# Influence of Temperature and Salt on Association and Thermodynamic Parameters of Micellization of a Cationic Gemini Surfactant

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**Abstract:** Association behavior of a gemini surfactant, N,N'-(ethane-1,2-diylbis(oxy))bis(2-oxoethane-2,1-diyl))bis(N,N-dimethylhexadecan-1-aminium) chloride, has been studied conductometrically at different temperatures (293.15 to 338.15 K) in aqueous and aqueous ethylene glycol solvents. The association studies were also performed in aqueous salt solution (sodium chloride, NaCl or sodium salicylate, NaSal). Critical micelle concentration (cmc) decreases and then increases with continuous increase in temperature (U-shaped behavior). The temperature ($T_m$) corresponds to lowest cmc ($cmc_m$) has been found ≈ 325 K for both the solvents (water and water + ethylene glycol). However, cmc increases in mixed solvent (water + ethylene glycol). The $T_m$ has been shifted to lower temperature in the presence of salt. The shifting in $T_m$ was dependent upon the nature of the counter ion. The cmc – temperature variation can be represented by a power law relationship. Relevant thermodynamic parameters have been evaluated and discussed on the basis of the nature of the solvent / counter ion. The enthalpy – entropy compensation plots exhibit linearity. The compensation temperature ($T_c$) and enthalpy change ($\Delta H^\circ_{mic}$) have been computed for various surfactant – solvent systems.

**Keywords:** Gemini surfactant, micellization, conductometry, thermodynamics, enthalpy – entropy compensation.

## INTRODUCTION

During the past few decades, association structures produced by a self-assembly processing have received considerable attention due to their dynamic nature [1]. For the purpose, various surfactants have been synthesized to explore water soluble supramolecular structures. Depending on the experimental conditions, molecular structure and shape, and relative volume fraction of hydrophilic and hydrophobic parts, the surfactant molecules self-assemble into various supramolecular structures e.g., spherical or cylindrical micelles. The molecular self-assembly of the surfactants is ideally suitable for the construction of the responsive material since the dynamic and reversible conformational changes can be triggered by external environment. The concentration at which the formation of surfactant micelle takes place is termed as critical micelle concentration (cmc). Inclusion of different types of additive is well-known to influence the micellar properties (e.g., cmc) of the surfactant solution by affecting the solvent structure or micellar morphology [2-5]. cmc is the first and foremost property to be known for all the surfactants before their use for any kind of application.

Dimeric or gemini surfactants are composed of two hydrophilic heads and two alkyl tails covalently linked through a spacer. These surfactants attracted attention both from industry and academic fields. They have shown superior solution properties in comparison with conventional surfactants e.g., very low cmc, more efficient in decreasing the surface tension of water, superior wetting properties, etc. [6-8]. Further, a few gemini surfactants have also shown interesting antimicrobial or antibacterial activities [9].

It is well documented that the cmc of surfactant varies with temperature. The variation of cmc with temperature observed for ionic surfactants is much different than their non-ionic counterparts. Generally, cmc of non-ionic surfactants decreases regularly with increase in temperature (till critical solution temperature). However, ionic surfactants show a more interesting behavior: cmc decreases to a certain value ($cmc_m$) and then increases with continuous increase in temperature (U-shaped behavior) [10-14]. The temperature at $cmc_m$ ($T_m$) for both non-ionic and ionic surfactants increases as the hydrophobicity of the surfactant decreases. However, $T_m$ was always higher for non-ionic surfactants than for ionic ones [5,11]. The temperature – cmc relationship can be represented by a power law [10,15]. The temperature effect on the cmc can also use to obtain various thermodynamic energetics of micellization. Further, the micellization process has been reported to exhibit an enthalpy – entropy compensation [16].

Recently, the temperature effect on micellization of gemini surfactants has been studied much [2,5,17-29].

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However, only a few studies reported a minimum in the cmc *vs* temperature plot in aqueous medium for gemini surfactants [20,29]. Similarly, no serious attempt has been made to study enthalpy – entropy compensation in gemini surfactant micellization process. Spacer has remarkable effect on the micellization properties of the surfactant. For hydrophilic spacer, the cmc increases with progressive increase in spacer chain length [30]. However, the cmc passes through a broad maximum with increasing the spacer length of a hydrophobic spacer [31].

