# Thermodynamic Energetics of Charged Micellar Solutions with and without Salts at the Cloud Point

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**ABSTRACT:** Cloud point (CP) data have been acquired for two anionic surfactants, namely, tetra-*n*-butyl ammonium dodecylsulfate (TBADS) and tetra-*n*-butylammonium dodecylbenzenesulfonate (TBADBS) with and without salts (Ca(NO$_3$)$_2$ and Al(NO$_3$)$_3$). The energetics of clouding process, standard Gibbs free energy change ($\Delta G^\circ_c$), standard enthalpy change ($\Delta H^\circ_c$), and standard entropy ($\Delta S^\circ_c$) were evaluated. The release of solvated water from the clouding component causes the phase separation. Hence CP was taken as the limit of its solubility. The $\Delta G^\circ_c$ for all of the systems with and without inorganic salts is found to be negative. However, both $\Delta H^\circ_c$ and $\Delta S^\circ_c$ are positive and negative depending upon concentration and charge on the counterion. The results are discussed in the light of exchange of counterions (TBA$^+$ by Ca$^{2+}$ or Al$^{3+}$) and formation of bridges through displaced TBA$^+$ among the anionic micelles present in the solution.
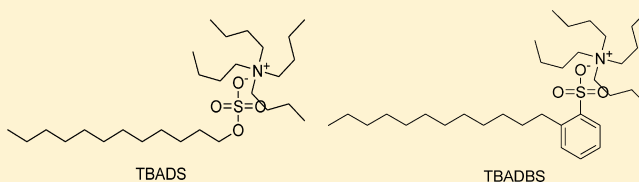
## INTRODUCTION

Surfactant or detergents are amphiphilic materials having potential applications in the solubilization of insoluble substrate in aqueous/nonaqueous solvents. Nonionic surfactant solutions have the property to undergo clouding on heating, followed by phase separation into two isotropic phases.[1] This separation is reversible when the system is cooled. The clouding has also been observed in solutions of ionic surfactants. However, the phenomenon occurs in ionic surfactant solutions rarely, which may be due to the presence of electrostatic repulsion between similar charged head groups in ionic micelles. The mixture of cationic and anionic surfactants produces an insoluble coacervate, which may form vesicular assemblies in an aqueous or aqueous/nonaqueous solvent mixture.[2−5] Ionic surfactants (for example, sodium dodecyl sulfate (SDS)) having inorganic counterions are not prone to clouding. Although clouding on heating an aqueous solution of dodecyl tributylammonium-bromide was reported, no such phenomenon was reported with head groups containing lower alkyl chains.[6] The clouding phenomenon was also reported with anionic surfactants containing large hydrophobic counterions such as tetra-*n*-butylammonium perfluoroalkanoate.[7,8] The above observations indicate that clouding phenomenon in anionic surfactant solution correlates with the presence of butyl chains either in the headgroup or counterion. The clouding phenomenon of some amphiphilic drugs[9] and the thermodynamics at the cloud point (CP) have been studied in the past.[10−12] Like ionic surfactants, many amphiphilic drugs show a similar clouding phenomenon under specific experimental conditions (pH, concentration, or temperature).

Keeping this view in mind, Kumar et al.[13−16] among others[17−20] studied a variety of systems in the context of clouding in charged micellar solutions. In most of the above studies the tetra-*n*-butyl ammonium (TBA$^+$) ion was driven from an added salt or was the counterion given by the surfactant (e.g., tetra-*n*-butylammonium dodecylsulfate (TBADS)). The clouding behavior of an anionic surfactant having other large counterions is not studied much.[13,21−23] Further, additives modify the phase behavior of surfactant solutions, and therefore, it is of considerable importance to acquire knowledge of clouding phenomenon of such surfactant systems to tune the phenomenon in desired way. Many studies are devoted to explain the mechanism of clouding phenomenon in charged micellar solution; it is yet to be completely resolved.[16,18,22,24]

