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Micellization of Sodium Dodecyl Sulfate in Sodium Acetate–Acetic Acid Buffer. A Conductivity Study

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Electrical conductivity of sodium dodecyl sulfate (SDS) in sodium acetate–acetic acid buffer solutions was measured as functions of concentration, temperature and pH. First and second critical micelle concentrations (cmcl and cmc2) of these solutions were estimated. Plot of cmcl versus pH passes through a minimum in the pH range 5.2 to 5.6. The decrease in cmcl with increasing pH is shown to be due to the Na^+ counterion and is described quantitatively by an analytical expression which also provides the value of counterion binding constant. The increasing tendency of cmcl with increase in pH is, on the other hand, caused by the acetate co-ion. The enthalpy and standard free energy changes due to micellization of SDS were estimated. The slope of the specific conductivity versus concentration plot above cmc2 is found to decrease with increasing concentration of sodium acetate which is contrary to the trend reported in sodium chloride solution. This study has revealed the effect of the nature of co-ion on micellization.

Surface potentials of ionic micelles are estimated experimentally by making spectral studies of indicator dyes in buffered micellar solutions of varying pH.[1—3] In such studies the surfactant concentration is always taken to be well above the cmc. The cmc of surfactants is however dependent on the pH of the solution. Moreover surfactants are known to have second cmc's also.[4—8] Information about the exact values of first and second cmc's of various surfactants in buffered media of varying pH is going to be useful in choosing the concentration range for the above spectral studies and also in the proper interpretation of the spectral data. Values of cmc of surfactants in different buffered solutions as a function of pH are not well-documented. With this aim in mind we have reported here cmcl and cmc2 of SDS in aqueous sodium acetate (NaAc) and acetic acid (AcH) buffer solutions as functions of pH and temperature using conductance method.

Experimental

SDS (SISCO, extra pure grade) was recrystallized from its ethanol solution and dried under vacuum. Sodium acetate (SD, analytical grade) and glacial acetic acid (Merck, analytical grade) were used without further purification. Buffer solutions of various pH were prepared by mixing appropriate amounts of 0.2 M ($1 M=1$ mol dm^{-3}) sodium acetate solution, 0.2 M acetic acid solution and conductivity water according to the standard buffer table.[9] The electrical conductance measurements were made using B905 Wayne Kerr Automatic Precision Bridge at a frequency of 1 kHz. The cell consisted of platinum electrodes having cell constant 121.11 m^{-1}. The temperature of the solutions was maintained in a thermostat having ±0.01°C thermal stability. Solutions of SDS in the buffers of various pH were prepared by weight. To check the purity of SDS we first measured the electrical conductance of aqueous solution of SDS at 25°C and the cmcl was found to be 0.0082 mol kg^{-1} which is in good agreement with the reported value.[10] The pH's of the buffer solutions were checked by a Systronics Model 335 digital pH-meter using glass and calomel electrodes and agreed within ±0.01 with the expected pH values. The effect of SDS on the pH of the solution was ignored.[11]

Results and Discussion

The measured specific conductivity (κ) data of SDS in NaAc+AcH buffer solutions of various pH when plotted against concentration (m) form three linear plots exhibiting thereby three different concentration regions. A typical plot of this type is shown in Fig. 1 for SDS solution of pH=4.8 at 25°C. Such a linear dependence of κ on m is well known in aqueous surfactant solutions.[4,12,13] The experimental values of κ of SDS solutions at different pH values and temperatures are therefore least-squares fitted to the linear equation

$$\kappa = a + bm \tag{1}$$

in the three concentration regions separately and the corresponding values of intercepts, a and slopes, b are listed in Table 1. The values of cmcl and cmc2 were