In the present study, we have synthesized a gemini surfactant (N,N'-((ethane-1,2-diyl bis(oxy)) bis (2–oxoethane–2,1–diyl)) bis (N,N–dimethylhexadecan–1–aminium) chloride) having a biodegradable spacer [32] and performed a study of temperature effect on the cmc under variety of solvent conditions (aqueous, aqueous + ethylene glycol mixed solvent, mass fraction ($\phi$ = 0.11), and in aqueous salt (sodium chloride, NaCl or sodium salicylate, NaSal, mole fractions ($x$) = 0.95 or 0.33, respectively)). The effect of temperature on cmc follows a power law. Thermodynamic parameters have been calculated by the temperature dependence of cmc.

## EXPERIMENTAL SECTION

### Materials

Chloroacetylchloride (98%, S.d.Fine Chemicals, used after simple distillation), ethylene glycol, EG (99%, Sigma Aldrich), N, N-hexadecyl dimethylamine (95%, Sigma Aldrich), sodium chloride, NaCl (99%, Merck) and sodium salicylate, NaSal (99%, Merck) were used as received. However, the salts were dried in a vacuum oven (3 – 4 h) before use. For preparation of the sample solution, water was demineralised in $KMnO_4$ solution and double distilled in all glass assembly. The specific conductivity of distilled water was 1 – 2 µS/cm.

### Synthesis of Gemini Surfactant with Biodegradable Spacer

The cationic gemini surfactant as shown in Scheme **1** was synthesized in two steps. Spacer, 1, 2 - bis-chloroacetoxy-ethane, was synthesized by drop by drop addition of chloro acetyl chloride in ethylene glycol followed by refluxing for 8 hrs as reported in the literature [33]. In the second step, 1, 2 - bis-chloroacetoxy-ethane and N, N-Hexadecyl dimethylamine was refluxed in dry ethyl acetate for 24

h. The solvent was removed under vacuum and a white solid mass was obtained. This solid mass recrystallized at least 3 – 4 times in ethyl acetate: DCM (8:2) mixture. The obtained white shiny powder was dried in a vacuum oven for several hours. The synthesized surfactant is named as gemini and used throughout in the manuscript.
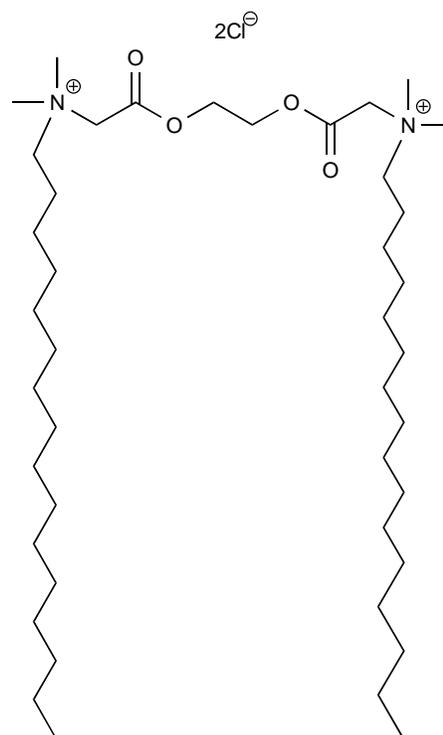


**Scheme 1:** Structure of N,N'-((ethane-1,2-diylbis(oxy))bis(2-oxoethane-2,1-diyl))bis(N,N dimethylhexadecan-1-aminium) chloride as Gemini Surfactant.

### Spectral Characteristics of Gemini Surfactant

The purity of the synthesized gemini was checked by ^{1}H NMR (Bruker, 400 MHz), FT-IR (8400S Shimadzu), elemental analysis and surface tensiometry. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta$ 0.867 – 0.900 (t, 6H), $\delta$ 1.256 – 1.349 (t, 52H), $\delta$ 1.781 (s, 4H), $\delta$ 3.555 (s, 12H), $\delta$ 3.795 – 3.837 (t, 4H), $\delta$ 4.487 (s, 4H), $\delta$ 5.111 (s, 4H). CHN Analysis, Anal. Calculated for $C_{42}H_{86}N_2O_4Cl_2$ (%) : C 66.90, H 11.50, N 3.72. Found C 65.63, H 11.87, N 3.12. FT-IR (KBr, cm$^{-1}$): 2920, 2853, 1751, 1636, 1472, 1187, 1048. The spectroscopic data were found in good agreement with the literature value reported earlier [34].

### Conductivity Measurements

Conductometric measurements were carried out by using a conductivity meter EUTECH cyberscan CON510 (cell constant 1 cm$^{-1}$) with an inbuilt

temperature sensor. A pre-calibrated conductivity cell was used to obtain a specific conductance at an appropriate concentration range. The temperature of the sample solution was precisely controlled by SCHOTT CT1650 thermostat with an accuracy of $\pm$ 0.01°C. The cell with the appropriate amount of the solvent in a vessel was placed in a thermostat for at least 30 minutes prior to the measurement.