The clouding in a surfactant solution can be considered as the solubility limit at or above which phase separation takes place. The clouded fraction releases their solvated water and yields two phases. Therefore, the standard free energy change ($\Delta G^\circ_c$) for clouding can be computed by the relation[25]

$$\Delta G^\circ_c = RT \ln x_s \tag{1}$$

where $x_s$ is the mole fraction of the surfactant at which clouding species passes from the soluble state to an insoluble state, $R$ is the gas constant (8.314 J·K$^{-1}$·mol$^{-1}$); and $T$ is the clouding temperature.

The standard enthalpy change of clouding, $\Delta H^\circ_c$, can be calculated from the slope of the $\Delta G^\circ_c/T$ versus $1/T$ plot

$$\Delta H^\circ_c = \partial(\Delta G^\circ_c/T)/\partial(1/T) \tag{2}$$

From relations 1 and 2 we can estimate the value of standard entropy change ($\Delta S^\circ_c$) using the relation

$$(\Delta S^\circ_c) = (\Delta H^\circ_c) - (\Delta G^\circ_c)/T \tag{3}$$

In the present communication, we are reporting the CP and thermodynamic data of clouding phenomenon in anionic surfactant solutions: tetra-*n*-butylammonium dodecylsulfate (TBADS) and tetra-*n*-butylammonium dodecylbenzenesulfonate (TBADBS) in the presence and absence of inorganic salts ($Ca(NO_3)_2$ and $Al(NO_3)_3$).

## EXPERIMENTAL SECTION

**Materials.** Sodium dodecyl sulfate, SDS (mass fraction purity ≥0.99), and tetrabutylammonium bromide, TBAB (mass fraction purity 0.99) were purchased from Sigma (St. Louis, MO, USA). Sodium dodecyl benzenesulfonate SDBS (mass fraction purity 99 %) was obtained from TCI (Japan) and used as received. TBADS has been prepared by mixing equimolar solutions of TBAB and SDS followed by extraction with dichloromethane. Similarly TBADBS has been prepared by mixing equimolar solutions of TBAB and SDBS. The purity of the TBADS and TBADBS was confirmed by $^1$H NMR, IR, and mass spectroscopy and by surface tensiometry. The structures of the above-synthesized surfactants are shown in Scheme 1.

**Scheme 1**
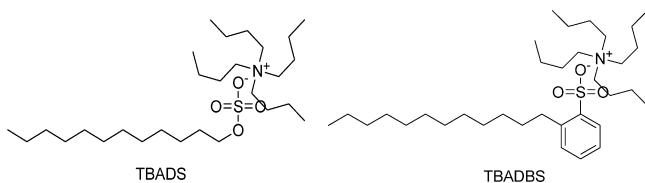


The critical micelle concentration (cmc) and other spectroscopic data of TBADS were in agreement with those reported earlier.[18,20] The inorganic nitrates, calcium nitrate tetrahydrate purified, $Ca(NO_3)_2 \cdot 4H_2O$ (mass fraction purity ≥0.98) and aluminum nitrate extra pure $Al(NO_3)_3 \cdot 9H_2O$ (mass fraction purity 0.98), were purchased from Merck and s.d. Fine-Chem Ltd., respectively. The water used to prepare the sample solutions was double-distilled in an all-glass distillation apparatus. The specific conductivity of the water was in the range (2 to 4)$\cdot 10^{-6}$ S·cm$^{-1}$.

**Sample Solutions.** CP measurements were carried out in pure surfactant (TBADS or TBADBS) solutions in the presence or absence of salts. To observe the salt effect on the CP, sample solutions were prepared by taking a requisite quantity of salt in standard volumetric flask and making up the volume with the stock solution of $5.4 \cdot 10^{-4}$ mole fraction ($x$) TBADS or TBADBS. After proper mixing, the sample solutions were kept in equilibration for ~24 h.