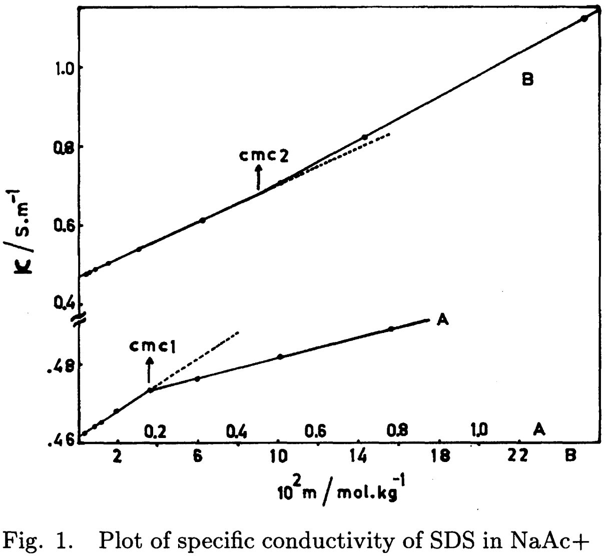

Fig. 1. Plot of specific conductivity of SDS in NaAc+AcH buffer of pH=4.8 at 25°C versus concentration.

Table 1. Least-Squares Fitted Values of the Parameters of Eq. 1 (Correlation Coefficient≥0.999)

t/°C	m≤cmc1		cmc1<m≤cmc2		m>cmc2	
	$a\times10^2$	b	$a\times10^2$	b	$a\times10^2$	b
	(a in $\mathrm{S\,m^{-1}}$ and b in $\mathrm{S\,m^{-1}\,mol^{-1}\,kg}$)					
			pH=3.6 ($m^{\mathrm{h)}}$=0.276 mol kg^{-1})			
15.0	6.197	5.357	8.139	2.010	6.211	2.245
20.0	6.954	6.065	9.091	2.338	6.929	2.599
25.0	7.732	6.802	10.05	2.704	7.698	2.973
30.0	8.537	7.569	11.11	3.065	8.547	3.359
35.0	9.348	8.371	12.25	3.448	9.468	3.763
40.0	10.15	9.238	13.44	3.841	10.47	4.172
45.0	11.03	10.01	14.71	4.254	11.58	4.600
			pH=4.0 ($m^{\mathrm{h)}}$=0.315 mol kg^{-1})			
15.0	12.57	5.029	13.91	1.909	11.21	2.236
20.0	14.16	5.754	15.64	2.235	12.58	2.591
25.0	15.81	6.412	17.39	2.577	13.95	2.965
30.0	17.52	7.043	19.29	2.916	15.46	3.352
35.0	19.26	7.890	21.27	3.285	17.02	3.759
40.0	21.06	8.455	23.30	3.667	18.85	4.166
45.0	22.90	9.340	25.50	4.051	20.64	4.598
			pH=4.4 ($m^{\mathrm{h)}}$=0.373 mol kg^{-1})			
15.0	24.75	5.470	25.75	1.711	22.15	2.112
20.0	27.88	6.224	28.98	1.983	24.88	2.449
25.0	31.15	6.747	32.26	2.357	27.76	2.800
30.0	34.50	7.582	35.74	2.672	30.75	3.167
35.0	37.99	7.896	39.35	3.004	33.90	3.545
40.0	41.54	8.683	43.04	3.374	37.18	3.933
45.0	45.15	8.588	46.67	3.834	40.69	4.332
			pH=4.8 ($m^{\mathrm{h)}}$=0.564 mol kg^{-1})			
15.0	36.71	5.111	37.35	1.768	35.13	2.008
20.0	41.32	5.937	42.05	2.058	39.67	2.321
25.0	46.17	6.437	46.92	2.359	44.32	2.652
30.0	51.13	7.022	51.98	2.675	49.28	2.989
35.0	56.27	7.413	57.17	3.005	54.39	3.341
40.0	61.54	7.775	62.51	3.341	59.68	3.702
45.0	66.69	9.504	68.03	3.701	65.17	4.073
			pH=5.2 ($m^{\mathrm{h)}}$=0.418 mol kg^{-1})			
15.0	47.14	4.200	47.56	1.747	44.95	1.960
20.0	53.08	4.751	53.53	2.021	51.16	2.244
25.0	59.24	5.171	59.69	2.333	56.38	2.602
30.0	65.58	5.717	66.05	2.675	62.52	2.938
35.0	72.08	5.838	72.53	3.017	68.80	3.291
40.0	78.81	6.448	79.33	3.334	75.38	3.647
45.0	85.15	10.37	86.33	3.680	82.69	4.004
			pH=5.6 ($m^{\mathrm{h)}}$=0.569 mol kg^{-1})			
15.0	53.17	2.985	53.45	1.714	51.87	1.890
20.0	59.79	3.861	60.11	2.001	58.47	2.189
25.0	66.61	4.761	67.02	2.293	65.31	2.501
30.0	73.68	5.733	74.20	2.543	72.36	2.827
35.0	80.95	6.015	81.47	2.927	79.70	3.157
40.0	88.32	7.803	89.07	3.173	85.71	3.591
45.0	95.96	8.538	96.80	3.609	93.26	3.947
			pH=6.0 ($m^{\mathrm{h)}}$=0.582 mol kg^{-1})			
15.0	58.09	2.452	58.26	1.745	57.37	1.859
20.0	65.30	2.915	65.54	1.988	64.50	2.157
25.0	72.76	3.371	73.01	2.312	72.02	2.463
30.0	80.36	4.183	80.78	2.617	79.88	2.778
35.0	88.28	4.795	88.68	2.936	87.73	3.109
40.0	96.36	5.058	96.85	3.256	96.20	3.435
45.0	104.5	6.091	105.3	3.589	104.6	3.779