## RESULTS AND DISCUSSION

### Determination of cmc, $T_m$ and Power Law Exponents

The cmc and degree of dissociation ($\alpha$) values for the gemini surfactant were determined from the intersection and the ratio of the slopes, respectively, of two straight lines in the plot of the specific conductance ($\kappa$) *vs* [surfactant] as reported earlier [3]. Figure **1** shows the dependence of the cmc on temperature for pure water, water + EG mixed solvent system, $\phi_{EG}$ = 0.11, aqueous NaCl and aqueous NaSal, $x_{NaCl}$ = 0.95 and $x_{NaSal}$ = 0.33, respectively. The cmc data are given in Tables **1** and **2**. $\alpha$ has shown weak dependence on temperature and hence an average value ($\alpha_a$) was used for whole temperature range and included in Tables **1** and **2**. It was observed that cmc decreases with temperature to a certain value ($cmc_m$) followed by an increase. The initial heating causes the decrease in hydration of the hydrophilic head group which favors micellization. Probably, this may be the reason for the decrease in the cmc (Figure **1**). However, when the surfactant molecules dissolve in aqueous medium the alkyl tail group distorts the water structure. Raising the

temperature also causes breakdown of structured water around the alkyl tail part which opposes the micellization. Above two factors, (i) decrease in head group hydration and (ii) break down of structured water around tail part, compete for the resulting effect on micellization phenomenon and the cmc value. The cmc increase in the latter part may be due to the predominance of second factor as indeed observed in Figure **1**. Generally, $T_m$ was reported between 273 K to 313 K for ionic surfactants [10] and $\approx$ 323 K for many non-ionic surfactants [35]. It is intriguing to note, though the present gemini is (cat) ionic in nature but $T_m$ was found $\approx$ 326 K (Table **3**) which is generally observed for non-ionic ones. This may be due to the hydration of the spacer which contains oxygen atoms of the carboxylate unit in addition to the usual hydration of the head group. This indicates that the head group hydration predominate the micellization process and even counteract the second factor up to a distinctly higher temperature.

The addition of a polar organic solvent to water is expected to change the physical properties (dielectric constant ($\varepsilon$) and dipole moment) [36]. The presence of EG in the solvent mixture can decrease the $\varepsilon$ than of pure water ($\varepsilon_{water}$ = 78.5 and $\varepsilon_{EG}$ = 37.7 at 293 K). An overall cmc increase was observed in 0.11 $\phi_{EG}$ (at different temperature) without affecting $T_m$ much. The addition of polar organic solvents may decrease the hydrophobic interaction between alkyl groups of the surfactant (diminishing of factor - ii). Additionally, when the $\varepsilon$ value of the solvent decreases, the repulsion between the head groups increases and thus cmc value increases (Table **1**).

The addition of salt to the aqueous solution, at a given temperature, causes a decrease in cmc (Figure **2** and Table **2**). It may be due to screening of the repulsion between cationic head groups of the surfactant in the presence of counter ions (Cl$^-$ or Sal$^-$) which facilitate early formation of the micelles. This indeed was observed in the present study and confirms the earlier reports [16,37]. However, a distinct fall in $T_m$ values was observed in the presence of salts (Table **3**). The decrease was more pronounced with the salt containing hydrophobic counterion (Sal$^-$). It has been reported earlier that hydrophobicity of the counterion plays an important role in the aggregation process [38]. Sal$^-$ is known for a strong binding with the cationic head groups and for screening the repulsive coulombic interactions. The presence of salt and increase of temperature may cause decrease in hydration of the hydrophilic group synergistically and therefore first



**Figure 1:** cmc *vs* Temperature for Gemini Surfactant in; ○, Pure Water; □, $\phi_{EG}$ = 0.11; △, $x_{NaCl}$ = 0.95; ◇, $x_{NaSal}$ = 0.33.

**Table 1:  Various Micellization (*cmc* and α_a) and Thermodynamic Parameters (ΔG°_mic, ΔH°_mic and ΔS°_mic) of Gemini Surfactant in Water + Ethylene Glycol Mixed Media at Different Temperatures**

