

Thermodynamic Parameters of Anionic Surfactant–Additive Systems at the Cloud Point

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The thermodynamic parameters of an aqueous anionic surfactant, tetrabutylammonium dodecyl sulfate (TBADS), are calculated in the presence of various additives (viz., quaternary bromides, alcohols, and amines) at the cloud point (CP) of the TBADS–additive system. As the clouding components release their solvated water, they separate out from the solution. Therefore, the CP of an amphiphile can be considered the limit of its solubility. The standard Gibbs energy change of solubilization ($\Delta_s G^\circ$) for all of the additives is found to be negative. The standard enthalpy change ($\Delta_s H^\circ$) and the standard entropy change ($T\Delta_s S^\circ$) values are found to be negative as well as positive depending upon the type and nature of the additive. The results are explained on the basis of their nature, effect on the water structure, and solubilization of these additives either in the micellar or aqueous phase.

Introduction

Clouding is a common phenomenon of nonionic surfactants. At the cloud point (CP), a homogeneous nonionic surfactant solution separates into two coexisting phases, one of which contains much of the surfactant, generally named as the surfactant-rich phase, while the other phase has largely water with surfactant concentration around its critical micelle concentration (cmc).¹ This phase separation is reversible; that is, when temperature decreases below CP, the two-phase system merges into a single homogeneous phase.

The CP of a surfactant is an important factor to be considered in surfactant screening for specific applications, because of the dramatic changes in physical properties and, hence, in the performance of a surfactant solution near the CP. Clouding is to be avoided in some applications, such as surfactant-mediated soil remediation, which is operated at a temperature range in which phase separation does not take place. In contrast, clouding phenomena are preferred in some other applications, for example, the CP extraction process, which is preferentially applicable in the two-phase region.^{2,3} The CP is very sensitive to the presence of additives in the system even at very low concentrations. The additives modify the surfactant–solvent interaction; in consequence, they change the cmc, the size of the micelles, and the phase behavior in the surfactant solutions.^{4,5} Thus, it is of considerable importance to acquire knowledge of the clouding phenomenon of a surfactant system, so that the CP can be tailored to desired levels to meet the requirements of applications.

Despite the number of applications and studies reported based upon the CP phenomenon, the mechanism by which the phase separation occurs is not yet very clear and continues to be a source of controversy among different researchers. Initially, this clouding was ascribed to an increase in size and aggregation number of the micelles and to the formation of giant micelles

which were believed eventually to become insoluble in water. Later, it was realized that the clouding results from the clustering of micelles as a result of attractive intermicellar interactions. Clouding is attributed to the dehydration of hydrophilic groups of the amphiphiles.⁶ It has also been reported that the increase of hydrophobicity near the headgroup region in an ionic surfactant increases the tendency to phase separate.^{7,8} Presently, two schools of thought are available for the appearance of the clouding in the ionic surfactant solutions: one by displacement of water by the counterions^{7–9} and another by the geometric constrictions due to micellar growth.^{10–12} Many theories were put forward to explain the occurrence of CP; it is still not completely resolved.^{13–15}

The CP of an amphiphile can be considered as the limit of its solubility as it phase separates at temperatures above the CP.¹⁶ The clouding components release their solvated water and separate out from the solution. Hence, the standard Gibbs energy of solubilization ($\Delta_s G^\circ$) of the surfactant can be evaluated from the relation¹⁶

$$\Delta_s G^\circ = RT \ln x_s \quad (1)$$

where x_s is the mole fraction of the species at CP; R is the gas constant; and T is the clouding temperature in the kelvin scale.

Here, the standard state is the hypothetical state of ideal solution of unit mole fraction.

The standard enthalpy of clouding, $\Delta_s H^\circ$, can then be calculated from the slope of the $\Delta_s G^\circ/T$ versus $1/T$ plot (see eq 2) and standard entropy of clouding, $\Delta_s S^\circ$, by use of the Gibbs–Helmholtz relation (eq 3)

$$\Delta_s H^\circ = \partial(\Delta_s G^\circ/T)/\partial(1/T) \quad (2)$$

$$\Delta_s S^\circ = (\Delta_s H^\circ - \Delta_s G^\circ)/T \quad (3)$$

In this article, we report the thermodynamics of phase separation of an anionic surfactant, tetrabutylammonium dodecyl

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sulfate (TBADS), in presence of various additives. The thermodynamics of such systems has also remained largely unexplored.