h) Highest concentration of the solution studied.

estimated from the least-squares fitted values of a and b for the three linear plots of κ vs. m and are listed in Table 2.

The variation of cmc1 with pH at 25°C is shown in Fig. 2. Below 40°C cmc1 decreases with increase in pH upto pH=5.2 and increases with pH thereafter. At temperatures ≥40°C the decrease in cmc1 with increasing pH is found to be up to pH=5.6 (Table 1). The lowering of cmc1 with increasing pH can be attributed to the increase in the $\mathrm{Na^+}$ ion concentration in the solution due to the increasing amount of NaAc as also is the case observed by the addition of NaCl to SDS solution.[14,15] However, for SDS solution no increase in cmc1 with increase in counterion concentration is reported up to 0.8 M NaCl concentration.[15] In the present system up to pH=6.0 the total concentration of $\mathrm{Na^+}$ ion is much less (about 0.1 M) than 0.8 M and therefore the increase in cmc1 with increase in pH above pH=5.2 or 5.6 is not due to the $\mathrm{Na^+}$ ion. It cannot be due to $\mathrm{H^+}$ ion also because at pH>5.2 the $\mathrm{H^+}$ ion concentration is much lower. Therefore it appears that the increase in cmc1 may be due to the co-ion, in this case acetate ion. Structurally SDS micelle is reported to undergo sphere–rod transitions around 0.45 M NaCl concentration[15] and the nature of the co-ions was found to affect the molecular weight of the large nonspherical micelle.[16] From the reported[17] values of cmc1 for 1-hexadecylpyridinium bromide (HDPB) in aqueous solution with added electrolytes it seems that co-ion has an influence on the cmc1 value of this cationic surfactant also. Reported cmc1 value of HDPB (6.86×10^{-4} M in $\mathrm{H_2O}$) decreases initially in KCl, NaCl, and HCl solutions and then it starts increasing somewhere between 0.01 M and 0.1 M KCl, 0.1 M and 1 M NaCl, and 0.2 M and 1 M HCl.[17] The decrease of cmc1 value is attributable to the counterion ($\mathrm{Cl^-}$ ion) binding whereas its increase can only be due to the effect of co-ion ($\mathrm{K^+/Na^+/H^+}$).