| $\phi_{EG}$ | $T$ | $cmc \cdot 10^5$ | $\alpha_a$ | $\Delta G^\circ_{mic}$ | $\Delta H^\circ_{mic}$ | $\Delta S^\circ_{mic}$ |
|---|---|---|---|---|---|---|
| | K | mol·kg⁻¹ | | kJ·mol⁻¹ | kJ·mol⁻¹ | kJ·K⁻¹·mol⁻¹ |
| 0.00 | 293.15 | 0.760 ± 0.02 | 0.72 ± 0.02 | -57.03 ± 0.07 | 11.65 ± 0.19 | 0.23 ± 0.001 |
| | 298.15 | 0.600 ± 0.04 | | -62.03 ± 0.23 | 73.45 ± 0.20 | 0.45 ± 0.002 |
| | 303.15 | 0.340 ± 0.03 | | -53.58 ± 0.28 | 94.15 ± 0.17 | 0.49 ± 0.002 |
| | 308.15 | 0.240 ± 0.01 | | -72.99 ± 0.20 | 144.14 ± 0.23 | 0.70 ± 0.001 |
| | 313.15 | 0.210 ± 0.01 | | -66.74 ± 0.18 | 123.45 ± 0.21 | 0.61 ± 0.001 |
| | 318.15 | 0.073 ± 0.004 | | -85.44 ± 0.21 | 109.45 ± 0.25 | 0.61 ± 0.001 |
| | 323.15 | 0.065 ± 0.003 | | -69.68 ± 0.18 | 30.88 ± 0.20 | 0.31 ± 0.001 |
| | 328.15 | 0.090 ± 0.004 | | -78.55 ± 0.19 | -61.75 ± 0.23 | 0.05 ± 0.001 |
| | 333.15 | 0.100 ± 0.005 | | -90.88 ± 0.25 | -223.13 ± 0.27 | -0.40 ± 0.002 |
| | 338.15 | 0.290 ± 0.02 | | -73.54 ± 0.21 | -350.73 ± 0.23 | -0.83 ± 0.001 |
| 0.11 | 293.15 | 0.890 ± 0.05 | 0.80 ± 0.03 | -50.11 ± 0.15 | 29.71 ± 0.18 | 0.27 ± 0.001 |
| | 298.15 | 0.650 ± 0.03 | | -45.69 ± 0.12 | 56.47 ± 0.16 | 0.34 ± 0.001 |
| | 303.15 | 0.460 ± 0.02 | | -51.56 ± 0.15 | 81.83 ± 0.18 | 0.44 ± 0.001 |
| | 308.45 | 0.260 ± 0.02 | | -61.20 ± 0.18 | 99.56 ± 0.21 | 0.52 ± 0.001 |
| | 313.15 | 0.230 ± 0.01 | | -52.89 ± 0.15 | 75.86 ± 0.18 | 0.41 ± 0.001 |
| | 318.15 | 0.130 ± 0.01 | | -51.85 ± 0.14 | 48.03 ± 0.17 | 0.31 ± 0.001 |
| | 323.15 | 0.090 ± 0.01 | | -75.85 ± 0.21 | 12.53 ± 0.24 | 0.27 ± 0.001 |
| | 328.15 | 0.145 ± 0.01 | | -63.58 ± 0.16 | -57.49 ± 0.21 | 0.02 ± 0.001 |
| | 333.15 | 0.170 ± 0.01 | | -62.05 ± 0.18 | -144.22 ± 0.21 | -0.25 ± 0.001 |

**Table 2:  Various Micellization (*cmc* and α_a) and Thermodynamic Parameters (ΔG°_mic, ΔH°_mic and ΔS°_mic) of Gemini Surfactant with Different Salt Mole Fraction (*x*) in Water at Different Temperatures**