Experimental Section

Materials. Sodium dodecyl sulfate, SDS (> 99 %), and the quaternary bromides (tetraethylammonium bromide, TEAB; tetrapropylammonium bromide, TPAB; and tetrabutylammonium bromide, TBAB) were purchased from Fluka, Switzerland ($\approx 99\%$) and used as received. TBADS has been prepared by mixing equimolar solutions of TBAB and SDS followed by extraction with dichloromethane.⁹ The purity of the TBADS was confirmed by ¹H, NMR, IR, and mass spectroscopy and by surface tensiometry. The aliphatic alcohols were propanol, C₃OH ($\geq 99.5\%$, BDH, England), butanol, C₄OH ($\geq 95\%$, Sarabhai M.Chemicals, India), pentanol, C₅OH ($\geq 99\%$, Fluka, Switzerland), hexanol, C₆OH ($\geq 99\%$, BDH, England), and heptanol, C₇OH ($\geq 99\%$, BDH, England). The aliphatic amines were ethylamine, C₂NH₂ (70 % in water, Fluka, Switzerland), butylamine, C₄NH₂ (98 %, Riedel-de-Haen, Germany), hexylamine, C₆NH₂ (98 %, Merck, Germany), and heptylamine, C₇NH₂ (98 %, Fluka, Switzerland). All of the salts were dried for at least 72 h before use in a vacuum drying oven. The temperature during drying was maintained according to the thermal stability and fusion point of the salt. The water used to prepare the sample solutions was demineralized and double-distilled in an all-glass distillation apparatus. The specific conductivity of this water was in the range $(1 \text{ to } 2) \cdot 10^{-6} \text{ S} \cdot \text{cm}^{-1}$.

Sample Solutions. To see the additive effect on CP, sample solutions were made by taking a requisite quantity of additives in standard volumetric flasks and making up the volumes with the stock solution of $0.03 \text{ mol} \cdot \text{L}^{-1}$ TBADS. After proper mixing, the sample solutions were kept overnight for equilibration. To avoid evaporation, the containers were kept properly stoppered during equilibration and measurement.

Methods. The CP values were obtained by placing several Pyrex glass tubes, each containing a fixed concentration of additive, into a temperature-controlled water bath (Brookfield model TC-200). The temperature was ramped at the rate of $0.1 \text{ K} \cdot \text{min}^{-1}$ near the CP. The onset of turbidity (visual observation) was taken as the CP. Similar CP measurements were made using different concentrations of additives. This was done by diluting the samples with stock solutions to lower concentrations and repeating the above procedure. The uncertainty in the measured CP was $\pm 0.1 \text{ K}$.

The thermodynamic parameters were calculated using eqs 1 to 3. $\Delta_s G^\circ/T$ versus $1/T$, a representative plot, is shown in Figure 1.

Results and Discussion

The data of thermodynamics of TBADS in the presence of additives are given in Tables 1 to 3. These parameters reveal that for all additives $\Delta_s G^\circ$ is negative. However, $\Delta_s H^\circ$ and $T\Delta_s S^\circ$ values are found to be negative or positive, depending upon the type and nature of the additive. For all quaternary salts and short chain amines, these values are negative at all mole fractions. For long chain amines and alcohols, these values are positive in the concentration range used.

i. Effect of Quaternary Bromides. It has already been mentioned that the CP of TBADS solution occurs due to the interaction of butyl chains of TBA⁺ counterions, which brings the charged micelles together (a sort of bridging of micelles through TBA⁺ counterions).^{13,14} Now, if TBA⁺ is exchanged with TEA⁺ or TPA⁺, the close interaction among the micelles