The variation of cmc1 with pH below pH=5.2 (5.6 above 35°C) is explained in the light of the expression

$$\log\,(\mathrm{cmc1}) = A - \beta \log\,[C^+] \tag{2}$$

suggested by Phillips[14] and also by Mukerjee et al.[18] In Eq. 2 β is the counterion binding constant and $[C^+]$ is the total counterion concentration. A is a constant related to the equilibrium constant of the equilibrium

$$n\mathrm{L}^- + n\beta C^+ \rightleftharpoons \mathrm{M}^{n(1-\beta)-}, \tag{3}$$

where $\mathrm{L^-}$ is the dodecyl sulfate monomer, n is the aggregation number and M is the micellar species. In the present solution $[C^+]$ is equal to the total $\mathrm{Na^+}$ ion concentration and is given by

$$[C^+] = \mathrm{cmc1} + [\mathrm{Na^+}]_\mathrm{b}, \tag{4}$$

where $[\mathrm{Na^+}]_\mathrm{b}$ is the concentration of the $\mathrm{Na^+}$ ion contributed by the buffer solution. Recently, Romsted and Zanette[11] have also used Eq. 2 to describe successfully

Table 2. Values of First and Second CMC of SDS in Sodium Acetate–Acetic Acid Buffer

t/°C	pH 3.6	4.0	4.4	4.8	5.2	5.6	6.0
	cmc1×10^3 and cmc2×10^2 (within parentheses)/mol kg^{-1}						
15.0	5.80	4.29	2.66	1.91	1.71	2.20	2.40
	(8.20)	(8.26)	(8.98)	(9.25)	(12.25)	(8.98)	(7.81)
20.0	5.73	4.20	2.59	1.88	1.65	1.72	2.59
	(8.28)	(8.60)	(8.80)	(9.05)	(10.63)	(8.72)	(6.15)
25.0	5.66	4.12	2.53	1.84	1.59	1.66	2.36
	(8.74)	(8.87)	(10.16)	(8.87)	(12.30)	(8.22)	(6.56)
30.0	5.71	4.29	2.53	1.95	1.55	1.63	2.68
	(8.72)	(8.78)	(10.08)	(8.60)	(13.42)	(6.48)	(5.59)
35.0	5.89	4.36	2.78	2.04	1.60	1.68	2.15
	(8.83)	(8.97)	(10.07)	(8.27)	(13.61)	(7.70)	(5.49)
40.0	6.10	4.68	2.83	2.19	1.67	1.62	2.72
	(8.97)	(8.92)	(10.48)	(7.84)	(12.62)	(8.04)	(3.63)
45.0	6.39	4.92	3.20	2.31	1.76	1.70	3.20
	(9.05)	(8.88)	(12.00)	(7.69)	(11.23)	(10.47)	(3.68)

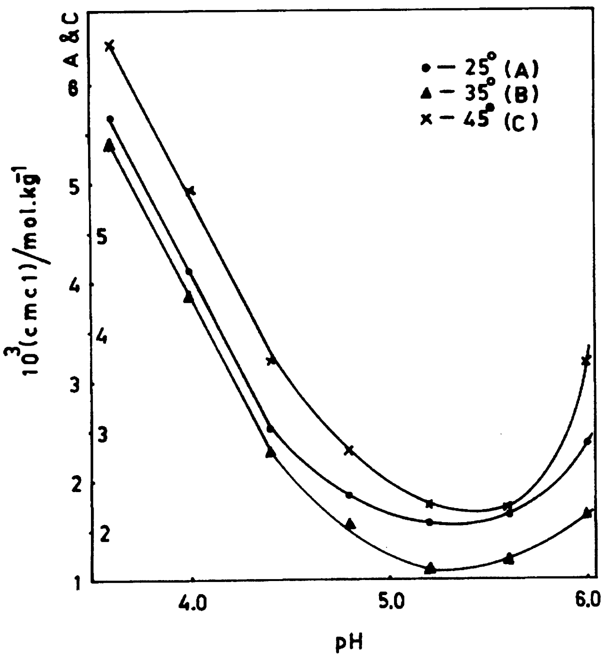

Fig. 2. Variation of cmcl of SDS in NaAc+AcH buffer with pH at different temperatures.