| Salt | $x$ | $T$ | $cmc \cdot 10^6$ | $\alpha_a$ | $\Delta G^\circ_{mic}$ | $\Delta H^\circ_{mic}$ | $\Delta S^\circ_{mic}$ |
|---|---|---|---|---|---|---|---|
| | | K | mol·kg⁻¹ | | kJ·mol⁻¹ | kJ·mol⁻¹ | kJ·K⁻¹·mol⁻¹ |
| NaCl | 0.95 | 293.15 | 1.46 ± 0.07 | 0.78 ± 0.02 | -51.90 ± 0.12 | 26.69 ± 0.23 | 0.27 ± 0.001 |
| | | 303.15 | 0.79 ± 0.04 | | -63.76 ± 0.15 | 70.20 ± 0.27 | 0.44 ± 0.001 |
| | | 313.15 | 0.53 ± 0.03 | | -71.16 ± 0.17 | 57.48 ± 0.29 | 0.41 ± 0.002 |
| | | 323.15 | 0.36 ± 0.02 | | -70.92 ± 0.16 | -28.40 ± 0.29 | 0.13 ± 0.001 |
| | | 333.15 | 0.89 ± 0.05 | | -84.52 ± 0.21 | -231.17 ± 0.36 | -0.44 ± 0.002 |
| NaSal | 0.33 | 293.15 | 0.53 ± 0.03 | 0.59 ± 0.02 | -72.02 ± 0.18 | 12.44 ± 0.11 | 0.29 ± 0.001 |
| | | 298.15 | 0.43 ± 0.02 | | -68.52 ± 0.17 | 55.97 ± 0.10 | 0.42 ± 0.001 |
| | | 303.15 | 0.34 ± 0.02 | | -94.38 ± 0.23 | 107.62 ± 0.14 | 0.67 ± 0.001 |
| | | 308.15 | 0.25 ± 0.01 | | -118.30 ± 0.29 | 134.17 ± 0.17 | 0.82 ± 0.002 |
| | | 313.15 | 0.17 ± 0.01 | | -120.46 ± 0.28 | 96.55 ± 0.17 | 0.69 ± 0.001 |
| | | 318.15 | 0.13 ± 0.01 | | -121.95 ± 0.27 | 18.05 ± 0.17 | 0.44 ± 0.001 |
| | | 323.15 | 0.16 ± 0.01 | | -76.08 ± 0.18 | -65.01 ± 0.11 | 0.03 ± 0.001 |
| | | 328.15 | 0.28 ± 0.02 | | -74.02 ± 0.19 | -169.77 ± 0.11 | -0.29 ± 0.001 |
| | | 333.15 | 0.59 ± 0.03 | | -66.11 ± 0.17 | -282.37 ± 0.10 | -0.65 ± 0.001 |

factor predominates much at lower temperature [11]. However, in the presence of salt above factor influences only up to a lower temperature because hydration is partially taken care by countering binding. Beyond this, break down of the structure of water around the alkyl tail (*vide supra*) starts predominating the micellization process and responsible for the lower $T_m$. The data in Table **3** are in consonance with this fact.

**Table 3: Temperature of Minimum cmc ($T_m$) and cmc at Minimum ($cmc_m$) of Gemini Surfactant in Different System**

| Gemini | $T_m$ | $cmc_m \cdot 10^5$ |
|---|---|---|
| | K | mol·kg$^{-1}$ |
| Pure water | 326.0 ± 0.7 | 0.065 ± 0.003 |
| $\phi_{EG}$ = 0.11 | 325.0 ± 0.5 | 0.090 ± 0.005 |
| $x_{NaCl}$ = 0.95 | 321.0 ± 0.4 | 0.036 ± 0.002 |
| $x_{NaSal}$ = 0.33 | 318.5 ± 0.5 | 0.013 ± 0.001 |
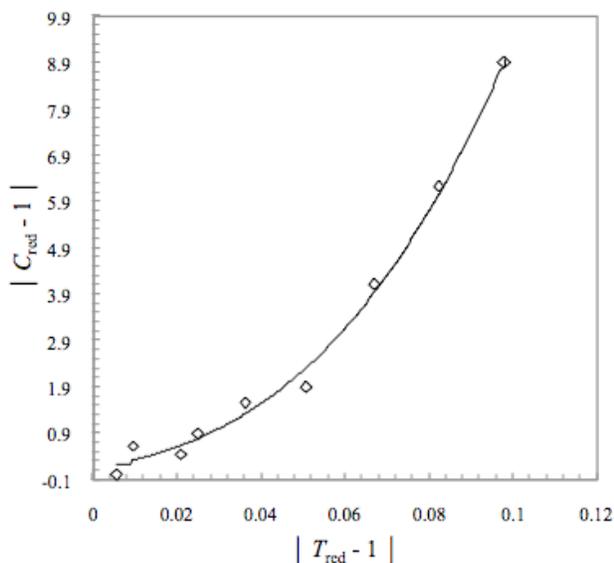


**Figure 2:** Reduced Variable Fit of cmc Data for the Gemini Surfactant in $\phi_{EG}$ = 0.11.

Temperature dependence of cmc can be fitted by a power law between reduced variables; where reduced variables are $C_{red} = C_{cmc} / cmc_m$ and $T_{red} = T / T_m$. $T_{red}$ and $C_{red}$ are related to each other by the relation;

$$(C_{red} - 1) = A (T_{red} - 1)^\gamma \tag{1}$$

Where, A is the constant and $\gamma$ is an exponent representing the nature of the surfactant system. Table **4** summarizes the results of the fitting of eq 1 from the cmc data of Tables **1** and **2**. The accuracy of the fit can be seen from the observance of experimental data on

the representative curve (Figure **2**) shown for 0.11 $\phi_{EG}$ (not shown for others). The Data in Table **4** indicate that the nature of the solvent has a significant effect on the value of A and $\gamma$ though the same surfactant was used each time. The value of $\gamma$ was derived from a logarithmic regression fit [10] and seems to be dependent on the nature of the additive. The data is not sufficient to comment more about the solvent effect (or additive effect) on fitting parameters ($\gamma$ and A). Different values of $\gamma$ were reported for various surfactant systems [15,39].