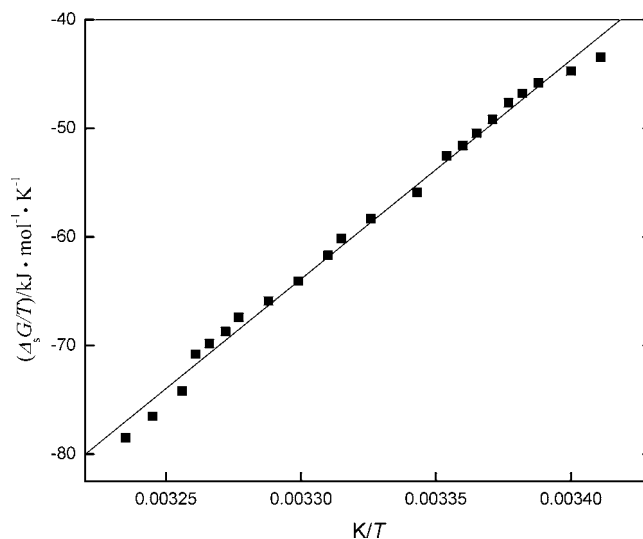


Figure 1. $\Delta_s G^\circ/T$ vs $1/T$ plot of the TBADS + TBAB system to derive the enthalpy change of clouding ($\Delta_s H^\circ$).

would be disturbed and thereby increase the overall entropy of the system. Further, at all concentrations of TEAB and TPAB, $\Delta_s H^\circ$ and $T\Delta_s S^\circ$ are negative, and $\Delta_s H^\circ > T\Delta_s S^\circ$. However, with externally added TBA⁺ (as TBAB), an opposite behavior is observed, that is, CP decreases. As the [TBA⁺] increases in the system, one can expect more connections of micelles through butyl chains with concomitant decreases in CP. As a result, $\Delta_s H^\circ$ and $T\Delta_s S^\circ$ are negative. The system is highly exothermic in the case of externally added [TBA⁺] as compared to [TEA⁺] and [TPA⁺].

ii. Effect of Alcohols. The values of $\Delta_s H^\circ$ and $T\Delta_s S^\circ$ were found to be positive for all alcohols. At standard conditions, the dissolution of one mole of TBADS in the presence of additives releases heat with overall ordering of the TBADS–additive systems. Alcohols are only partially soluble in water and hence solubilize more in micelles with their headgroups toward the surface and alkyl chains penetrating into the micelle.¹⁷ This results in the formation of a larger aggregate that ends up with the release of heat with the overall ordering of the system.

iii. Effect of Amines. The values of thermodynamic parameters ($\Delta_s H^\circ$ and $T\Delta_s S^\circ$) change sign from negative to positive in the concentration range used. In case of short chain amines the values of $\Delta_s H^\circ$ and $T\Delta_s S^\circ$ are negative. These additives are highly miscible in water and, therefore, disrupt the water structure; their presence always results in a decrease in the aggregation number.¹⁸ No micelle formation takes place when enough of these additives are added to the micellar solution.¹⁹ These additives get adsorbed at the micelle–water interface²⁰ and would hinder the micellar aggregation. Hence, the $T\Delta_s S^\circ$ value comes out to be negative and large in magnitude. However, in case of higher amines, the values of $\Delta_s H^\circ$ and $T\Delta_s S^\circ$ are positive. Higher chain amines are poorly soluble in water and seem to solubilize inside the micelles with the hydrophilic group toward the micellar surface and chain penetrating into the micelle. The positive $T\Delta_s S^\circ$ manifests parallelism with the micelle formation.

Conclusions

The clouding behavior witnessed with TBADS in presence of quaternary salts and short chain amines is exothermic. The release of sufficient solvated water from the domain of micellar aggregation on increasing temperature makes the

Table 1. Cloud Point (T_{cp}) and Thermodynamic Parameters for Clouding in 0.03 mol·L⁻¹ TBADS Aqueous Solution in the Presence of Quaternary Bromides of Mole Fractions x