**Methods.** The CP values were obtained by placing sample tubes, containing surfactant solution with a fixed concentration of salt or no salt, into a temperature-controlled water bath. The onset of turbidity (visual observation) was taken as the CP. Similar CP measurements were also made by diluting the samples with stock surfactant solutions in order to collect CP data at various concentrations of salt. The uncertainty in the measured CP was ± 1.0 K.

## RESULTS AND DISCUSSION

The clouding phenomenon is a phase-changing process which is very common in the case of nonionic surfactants. The temperature required for observing this phenomenon is called CP. In the case of ionic surfactants the dehydration of head groups, depletion of the electrostatic interaction among dodecyl sulfate

anions, and micelle–micelle interaction via bridging with tetrabutyl ammonium have been considered as the causes for the clouding phenomenon.[13,16,18,20] Figure 1 shows the decrease
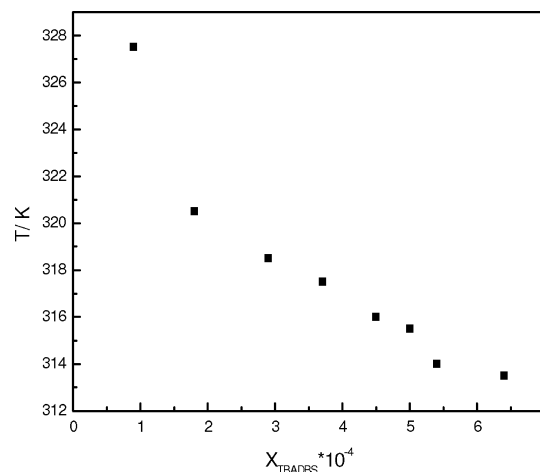


**Figure 1.** Variation of the cloud point at different mole fractions of TBADBS.

in CP with [TBADBS]. This may be due to the fact that, as [TBADBS] increases, the number of TBA$^+$ ions would increase and therefore the bridging of micelle is expected to facilitate clouding with a concomitant decrease in CP. This indeed was observed in Figure 1.

The CP data for TBADS and TBADBS are summarized in Table 1. The values of CP for TBADS were plotted together

**Table 1. CP Data for TBADS and TBADBS at Different Mole Fractions $x$**

| [TBADS] | | [TBADBS] | |
|---|---|---|---|
| $10^4 \cdot x_{TBADS}$ | CP/K | $10^4 \cdot x_{TBADBS}$ | CP/K |
| 2.72 | 320.5 | 0.9 | 327.5 |
| 3.56 | 319.0 | 1.8 | 320.5 |
| 4.64 | 316.0 | 2.9 | 318.5 |
| 5.79 | 315.0 | 3.7 | 317.5 |
| 6.64 | 314.5 | 4.5 | 316.0 |
| 7.73 | 313.0 | 5.0 | 315.5 |
| 9.28 | 312.0 | 5.4 | 314.0 |
| 17.97 | 304.8 | 6.4 | 313.5 |

with the values given in literature[18] (Figure 2). The CP data for TBADS are found in close agreement. The CP for TBADBS was found lower than the corresponding values obtained with TBADS at different concentrations (Table 1). The lower CP value with TBADBS may be due to the presence of the benzene ring in the dodecyl benzene sulfonate anion (DBS$^-$) moiety. This structural difference is responsible for greater hydrophobic interactions between the DBS$^-$ and the alkyl chains of TBA$^+$. It has been reported that the critical micelle concentration (cmc) of SDBS was found to be lower than SDS.[26] The same analogy can be drawn here and may be responsible for lower CP values with TBADBS in Table 1.