**Table 4: Exponent ($\gamma$) and Constant (A) of Gemini Surfactant in Different System**

| Gemini | $\gamma$ | A |
|---|---|---|
| Pure water | 3.19 ± 0.08 | 14.15 ± 0.32 |
| $\phi_{EG}$ = 0.11 | 2.55 ± 0.12 | 11.57 ± 0.46 |
| $x_{NaCl}$ = 0.95 | 1.03 ± 0.02 | 4.82 ± 0.29 |
| $x_{NaSal}$ = 0.33 | 0.62 ± 0.03 | 3.56 ± 0.15 |

## Thermodynamics of Micellization

As we mentioned earlier, micellization in surfactant solution is sensitive to temperature and therefore thermodynamic parameters have been calculated by the temperature dependence of the cmc values (Figure **1**). Two models are generally used to evaluate thermodynamic parameters; (1) phase separation model (pseudo-phase model) regards that micelles act as separate phase and assumes that monomer activity remains constant over the cmc and (2) mass action model (equilibrium model) regards micelle formation as an equilibrium condition in which the monomer activity continues to increase, although at a much reduced rate, above the cmc [40]. In our study, the phase separation model has been chosen to get thermodynamic energetics. For ionic gemini surfactants, the standard Gibbs free energy of micellization, $\Delta G°_{mic}$, can be written as [7],

$$\Delta G°_{mic} = 2RT (1.5 - \alpha_a) \ln X_{cmc} \tag{2}$$

Where, $R$, $T$ and $X_{cmc}$ are ideal gas constant, absolute temperature and cmc expressed in mole fraction unit, respectively.

The standard enthalpy change for micellization, $\Delta H°_{mic}$, can be calculated by using Gibbs-Helmholtz eq 3,

$$\Delta H°_{mic} = - 2RT^2 (1.5 - \alpha_a) (\partial \ln X_{cmc} / \partial T) \tag{3}$$
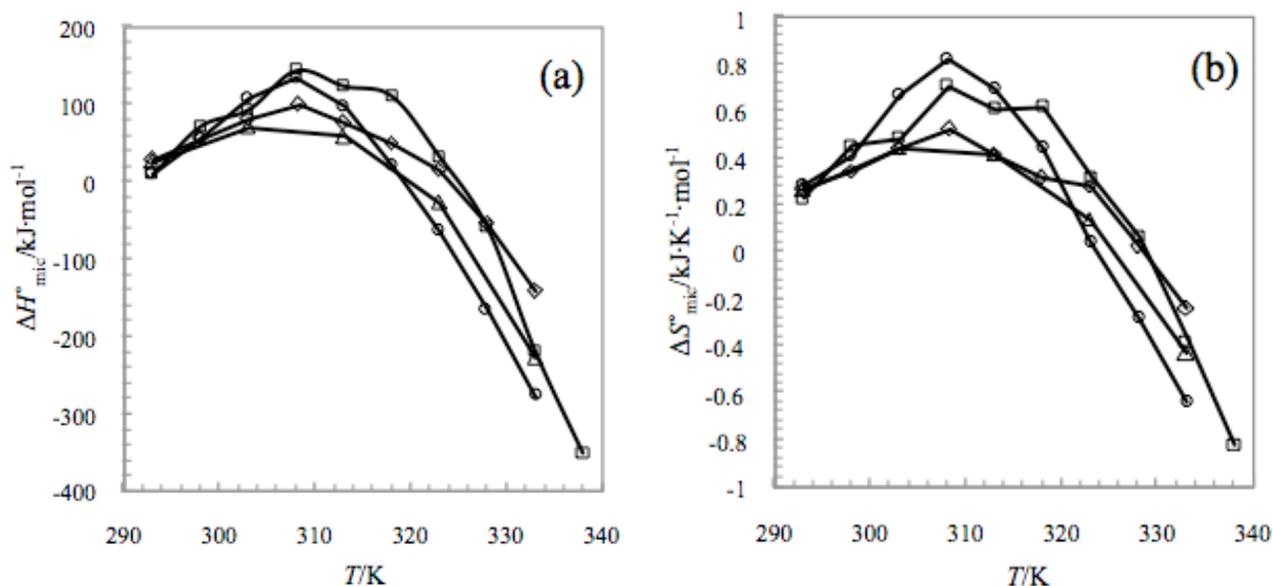
**Figure 3:** Thermodynamic Parameters (**a**) Standard Enthalpy ($\Delta H^{\circ}_{mic}$) and (**b**) Standard Entropy ($\Delta S^{\circ}_{mic}$) of Gemini Surfactant in; □, Pure Water; ◊, $\phi_{EG} = 0.11$; △, $x_{NaCl} = 0.95$; ○, $x_{NaSal} = 0.33$.