$10^4 \cdot x$	T_{cp} K	$\Delta_s G^\circ$ kJ·mol ⁻¹	$\Delta_s H^\circ$ kJ·mol ⁻¹	$T\Delta_s S^\circ$ kJ·mol ⁻¹
Tetraethylammonium Bromide				
0	311.65			
0.90	313.15	-24.25	-111.43	-87.18
1.08	313.65	-23.82		-87.61
1.35	314.15	-23.27		-88.16
1.80	315.15	-22.59		-88.84
2.70	316.15	-21.59		-89.84
3.37	317.65	-21.12		-90.31
4.50	318.65	-20.41		-91.02
5.40	319.65	-19.99		-91.44
6.75	321.15	-19.49		-91.94
7.68	322.15	-19.21		-92.22
9.00	323.15	-18.84		-92.59
10.79	324.65	-18.44		-92.99
13.49	326.65	-17.95		-93.48
15.41	328.15	-17.67		-93.76
17.98	329.65	-17.32		-94.11
19.61	331.15	-17.16		-94.27
21.56	332.65	-16.98		-94.45
23.95	334.15	-16.76		-94.67
26.94	336.15	-16.53		-94.90
30.77	339.15	-16.31		-95.12
35.89	342.15	-16.01		-95.42
Tetrapropylammonium Bromide				
0	311.65			
1.82	314.65	-22.53	-87.33	-64.80
2.12	315.15	-22.16		-65.17
2.54	315.65	-21.73		-65.60
3.17	316.65	-21.21		-66.12
3.64	317.65	-20.91		-66.42
4.23	318.65	-20.58		-66.75
5.08	319.65	-20.16		-67.17
6.35	321.15	-19.65		-67.68
7.20	322.15	-19.38		-67.95
8.31	323.65	-19.08		-68.25
9.80	325.15	-18.73		-68.60
12.00	326.15	-18.24		-69.09
13.49	327.65	-18.00		-69.33
15.41	329.15	-17.72		-69.61
17.98	331.65	-17.43		-69.90
21.56	334.15	-17.05		-70.28
26.94	336.65	-16.56		-70.77
35.89	341.15	-15.97		-71.36
44.82	345.15	-15.52		-71.81
53.73	350.15	-15.21		-72.12
Tetrabutylammonium Bromide				
0	311.65			
0.79	309.15	-24.27	-201.71	-177.44
1.01	308.15	-23.57		-178.14
1.33	307.15	-22.79		-178.92
2.00	306.65	-21.72		-179.99
2.25	306.15	-21.39		-180.32
2.57	305.65	-21.00		-180.71
3.01	305.15	-20.57		-181.14
3.60	304.15	-20.05		-181.66
4.50	303.15	-19.42		-182.29
5.99	302.15	-18.64		-183.07
7.20	301.65	-18.15		-183.56
9.00	300.65	-17.53		-184.18
12.00	299.15	-16.73		-184.98
17.98	298.15	-15.67		-186.04
20.22	297.65	-15.35		-186.36
23.11	297.15	-14.99		-186.72
26.94	296.65	-14.59		-187.12
32.31	296.15	-14.12		-187.59
35.89	295.65	-13.84		-187.87
40.36	295.15	-13.53		-188.18
46.09	294.15	-13.16		-188.55
53.73	293.15	-12.74		-188.97

Table 2. Cloud Point (T_{cp}) and Thermodynamic Parameters for Clouding in 0.03 mol·L⁻¹ TBADS Aqueous Solution in the Presence of Aliphatic Alcohols of Mole Fractions x

$10^4 \cdot x$	T_{cp} K	$\Delta_s G^\circ$ kJ·mol ⁻¹	$\Delta_s H^\circ$ kJ·mol ⁻¹	$T\Delta_s S^\circ$ kJ·mol ⁻¹
Propanol				
0	311.65			
19.97	310.65	-16.05	222.32	238.37
25.67	310.15	-15.38		237.70
29.93	309.65	-14.96		237.28
35.89	309.15	-14.47		236.79
44.82	308.65	-13.88		236.20
51.19	308.15	-13.51		235.83
59.66	307.15	-13.10		235.42
71.52	306.15	-12.57		234.89
Butanol				
0	311.65			
4.00	309.65	-20.14	97.36	117.50
5.00	309.15	-19.53		116.89
6.66	308.65	-18.77		116.13
7.99	308.15	-18.27		115.63
10.00	307.15	-17.64		115.00
13.33	305.65	-16.82		114.18
19.95	303.15	-15.67		113.03
25.67	301.65	-14.96		112.32
29.93	300.65	-14.53		111.89
35.89	297.65	-13.93		111.29
44.82	295.15	-13.27		110.63
51.19	293.15	-12.86		110.22
59.66	291.15	-12.40		109.76
71.52	289.15	-11.87		109.23
Pentanol				
0	311.65			
2.5	307.15	-21.18	66.82	88.00
2.86	306.65	-20.80		87.62
3.33	306.15	-20.38		87.20
4.00	305.15	-19.85		86.67
5.00	303.15	-19.15		86.34
6.66	300.65	-18.28		85.10
7.99	299.15	-17.74		84.56
9.98	296.65	-17.04		83.86
13.33	293.15	-16.14		82.96
19.97	287.65	-14.87		81.69
22.46	285.15	-14.46		81.28
25.67	282.65	14.02		80.84
Hexanol				
0	311.65			
0.66	309.15	-24.72	73.09	97.81
0.79	308.15	-24.19		97.28
0.99	307.15	-23.54		96.63
1.13	306.15	-23.12		96.21
1.33	305.15	-22.64		95.73
1.60	304.15	-22.09		95.18
2.00	301.65	-21.36		94.45
2.66	299.65	-20.50		93.59
4.00	295.15	-19.20		92.29
5.15	291.65	-18.36		91.45
5.99	289.65	-17.87		90.96
7.20	287.65	-17.31		90.39
9.00	285.65	-16.65		89.74
10.27	282.15	-16.14		89.23
Heptanol				
0	311.65			
0.57	306.15	-24.85	58.98	83.83
0.66	305.15	-24.39		83.37
0.79	304.15	-23.88		82.86
0.88	303.15	-23.53		82.51
0.99	302.15	-23.16		82.14
1.13	301.15	-22.74		81.72
1.33	299.65	-22.23		81.21
1.60	297.65	-21.62		80.60
2.00	294.65	-20.87		79.85
2.66	290.15	-19.85		78.83
4.00	285.15	-18.55		77.53
5.15	281.15	-17.70		76.68
5.99	279.15	-17.22		76.20