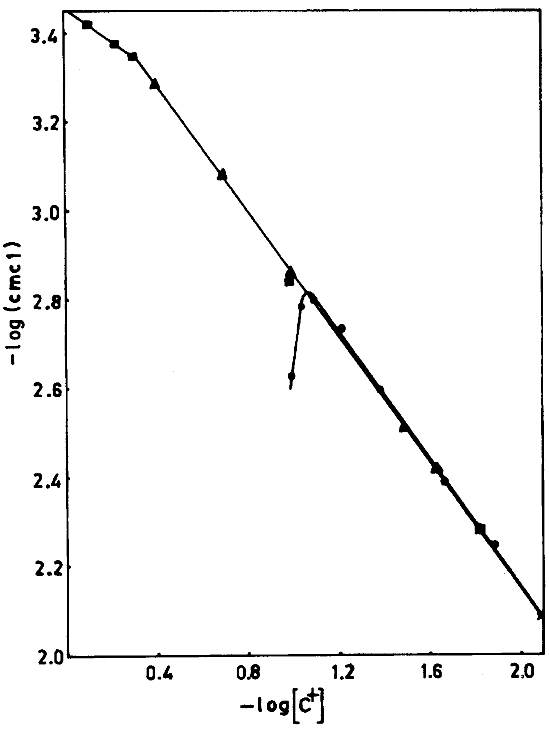

Fig. 3. Plot of log (cmcl) of SDS in NaAc+AcH buffer (●), in H_2O (×), and in NaCl solutions (reported data; ▲ - Ref. 14 and ■ - Ref. 15) at 25°C versus log [C^+].

the effect of added electrolyte on cmcl. The plot of log (cmcl) vs. log [C^+] at 25°C is shown in Fig. 3 and is linear in the region where pH$\leqslant$5.2. The least-squares fitted value of the slope of this linear plot is 0.72 which is in good agreement with the value of counterion binding constant reported for aqueous SDS solution.[11,13] The value of $A=-3.59$ is also in good agreement with the value reported for SDS+NaCl solutions.[19] From the present study it is evident that Eq. 2 is not applicable all the time, instead there is a counterion concentration limit for the applicability of this equation. In order to examine the counterion concentration limit for the applicability of Eq. 2 we also plotted in Fig. 3 the reported[14,15] values of log (cmcl) against Na^+ ion concentration for SDS in NaCl solutions. From this plot (Fig. 3) it may be seen that there is a deviation from Eq. 2 in the region 0.4—0.5 M NaCl concentration where a structural transition of the SDS micelle is reported to occur.[15] log (cmcl) values corresponding to NaCl concentration[15] lying above 0.45 M fall on a separate straight line (Fig. 3). Therefore a deviation from Eq. 2 envisages a structural transition of the micelles taking place. It may further be noted from Fig. 3 that the plots of log (cmcl) vs. log $[C^+]$ in the low Na^+ ion concentration region (up to ca. 0.08 M) corresponding to both SDS in NaCl solution and SDS in NaAc+AcH buffer solution almost overlap thereby indicating that the variation in cmcl with pH ($pH \leqslant 5.2$) observed in the present study is solely due to the Na^+ ion. This also suggests that the increase in cmcl with pH above pH=5.2 is not due to the Na^+ ion because, if it is so, no deviation in the plot of log (cmcl) vs. log $[C^+]$ would be expected up to $[Na^+] \approx 0.45$ M. Therefore from this analysis it is ascertained that the variation in cmcl with pH above pH=5.2 is governed by the acetate co-ion. It can only be concluded from the present study that the acetate co-ion does not favor micelle formation unlike Na^+ counterion. In order to further verify this conclusion we measured the cmcl of SDS in acetic acid solution of pH=1.79 by conductance method. We observed cmcl of 0.006 M. On the other hand, the cmcl of SDS in HCl solution of same pH is estimated to be 0.0019 M from the reported data.[20] Therefore it is evident that acetate ion hinders significantly the micelle formation unlike halide co-ions. Although the decrease in cmcl with increasing counterion concentration is normally attributed to the electrostatic effect, at the moment we do not know the actual reason for the observed dependence of cmcl on co-ion concentration. The co-solvent (acetic acid) effect as a probable explanation for the increase in cmcl may not be ruled out also.