Since, $\Delta H^{\circ}_{mic}$ is not constant with respect to temperature; the values were obtained by using following polynomial equation [11,19]

$$\ln X_{cmc} = a + bT + cT^2 + dT^3 \qquad (4)$$

On differentiating eq 4, one can get the value of $\partial \ln X_{cmc} / \partial T$ as,

$$\partial \ln X_{cmc} / \partial T = b + 2cT + 3dT^2 \qquad (5)$$

The polynomial constants (a, b, c and d) are obtained by least square regression analyses. By substituting the value $\partial \ln X_{cmc} / \partial T$ in to eq 3, we get

$$\Delta H^{\circ}_{mic} = -2RT^2 (1.5 - \alpha_a)(b + 2cT + 3dT^2) \qquad (6)$$

Finally, the standard entropy of the micellization, $\Delta S^{\circ}_{mic}$, evaluated from the values of $\Delta H^{\circ}_{mic}$ and $\Delta G^{\circ}_{mic}$ as follows,

$$\Delta S^{\circ}_{mic} = (\Delta H^{\circ}_{mic} - \Delta G^{\circ}_{mic}) / T \qquad (7)$$

The results of $\Delta G^{\circ}_{mic}$, $\Delta H^{\circ}_{mic}$ and $\Delta S^{\circ}_{mic}$ obtained by the eqs 2, 3 and 7 are also summarized in Tables **1** and **2**. The data show that the micellization process is endothermic at low temperature ($\Delta H^{\circ}_{mic} > 0$) and become exothermic at higher temperature ($\Delta H^{\circ}_{mic} < 0$). However, $\Delta G^{\circ}_{mic} < 0$ which may be due to entropy effect, especially at low temperature. The value of negative enthalpy indicates that the London dispersion forces have a significant role in the micellization process at higher temperature. These forces are of predominant in nature and facilitating the micellization

[41]. The data of temperature dependence of $\Delta H^{\circ}_{mic}$ and $\Delta S^{\circ}_{mic}$ are plotted in Figures **3**.

In general, the compensation phenomenon between the $\Delta H^{\circ}_{mic}$ and $\Delta S^{\circ}_{mic}$ in the micellization process can be described in the form of a straight line equation (see Figure **4**) of the type
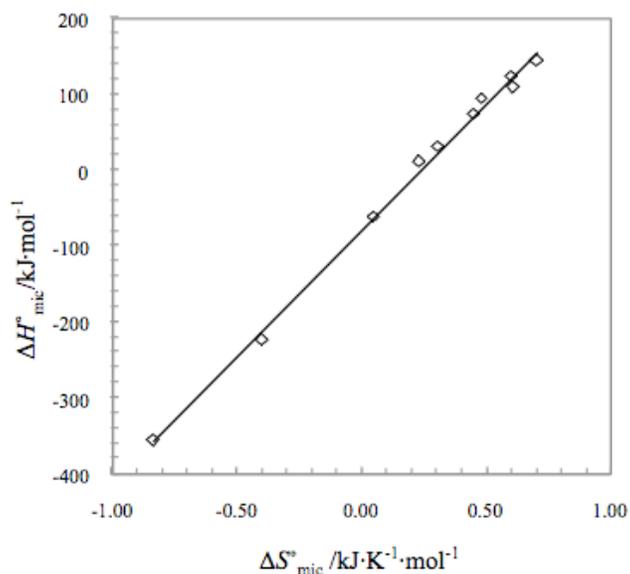


**Figure 4:** Plot of Standard Enthalpy ($\Delta H^{\circ}_{mic}$) *vs* Standard Entropy ($\Delta S^{\circ}_{mic}$) of Gemini Surfactant in Pure Water.

$$\Delta H^{\circ}_{mic} = T_c \Delta S^{\circ}_{mic} + \Delta H^{*}_{mic} \qquad (8)$$

The slope is the compensation temperature ($T_c$) and is a characteristic of solute-solute and solute – solvent interaction. $T_c$ can be considered as a measure of