resultant entropy values fairly negative. On the other hand, higher chain amines and alcohols increase the micelle size

Table 3. Cloud Point (T_{cp}) and Thermodynamic Parameters for Clouding in 0.03 mol·L⁻¹ TBADS Aqueous Solution in the Presence of Aliphatic Amines of Mole Fractions x

$10^5 \cdot x$	T_{cp} K	$\Delta_s G^\circ$ kJ·mol ⁻¹	$\Delta_s H^\circ$ kJ·mol ⁻¹	$T\Delta_s S^\circ$ kJ·mol ⁻¹
Ethylamine				
0	311.65			
5.76	311.65	-25.29	-865.72	-840.43
9.90	312.15	-23.93		-841.79
16.00	312.65	-22.71		-843.01
26.60	313.15	-21.43		-844.29
59.90	313.65	-19.35		-846.37
102.70	313.65	-17.94		-847.78
120.00	314.15	-17.56		-848.16
143.90	314.65	-17.12		-848.60
179.80	315.15	-16.56		-849.16
Butylamine				
0	311.65			
51.50	312.15	-19.65	-239.52	-219.87
59.90	312.15	-19.25		-220.27
72.00	312.65	-18.81		-220.71
90.00	313.15	-18.26		-221.26
102.70	313.65	-17.94		-221.58
120.00	314.15	-17.56		-221.96
143.90	315.15	-17.15		-222.37
179.80	316.15	-16.61		-223.36
Hexylamine				
0	311.65			
2.16	310.65	-27.74	812.76	840.50
2.88	310.15	-26.96		839.72
4.50	309.65	-25.77		838.53
5.04	309.65	-25.47		838.23
7.92	309.15	-24.27		837.03
9.90	309.15	-23.69		836.45
13.30	309.15	-22.93		835.69
16.00	308.65	-22.42		835.18
20.00	308.65	-21.86		834.62
26.60	308.15	-21.08		833.84
40.00	307.65	-20.01		832.77
59.90	307.15	-18.95		831.71
90.00	307.15	-17.91		830.67
102.70	307.15	-17.57		830.33
143.90	306.65	-16.68		829.44
179.80	306.15	-16.08		828.84
Heptylamine				
0	311.65			
4.50	310.65	-25.85	214.80	240.65
5.04	310.15	-25.51		240.31
5.76	309.65	-25.13		239.93
6.66	309.15	-24.72		239.52
7.92	308.65	-24.23		239.03
9.90	308.15	-23.62		238.42
13.30	307.15	-22.79		237.59
16.00	306.15	-22.24		237.04
20.00	305.15	-21.61		236.41
26.60	304.15	-20.81		235.61
40.00	302.65	-19.68		234.48

and decrease the randomness of the system; hence the $T\Delta_s S^\circ$ value becomes positive. The Gibbs energy change, $\Delta_s G^\circ$, is negative for all of systems which shows the spontaneity of the clouding phenomenon.

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