Furthermore, Eq. 2 can also be modified to the form

$$\log\,(\mathrm{cmcl}) = (1+\beta)\log\,(\mathrm{cmcl})_0 - \beta\log\,[C^+] \qquad (5)$$

where $(\mathrm{cmcl})_0$ is the cmcl of SDS in aqueous solution without the presence of buffer or added electrolyte. Substituting the measured value of $(\mathrm{cmcl})_0=0.0082$ M and $\beta=0.72$ we get $(1+\beta)\log\,(\mathrm{cmcl})_0=-3.588$ which is in excellent agreement with the value of A obtained above. Recently De Vijlder[8] used an empirical equation of the form

$$\log\,(\mathrm{cmcl}) = \log\,(\mathrm{cmcl})_0 + (a_\pm)^{\frac{1}{2}} \qquad (6)$$

for describing the variation of cmcl with the concentration of added uni-univalent electrolyte. In Eq. 6 $a_\pm$ is the mean activity of the added electrolyte. Comparison of Eqs. 5 and 6 provides an empirical relation between $\log\,[(\mathrm{cmcl})_0/[C^+]]$ and the mean activity of the added electrolyte.

From Table 2 it is apparent that for SDS solutions having $pH \leqslant 5.2$ cmcl decreases with increasing temperature and passes through a minimum in the temperature region from 25 to 30 °C. This observation is in accordance with the temperature dependence of cmcl reported for aqueous SDS solution.[12] For SDS solutions of pH=5.6 and 6.0 no regular trend in the temperature dependence of cmcl is observed. It may however be pointed out that the uncertainties in the values of cmcl at pH=5.6 and 6.0 are relatively more than those at other pH's. This is because the precision of cmcl determination is found to be dependent on the difference in the respective values of a and b in the $m \leqslant \mathrm{cmc1}$ and $\mathrm{cmc1} < m \leqslant \mathrm{cmc2}$ regions of concentration and this difference decreases with increasing pH. Plots of log (cmcl) vs. $1/T$ for SDS solutions of $pH \leqslant 5.2$ form two straight lines as shown in Fig. 4. We therefore estimated the enthalpy change due to micelle formation, ΔH_m for SDS solutions of $pH \leqslant 5.2$ from the expression[12]

$$\Delta H_m = 2.303R[\mathrm{dlog}\,(\mathrm{cmcl})/\mathrm{d}(1/T)], \qquad (7)$$

where R is the gas constant and the values of dlog (cmcl)/d $(1/T)$ were obtained by the least-squares fittings. The values of ΔH_m estimated thus in the two temperature regions are listed in Table 3. ΔH_m has positive values below 25°C and negative values above 35°C. Positive ΔH_m values indicate that below 25°C entropy factor is the driving force to micellizaton. We also estimated the standard free energy change per mole of micelle formed, ΔG° from the expression[14]

$$\Delta G^\circ = 2.303RT(\log\,(\mathrm{cmcl}) + \beta\log\,[C^+]). \qquad (8)$$

The standard state is chosen as that of mole fraction unity. Expressing therefore the concentrations in mole fractions and substituting the value 0.72 for β we calculated $\Delta G^\circ/RT$ at 25°C for SDS solutions of different pH and the values are listed in Table 3. These values of $\Delta G^\circ/RT$ are in agreement with the value reported by