Tables 2 and 3 contain thermodynamic data ($\Delta G^\circ_c$, $\Delta H^\circ_c$, and $\Delta S^\circ_c$) for TBADS and TBADBS, respectively. $\Delta G^\circ_c$ data shows close agreement with the literature values.[20] However, we found discrepancy in the value of $\Delta H^\circ_c$ ($\Delta H^\circ_c$ = 116.7 kJ·mol$^{-1}$ (Table 2) while the value reported for $\Delta H^\circ_c$ in an earlier work[20]

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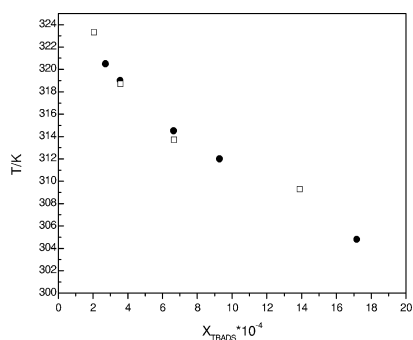dx.doi.org/10.1021/je200909j | *J. Chem. Eng.Data* 2012, 57, 521−525

**Figure 2.** Variation of cloud points at different mole fractions of TBADS: ●, present study; □, data taken from ref 18.

**Table 2. Thermodynamic Parameters for Clouding in TBADS at Different Mole Fractions $x$[a]**

| $10^4 \cdot x_{TBADS}$ | $\Delta G^{\circ}_c$ kJ·mol⁻¹ | $\Delta H^{\circ}_c$ kJ·mol⁻¹ | $\Delta S^{\circ}_c$ kJ·K⁻¹·mol⁻¹ |
|---|---|---|---|
| 2.72 | −21.9 | 116.7 | 0.432 |
| 3.56 | −21.1 | | 0.432 |
| 4.64 | −20.2 | | 0.433 |
| 5.79 | −19.5 | | 0.432 |
| 6.64 | −19.1 | | 0.432 |
| 7.73 | −18.6 | | 0.432 |
| 9.28 | −18.1 | | 0.432 |

[a]The relative uncertainties of $\Delta G^{\circ}_c$, $\Delta H^{\circ}_c$, and $\Delta S^{\circ}_c$ are within ± 0.4, ± 5.4, and ± 4.6, respectively.

**Table 3. Thermodynamic Parameters for Clouding in TBADBS at Different Mole Fractions $x$[a]**

| $10^4 \cdot x_{TBADS}$ | $\Delta G^{\circ}_c$ kJ·mol⁻¹ | $\Delta H^{\circ}_c$ kJ·mol⁻¹ | $\Delta S^{\circ}_c$ kJ·K⁻¹·mol⁻¹ |
|---|---|---|---|
| 0.9 | −25.4 | 122.5 | 0.451 |
| 1.8 | −22.9 | | 0.454 |
| 2.9 | −21.6 | | 0.452 |
| 3.7 | −20.9 | | 0.451 |
| 4.5 | −20.2 | | 0.452 |
| 5.0 | −19.9 | | 0.451 |
| 5.4 | −19.6 | | 0.453 |
| 6.4 | −19.2 | | 0.452 |

[a]The relative uncertainties of $\Delta G^{\circ}_c$, $\Delta H^{\circ}_c$, and $\Delta S^{\circ}_c$ are within ± 0.007, ± 0.062, and ± 0.053, respectively.

was 0.12 kJ·mol⁻¹. This indicates that there is a difference of 3 orders of magnitude.[27] The endothermic process was associated with a similar $\Delta H^{\circ}_c$ value as reported for other nonionic amphiphiles.[28,29] By using the values of $\Delta G^{\circ}_c$ and $\Delta H^{\circ}_c$, we can obtain $\Delta S^{\circ}_c$ using eq 3 (supravide). The thermodynamic parameters presented in Tables 2 and 3 show that the clouding process is spontaneous and the mechanism of clouding seems to be similar with both surfactants (TBADS and TBADBS). Figure 3 shows the representative plots of $\Delta G^{\circ}_c/T$ vs $1/T$ to calculate $\Delta H^{\circ}_c$ from slope.

