.0007
0.0612	2.1	0.68 ± 0.01	62 ± 10	0.0004
0.0923	1.7	0.61 ± 0.01	60 ± 5	0.0011
0.1512	1.6	0.55 ± 0.02	69 ± 5	0.0007
0.1749	1.5	0.49 ± 0.03	58 ± 8	0.0008
0.2029	1.8	0.50 ± 0.05	61 ± 10	0.0009
0.2139	1.9	0.51 ± 0.05	60 ± 10	0.0009
0.2486	2.1	0.53 ± 0.05	63 ± 10	0.0013

with a further increase in NaAc or NaPr concentration. Shanks and Franses[8] also observed a decrease of b for SDS with an increase in salinity up to 0.1 mol dm^{-3} of NaCl solution studied by them. The minima in the plots of b versus concentration of NaAc and NaPr seem to coincide with the minima in the cmc versus concentration of these two electrolytes (Figure 4). To understand the anomalous behavior of cmc with respect to NaAc and NaPr concentration, it may be worthwhile to compute the free energy parameter of micellization. The free energy change of ionic micelle formation per mole of monomer, $\Delta G^0{}_m$ has been considered to comprise two factors and is written as

$$\Delta G^0{}_{\mathrm{m}} = \Delta G^0{}_{\mathrm{HC}} + \Delta G^0{}_{\mathrm{el}} \tag{14}$$

where $\Delta G^0{}_{\mathrm{HC}}$ is the hydrophobic free energy and is closely related to the free energy of transfer of a hydrocarbon chain from water to a liquid hydrocarbon equivalent to the interior of a regular micelle and is a negative term. $\Delta G^0{}_{\mathrm{el}}$ is an electrostatic free energy and is positive, as it represents the repulsive force. The decrease of cmc with increasing electrolytic concentration, which is a normal trend, has been attributed to the decrease in $\Delta G^0{}_{\mathrm{el}}$. The increase in cmc caused by the acetate and propionate co-ions may therefore be considered to be attributable to the influence of co-ion on the hydrophobic interactions causing $\Delta G^0{}_{\mathrm{HC}}$ to increase on addition of electrolyte. To ascertain the above plausible interpretation of the effect of co-ion on cmc, it is therefore necessary to estimate first the value of $\Delta G^0{}_{\mathrm{m}}$ and then to separate it into the contributions from $\Delta G^0{}_{\mathrm{el}}$ and $\Delta G^0{}_{\mathrm{HC}}$. The values of $\Delta G^0{}_{\mathrm{m}}$ were computed using eq 11 by considering A to be almost equal to $\Delta G^0{}_{\mathrm{m}}/RT$, where R is the gas constant. For calculating A from eq 11 the values of b are taken from Tables 2 and 3. The computed values of $\Delta G^0{}_{\mathrm{m}}$ for SDS in NaAc and NaPr solutions are given in Tables 4 and 5.

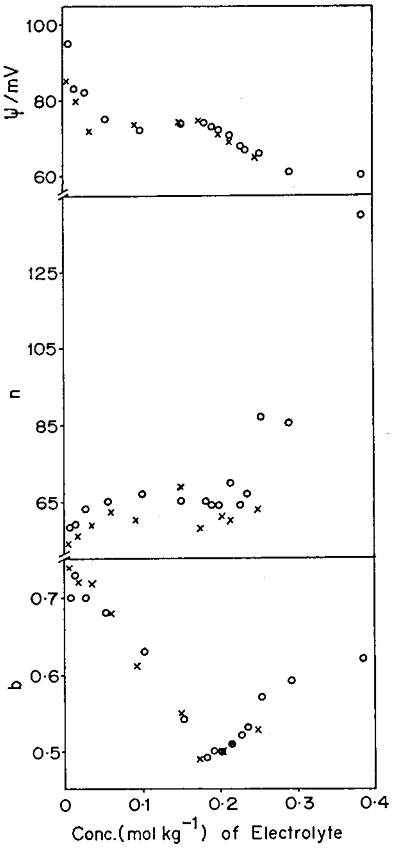

Figure 4. Plots of b, n, and Ψ versus concentration of NaAc (○) and NaPr (×).

TABLE 4: Values of Surface Potential and Free Energy Terms for SDS Micelles in NaAc Solutions at 25 °C

conc of NaAc (mol kg^{-1})	Ψ (mV)	$-\Delta G^0$ (kJ mol^{-1})	$\Delta G^0{}_{\mathrm{el}}$ (kJ mol^{-1})	$-\Delta G^0{}_{\mathrm{HC}}$ (kJ mol^{-1})
0.0071	94.7	37.3	9.1	46.4
0.0135	83.5	37.7	8.1	45.8
0.0275	81.7	37.2	7.9	45.1
0.0548	74.9	36.8	7.2	44.0
0.1014	72.1	35.7	7.0	42.7
0.1522	73.9	35.1	7.1	42.2
0.1833	74.2	34.3	7.2	41.5
0.1934	73.2	34.0	7.1	41.1
0.2005	72.1	33.6	7.0	40.6
0.2154	71.2	33.3	6.9	40.2
0.2271	67.9	33.0	6.6	39.6
0.2364	67.0	33.1	6.5	39.6
0.2539	66.2	33.4	6.4	39.8
0.2918	60.8	32.9	5.9	38.8
0.3858	60.6	32.0	5.8	37.8