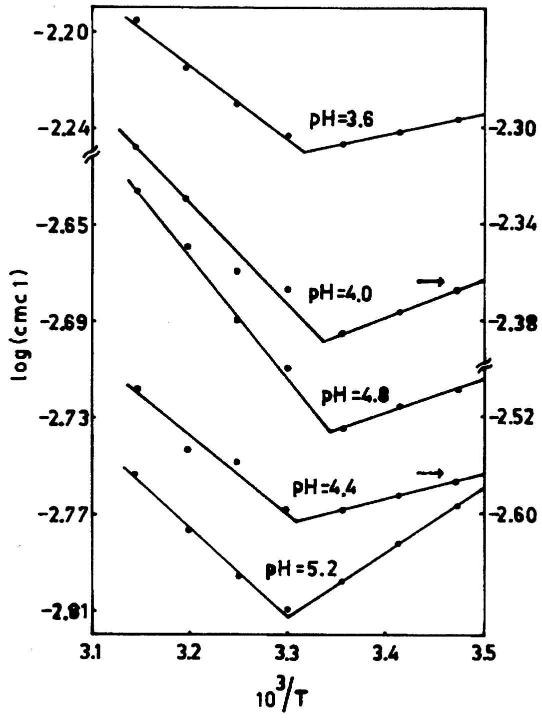

Fig. 4. Plot of log (cmcl) of SDS in NaAc + AcH buffer versus reciprocal of temperature.

Table 3. Values of Enthalpy and Standard Free Energy Changes Due to Micellization of SDS in Sodium Acetate–Acetic Acid Buffer

pH	ΔH_m/kJ mol^{-1} at 15—25°C	35—45°C	$\Delta G^\circ/RT$ at 25°C
3.6 (0.0074M$^{a)}$; 0.0926M$^{b)}$)	1.76	−6.61	−15.20 (−15.9$^{c)}$)
4.0 (0.018M; 0.082M)	2.89	−9.87	−15.14
4.4 (0.039M; 0.061M)	3.59	−12.88	−15.17
4.8 (0.06M; 0.04M)	2.68	−10.13	−15.20
5.2 (0.079M; 0.021M)	5.23	−7.82	−15.18
5.6 (0.0904M; 0.0096M)	—$^{d)}$	—$^{d)}$	−15.02
6.0 (0.096M; 0.004M)	—$^{d)}$	—$^{d)}$	−14.59

a) Concentration of NaAc in the buffer solution. b) Concentration of AcH in the buffer solution. c) Average value of $\Delta G^\circ/RT$ reported for SDS in NaCl solutions (Ref. 14). d) No regular trend of cmcl with temperature.

Phillips[14] for solution of SDS in NaCl solutions. ΔG° is found to have negligible effect on pH up to pH=5.2 and on temperature. Negligible dependence of ΔG° on pH below pH=5.2 shows that ΔG° is virtually independent of electrolyte concentration as observed by others.[14] However, above pH=5.6 ΔG° tends to show a dependence on pH or electrolytic concentration and its value appears to become higher than that below pH=5.2.

The values of cmc2 estimated for SDS solutions of different pH are given in Table 2. These values of cmc2 are however less precise because cmc2 value generally depends on the concentration region ($m>$cmc2) covered in the conductance measurement and the plot of κ vs. m becomes curved when the concentration is extended to high m. We also measured cmc2 for aqueous SDS solution at 25°C which was found to be 0.062 mol kg^{-1} and is in agreement with the reported value.[4] No regular trend is observed in the dependence of cmc2 on temperature or pH. However, the slope, b_3 of the κ vs. m plot in the region $m>$cmc2 decreases at all temperatures with increasing pH or NaAc amount. For SDS in NaCl solution the slope, b_3 is, on the other hand, reported to increase with increasing concentraiton of NaCl.[4] The opposite trend in the variation of b_3 with the addition of NaCl and NaAc solutions therefore suggests that the acetate co-ion also affects the second micellization process. The slope, b_3 is found to be always greater than the slope of κ vs. m plot in the region cmc1$<m\leqslant$cmc2 as reported for aqueous SDS solutions.[4]

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