**Table 5:** Correlation Coefficient (R), Compensation Temperature ($T_C$) and Intercept ($\Delta H^*_{mic}$) of Gemini Surfactant in Different System and Compare with Literature Data

| Gemini surfactants | Medium | R | $T_c$ | $\Delta H^*_{mic}$ | Ref. [c] |
|---|---|---|---|---|---|
| | | | K | kJ·mol$^{-1}$ | |
| Gemini | Aqueous | 0.996 | 332 ± 0.02 | -79.496 ± 0.05 | This work |
| Gemini | $\phi_{EG} = 0.11$ | 0.990 | 327 ± 0.04 | -62.858 ± 0.06 | This work |
| Gemini | $x_{NaCl} = 0.95$ | 0.996 | 343 ± 0.03 | -77.100 ± 0.05 | This work |
| Gemini | $x_{NaSal} = 0.33$ | 0.990 | 283 ± 0.04 | -86.258 ± 0.07 | This work |
| 12-2-12 | Aqueous | - | 293[b] | -34.780[b] | [29] |
| 12-4-12 | Aqueous | - | 290[b] | -32.090[b] | [29] |
| 12-5-12 | Aqueous | 0.999[a] | 306[b] | -67.670[a] | [24] |
| 14-2-14 | Aqueous | - | 304[b] | -40.400[b] | [29] |
| 14-4-14 | Aqueous | - | 296[b] | -36.090[b] | [29] |
| 14-5-14 | Aqueous | 0.976[a] | 288[b] | -73.350[a] | [21] |
| 14-5-14 | $\phi_{EG} = 0.11$ | 0.995[a] | 310[b] | -73.396[a] | [21] |
| 14-6-14 | Aqueous | 0.972[a] | 204[a] | -57.114[a] | [5, 22] |

[a]Compensation temperature and intercept, Correlation Coefficient calculated by using thermodynamic parameters of respective reference.
[b]Data used as such given in the reference.
[c]Data obtained from conductance measurements.

desolvation part of the micellization (dehydration of the hydrocarbon tail). The intercept, $\Delta H^*_{mic}$, characterizes the solute –solute interaction and can be considered as an index of the chemical part of the micellization (aggregation of hydrocarbon tails in to the micelle). Compensation plots were drawn with each type of solvent (water, water + EG, Water + NaCl or Water + NaSal) but a representative plot is given for pure water (Figure **4**). The $\Delta H^*_{mic}$ stands for the enthalpy effect when $\Delta S^\circ_{mic} = 0$. The decrease in $\Delta H^*_{mic}$ corresponds to micelle of higher stability. With NaSal, the value of $\Delta H^*_{mic}$ is found much lower than the reported literature values (Table **5**). In other words, the effect of chemical part of the process in micellization predominates in presence of the salt (especially for NaSal). The data in Table **5** suggest that $T_c$ values in our systems are comparatively higher than the conventional gemini surfactants with polymethylene spacers. Further, $T_c$ values are reported higher for non-ionic surfactants than their ionic counterparts [11]. This can be understood in the light of the fact that the hydration natures of the head groups are different in two classes of surfactant. It is interesting to note in our case that the $T_c$ value matches with the values of non-ionic surfactants though gemini is ionic. This may be due to the presence of additional hydrophilicity in the spacer chain of the gemini surfactant to that of head group itself (Scheme **1**).

## CONCLUSIONS

The micellization behavior of gemini surfactant has been examined under various solvent conditions (water, 0.11 $\phi_{EG}$, 0.95 $x_{NaCl}$ or 0.33 $x_{NaSal}$) at different temperatures. The cmc value decreases up to a certain value of temperature ($T_m$) for all the systems. However, the decrease was more pronounced with higher binding counterion (Sal$^-$). Temperature dependence of cmc can be fitted by a power law. The enthalpy of micellization ($\Delta H^*_{mic}$) passes through zero in all the systems which ascribed to the balance between enthalpy and entropy of the process coming from the hydrophobic effect. The compensation temperature, $T_c$, was found similar to non-ionic surfactants which ascribes the higher hydration of the present cationic gemini surfactant. $\Delta H^*_{mic}$ values indicate that the micelle forms are more stable [11].

## ACKNOWLEDGEMENT

## APPENDIX

$T_m$ = Temperature of minimum cmc (Temperature minima)

$cmc_m$ = cmc at minimum temperature (cmc minima)

$T_c$ = Compensation Temperature

cmc = Critical micelle concentration

$\alpha_a$ = Average degree of dissociation

$\Delta G^\circ_{mic}$ = Standard Gibbs free energy of micellization

$\Delta H^\circ_{mic}$ = Standard enthalpy of micellization

$\Delta S^\circ_{mic}$ = Standard entropy of micellization

$\phi_{EG}$ = mass fraction of ethylene glycol

$x_{NaCl}$ = mole fraction of sodium chloride

$x_{NaSal}$ = mole fraction of sodium salicylate

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