The CP data in the presence of salts Ca(NO₃)₂ and Al(NO₃)₃ are summarized in Table 4. A perusal of data indicates that the presence of salt counterion increases and decreases the CP with continuous increase of [salt]. The initial increase may be due to exchange of monovalent TBA⁺ counterion with multivalent inorganic counterions. In doing so the multivalent counterion

**Table 4. CP Data for $5.4\cdot10^{-4}$ $x$ Surfactants in the Presence of Salts at Different Mole Fractions $x$**

| | TBADS | | | | TBADBS | | |
|---|---|---|---|---|---|---|---|
| $10^4 \cdot x_{Ca}$ | CP/K | $10^5 \cdot x_{Al}$ | CP/K | $10^5 \cdot x_{Ca}$ | CP/K | $10^6 \cdot x_{Al}$ | CP/K |
| 0.81 | 315.5 | 2.39 | 309.1 | 0.53 | 312.5 | 0.90 | 313.5 |
| 1.30 | 317.0 | 2.61 | 309.5 | 0.59 | 312.5 | 1.80 | 313.4 |
| 1.83 | 317.8 | 3.60 | 310.0 | 0.85 | 313.3 | 3.70 | 312.2 |
| 2.75 | 318.5 | 4.79 | 308.5 | 0.94 | 312.8 | 5.63 | 311.6 |
| 3.67 | 316.5 | 5.76 | 306.9 | 1.78 | 306.5 | 7.48 | 311.1 |
| 4.40 | 315.0 | 7.20 | 301.8 | 2.66 | 303.5 | 9.00 | 310.5 |
| 5.50 | 313.0 | | | 3.56 | 297.5 | | |
| 7.33 | 311.5 | | | 4.26 | 293.5 | | |
| 8.99 | 310.0 | | | | | | |

**Table 5. Thermodynamic Parameters for Clouding in $5.4\cdot10^{-4}$ $x$ TBADS Aqueous Solution in the Presence of Ca(NO₃)₂ of Different Mole Fractions $x$[a]**

| $10^4 \cdot x_{ca}$ | $\Delta G^{\circ}_c$ kJ·mol⁻¹ | $\Delta H^{\circ}_c$ kJ·mol⁻¹ | $\Delta S^{\circ}_c$ kJ·K⁻¹·mol⁻¹ |
|---|---|---|---|
| 0.81 | −24.7 | −333.2 | −0.978 |
| 1.30 | −23.6 | | −0.977 |
| 1.83 | −22.7 | | −0.977 |
| 2.75 | −21.7 | 113.8 | 0.423 |
| 3.67 | −20.8 | | 0.423 |
| 4.40 | −20.2 | | 0.424 |
| 5.50 | −19.5 | | 0.424 |
| 7.33 | −18.7 | | 0.423 |
| 8.99 | −18.1 | | 0.423 |

[a]The relative uncertainties of $\Delta G^{\circ}_c$, $\Delta H^{\circ}_c$, and $\Delta S^{\circ}_c$ are within ± 0.013, ± 0.105, and ± 0.115, respectively.

carries more water toward the micelle and hence needs higher temperatures to observe CP. However, at higher [salt] a decrease in CP may be due to the fact that the above-exchanged TBA⁺ counterion could be responsible for bridging of two or more micelles and hence facilitating the clouding phenomenon and lowering of CP. The similar salt effect on CP was reported earlier also with monovalent counterions (e.g., Na⁺). However, the increasing and decreasing effect on CP is observed at a very low concentration of multivalent counterions. This indicates that the charge of the added counterion plays a significant role in observing the CP.