$\Delta G^0{}_{\mathrm{el}}$ can be calculated if the surface potentials of the SDS micelle are known as a function of electrolyte concentration. As mentioned above, the surface potentials, Ψ, of SDS micelles were computed by writing a computer program to solve numerically eq 7 using a fourth-order Runge–Kutta method and an iteration procedure. In the computation of Ψ also, I was calculated from model 1 (Table 1) in which the additional contribution from NaAc or NaPr was included. To start the calculation, it is necessary to supply the initial values of x, y, and dy/dx. The initial value of x was chosen arbitrarily in light of the cell model.[21,22] The initial values of y and dy/dx were taken as equal to $-x$ (initial value) and 1, respectively. If the boundary conditions were not satisfied in the first cycle, the second cycle of calculation begins with a modified initial value of x depending upon the given increment. The iteration of x

TABLE 5: Values of Surface Potential and Free Energy Terms for SDS Micelles in NaPr Solutions at 25 °C

conc of NaPr (mol kg^{-1})	Ψ (mV)	$-\Delta G^0$ (kJ mol^{-1})	ΔG^0_{el} (kJ mol^{-1})	$-\Delta G^0_{HC}$ (kJ mol^{-1})
0.0049	85.2	37.8	8.2	46.0
0.0175	79.6	37.5	7.7	45.2
0.0356	71.9	37.2	6.9	44.1
0.0612	71.4	36.6	6.9	43.5
0.0923	73.5	35.4	7.1	42.5
0.1512	74.2	33.9	7.2	41.1
0.1749	74.7	32.9	7.2	40.1
0.2029	71.2	32.5	6.9	39.5
0.2139	68.8	32.5	6.6	39.1
0.2486	65.3	32.3	6.3	38.6

continues until the boundary condition given by eq 9 was fulfilled up to <0.001%, and the corresponding value of Ψ was then accepted as the surface potential of the micelle. In this fashion we first computed the surface potentials of known systems, and complete agreement with the reported[10,23] Ψ values was obtained, thereby confirming the correctness of our computation method. Subsequently we computed the surface potentials of SDS micelles in NaAc and NaPr solutions using c_0, n, and b values listed in Tables 2 and 3. The values of Ψ computed thus are given in Tables 4 and 5. The variation of Ψ with electrolyte concentration is shown in Figure 4. Ψ decreases with increasing concentration of NaAc and NaPr as in the case of other electrolytes.[10,23] However, the plot of Ψ versus concentration of NaAc or NaPr has an almost concentration-independent region for Ψ between ~0.05 to ~0.15 mol kg^{-1} of electrolyte, unlike the trend in NaCl solution.[23] Using these Ψ values, ΔG^0_{el} were calculated (Tables 4 and 5) since $\Delta G^0_{el} = F\Psi$. Knowing the values of ΔG^0_m and ΔG^0_{el}, the values of ΔG^0_{HC} for SDS micelles in NaAc and NaPr solutions were calculated (Tables 4 and 5). From the computed values of ΔG^0_{el} and ΔG^0_{HC} it is apparent that with increasing electrolyte concentration ΔG^0_{el} decreases whereas ΔG^0_{HC} increases. Therefore the observed trend in the dependence of cmc on electrolyte concentration can be explained if cmc is controlled by ΔG^0_{el} in the decreasing region of cmc and it is controlled, on the other hand, by ΔG^0_{HC} in the increasing region of cmc. It may however be commented that the increase in ΔG^0_{HC} above the cmc minimum is not very significant.

A similar type of dependence of cmc on the concentration of additive was reported[24] in aqueous SDS solution by the addition of butylurea (BU). The decrease of cmc of SDS by the addition of BU was explained as due to the dissolution of the butyl end at the interstitial sites in water, which in turn forces the surfactant to micellize at a lower concentration. The increase in the cmc of SDS with the addition of BU (above ~0.2 mol dm^{-3} BU) was explained, on the other hand, as either due to regular mixing of SDS with water after all its interstitial sites are occupied by the hydrophobic end of BU or due to penetration of the SDS micelle by BU, forming the mixed micelle. In the present systems under study the acetate and propionate co-ions contributed by the added electrolyte have hydrophobic surfaces equal to that of methanol and ethanol, respectively. Therefore, the effect of added NaAc and NaPr in lowering the cmc of SDS might be partly electrical, partly interstitial mixing, and partly order-destroying of the solvent.[25] Infact, hydrophobic hydration of acetate and propionate ions has been reported by others.[26] However, in lowering the cmc of SDS the electrical effect of NaAc and NaPr dominates over the other two effects. The increase in the cmc of SDS with an increase in NaAc (above ~0.183 mol kg^{-1}) and NaPr (above ~0.175 mol kg^{-1}) concentration may be attributed to the penetration of the SDS micelle by acetate and propionate co-ions from their hydrocarbon end with the ionic (COO$^-$) group projecting out of the micelle surface. A similar penetration of anionic SDS micelle by negatively charged deprotonated species of methyl red was reported by Drummond et al.[27] Recently the existence of like-ion pairs was reported[28] in aqueous sodium sulfate solution also. The increase in cmc of SDS by the addition of methanol and ethanol is also described by the penetration of SDS micelles by these two alcohols.[29,30]

It may therefore be concluded that co-ions like acetate, propionate, etc., behave differently from other inorganic co-ions, as they can fill the interstitial sites in water and can penetrate the micelle from their hydrocarbon chain end, causing a minimum in the plot of cmc versus concentration of added electrolyte.

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