The thermodynamic data of TBADS in the presence of Ca(NO₃)₂ and Al(NO₃)₃ are given in Tables 5 and 6. The data reveal that for both the salts $\Delta G^{\circ}_c$ is negative. However, $\Delta H^{\circ}_c$ and $\Delta S^{\circ}_c$ are found to be negative or positive depending upon [salt]. At lower [salt] all thermodynamic parameters are found negative. At higher [salt], only $\Delta G^{\circ}_c$ is negative. This indicates that, at lower [salt], the micellar structures are more ordered and $\Delta H^{\circ}_c$ values are in a similar range as were found for nonionic amphiphiles.[28,29] This also suggests that the clouding phenomenon in the presence of salts is an exothermic process which changes to endothermic at higher [salt]. Moreover, the $\Delta S^{\circ}_c$ value suggests that micelles are more ordered initially in the presence of Al³⁺. This may be due to the presence of higher charge on Al³⁺ which may replace three TBA⁺ ions from the micelle−water interface. However, it seems that disordering increases at higher [salt], as more TBA⁺ ions are available to form loose bridges of the micelles. This indeed reflects from data given in Tables 5 and 6. Tables 7 and 8 contain
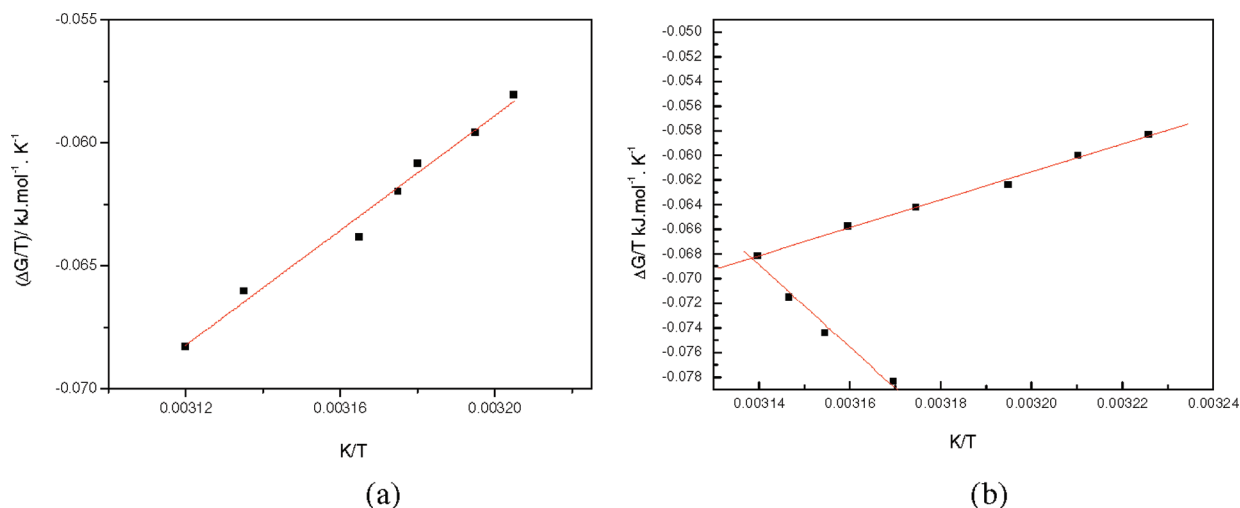
Figure 3. $\Delta G°_c/T$ vs $1/T$ plot of (a) TBADS and (b) TBADS + CaNO$_3$ to derive the enthalpy change of clouding.

**Table 6. Thermodynamic Parameters for Clouding in $5.4\cdot10^{-4}$ $x$ TBADS Aqueous Solution in the Presence of Al(NO$_3$)$_3$ of Different Mole Fractions $x$**

|  | $\Delta G°_c$ | $\Delta H°_c$ | $\Delta S°_c$ |
|---|---|---|---|
| $10^5\cdot x_{Al}$ | kJ·mol$^{-1}$ | kJ·mol$^{-1}$ | kJ·K$^{-1}$·mol$^{-1}$ |
| 2.39 | −27.3 | −367.3 | −1.10 |
| 2.61 | −27.2 |  | −1.10 |
| 3.60 | −26.4 |  | −1.10 |
| 4.79 | −25.5 | 59.6 | 0.28 |
| 5.76 | −24.9 |  | 0.28 |
| 7.20 | −23.9 |  | 0.28 |

**Table 7. Thermodynamic Parameters for Clouding in $5.4\cdot10^{-4}$ $x$ TBADBS Aqueous Solution in the Presence of Ca(NO$_3$)$_2$ of Different Mole Fractions $x^a$**

|  | $\Delta G°_c$ | $\Delta H°_c$ | $\Delta S°_c$ |
|---|---|---|---|
| $10^5\cdot x_{Ca}$ | kJ·mol$^{-1}$ | kJ·mol$^{-1}$ | kJ·K$^{-1}$·mol$^{-1}$ |
| 0.53 | −31.6 | −432.3 | −1.28 |
| 0.59 | −31.3 |  | −1.28 |
| 0.85 | −30.4 |  | −1.28 |
| 0.94 | −30.1 |  | −1.29 |
| 1.78 | −27.9 | 59.4 | 0.28 |
| 2.66 | −26.6 |  | 0.28 |
| 3.56 | −25.3 |  | 0.28 |
| 4.26 | −24.6 |  | 0.29 |

$^a$The relative uncertainties of $\Delta G°_c$, $\Delta H°_c$, and $\Delta S°_c$ are within ± 0.121, ± 0.646, and ± 0.706, respectively.

thermodynamic data of TBADBS in the presence of Ca(NO$_3$)$_2$ and Al(NO$_3$)$_3$. The behavior of Ca(NO$_3$)$_2$ and Al(NO$_3$)$_3$ are similar with a difference that with Ca(NO$_3$)$_2$ system is also showing negative $\Delta H°_c$ and $\Delta S°_c$ at higher [salt]. The similar behavior could have been observed with Al(NO$_3$)$_3$. But poor solubility
of Al(NO$_3$)$_3$ in TBADBS micellar solution hampered the CP determination at higher [Al(NO$_3$)$_3$]. However, $\Delta H°_c$ and $\Delta S°_c$ are higher for Al(NO$_3$)$_3$ than the Ca(NO$_3$)$_2$ case until Al(NO$_3$)$_3$ was added. This shows that with Al(NO$_3$)$_3$ the process is mainly endothermic.

**Table 8. Thermodynamic Parameters for Clouding in $5.4\cdot10^{-4}$ $x$ TBADBS Aqueous Solution in the Presence of Al(NO$_3$)$_3$ of Different Mole Fractions $x^a$**

|  | $\Delta G°_c$ | $\Delta H°_c$ | $\Delta S°_c$ |
|---|---|---|---|
| $10^6\cdot x_{Al}$ | kJ·mol$^{-1}$ | kJ·mol$^{-1}$ | kJ·K$^{-1}$·mol$^{-1}$ |
| 0.90 | −36.3 | 464.0 | 1.59 |
| 1.80 | −34.5 |  | 1.59 |
| 3.70 | −32.4 |  | 1.59 |
| 5.63 | −31.3 |  | 1.59 |
| 7.48 | −30.5 |  | 1.59 |
| 9.00 | −30.0 |  | 1.60 |

$^a$The relative uncertainties of $\Delta G°_c$, $\Delta H°_c$, and $\Delta S°_c$ are within ± 0.004, ± 0.054, and ± 0.046, respectively.

### ■ CONCLUSIONS

The clouding behavior of TBADS and TBADBS in the pure state is an endothermic process. However, the presence of salt makes the process endo- or exothermic depending upon the [salt] as well as the charge on the salt counterion. Further the Gibbs free energy change $\Delta G°_c$ is found negative for all of the systems which indicate that the clouding phenomenon is a spontaneous process.

### ■ AUTHOR INFORMATION

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### ■ ACKNOWLEDGMENTS

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