Thermodynamic Micellization of Cationic-Nonionic Surfactants in Aqueous Solution Using Conductivity and Surface Tension Measurements

Inaam H. Ali1*, Sameer H. Kareem2, Fouad A.A. AL-Saady3

Abstract

In the current work, we discuss the mixed micelles and thermodynamic micellization of aqueous binary mixture of polyoxyethylene - 20 sorbitan-monododecanoate (Tween 20) as nonionic surfactant and Benzylidimethylhexadecyl ammonium chloride (HDBAC) as cationic surfactant using conductivity and surface tension (γ) estimations in the temperatures range (288 -318K). Critical micelle concentration (CMC) and variables of micellization, like the standard thermodynamic functions: Gibbs free energy (ΔG°m), enthalpy (ΔH°m) and entropy (ΔS°m) were calculated using the variation of conductivity and γ with molar concentration and the variation of lnXm with temperature. The experimental CMC values were applied to calculate the mole fractions of surfactant in the mixed micelle (X1m), the β parameter and the coefficient of activity f1 and f2 using the equations proposed by Clint and Rubingh, which indicate the β parameter, is always negative. In addition, the results of thermodynamic parameters show that ΔG°m are negative for both individual and mixture of HDBAC-Tween20 surfactants and the values negatively increased with increasing temperature while its negative values decreasing with decreasing initial mole fraction of HDBAC.

Key Words: Thermodynamic Micellization, Tween 20, HDBAC, Conductivity Measurement.

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Introduction

The researches on surface properties of the mixed surfactants system were thoroughly performed and its application is still growing widely and applied in field of dispersion, moistening, emulsification, and different orientations [Bunton, 1991]. These mixtures often have lower CMC (critical micelle concentration), have better solubility, improved surface activity and improved rheology [Lan, 2007]. Micelles may be viewed as a separate step within a surfactant solution and their physical and chemical properties change dramatically depending on the concentration of surfactant. These properties can be measured as a function of the concentration of surfactant concentration from sharp inconsistency in the profile which leads to determine the CMC of the surfactant. Various techniques attempts were applied to determine the CMC values of different surfactant systems, like tensiometry [Fainerman, 2009; Inaam, 2019; Fouad, 2020], conductometry study [Akhtar, 2006; Pornpen, 2009; Zarganian, 2011], fluorescence techniques [Kabir, 2010], calorimetric study [Chakraborty, 2007], light scattering [Mohamed, 2015], etc. The micelle behaviors and associated thermodynamics of the different surfactants are depend on their compositions and the temperature paly important role on self-assembled structures in solutions such as micellar composition and aggregation number formation in aqueous media.

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There are many attempts to examine the surface properties, mole fractions of the mixed components containing cationic-nonionic surfactant [Rub, 2016; Sanjeev, 2012; Azum, 2013; Bagheri, 2017], which have been studied using a variety of theories like Clint [Clint, 1975] Motomura, [Motomura, 1984] Rosen [Rosen, 1993] Rubingh, [Rubingh, 1979]. These approaches suggest that the electrostatic interactions between cationic amphiphilic surfactant and the nonionic one lead to nonideality of the surfactant mixtures. Also, it predicts type of interactions in air – water interface and micelle between various compositions of surfactant which may be included many interactions such as: electrostatic; steric; van der Waals, and hydrogen bonding among surfactant molecules [Hadgivanov, 2009].

In this study, thermodynamic functions and parameters were estimated from the interfacial interaction of binary mixture of the surfactant Tween 20 (polyoxyethylene - 20 sorbitan-monododecanoate with 12 Carbon atoms) and Benzyldimethylhexadecylammonium chloride (HDBAC) using both surface tension and conductivity measurements.

**Experimental**

**Materials**

Tween 20 was purchased from Sigma Chemical Co., Benzyldimethylhexadecylammonium chloride (HDBAC) purchased from (BDH) Chemicals Ltd. Both the individual and mixtures of HDBAC-Tween20 solutions are made using deionized water (2-3 μS cm⁻¹). Before measuring conductivity and γ, the prepared solution were kept for about 30 minutes to attain equilibrium at certain temperature. Surfactant solution with different concentration and percentage of mixture were prepared by diluting certain amounts of stock solution in 50 ml volumetric flask with fresh distilled water.

**Surface Tension Measurements**

Du Nouys platinum ring on S.E.O. Co. Ltd, tension meter (Korea) was used to measure γ. This ring was cleaned before each measurement and the results were the average of three measurements. The CMC values were estimated from drawing a graph of surface tension against log C and were extrapolated from the break point of after and before micelle areas.

**Conductivity Measurements**

Electrical conductance measurements at four temperatures (288K, 298K, 308K and 318K) were carried with the help of conductometer type (Cyber Scan 350) from Eutech Instruments equipped with platinum electrode which was washed with deionized water after each reading, the accuracy of conductivity measurements was 0.5%. The conductometer cell was calibrated initially with standard potassium chloride solutions.

**Results and Discussion**

**Conductivity and Surface Tension Results**

The conductivity and γ measurements are useful techniques for studying association behavior of many combined systems. The specific conductance and γ for individual and mixtures of HDBAC - Tween20 were established at four different temperatures (288K, 298K, 308K and 318K). Figure 1 represents the relation between conductivity measurements and concentration of pure HDBAC and different mole fraction of binary mixture HDBAC-Tween20 at 298K while figure 2 shows the relation between γ and concentration of pure Tween 20.

From crossing point of the two above and below straightforward lines, CMC values can be estimated, and show from the figure, the CMC of HDBAC (4×10^{-4} mol/L) was drop to around 1×10^{-4} mol/L for different mole ratio of mixture. The magnitude of CMC for single and different mole ratio of mixture at four temperature (288K-318K) was tabulated in Table (1) revealing increasing in the magnitude of CMC with decreasing in the initial mole ratio of HDBAC and also the CMC increasing as the temperature increased. This rise in temperature makes it difficult to form the micelles, owing to the greatly increased hydration of the ion. This may be making the electrostatic interaction of micellization weak [Li, 2017].

**Mixed Micelles Formation**

In the mixture of two surfactants, two critical micelle concentrations were existing, one is the ideal value (CMC_{ideal}), which is predicted if no interaction between the components was present, and the other is real value (CMC_{Exp}) which depends on the form of interactions between the components. For non-

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**Table 1.** Values of CMC for individual HDBAC and different molar ratio of binary mixture of (HDBAC + Tween20)

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>CMC (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDBAC</td>
<td>0.00038</td>
</tr>
<tr>
<td>0.9 HDBAC</td>
<td>0.000087</td>
</tr>
<tr>
<td>0.7 HDBAC</td>
<td>0.000093</td>
</tr>
<tr>
<td>0.5 HDBAC</td>
<td>0.000103</td>
</tr>
<tr>
<td>0.3 HDBAC</td>
<td>0.000126</td>
</tr>
<tr>
<td>0.1 HDBAC</td>
<td>0.000143</td>
</tr>
<tr>
<td>Tween20</td>
<td>0.000176</td>
</tr>
</tbody>
</table>

---

**Figure 1.** Conductivity measurement against concentration of different mole fraction for HDBAC and Tween 20 at 298K

**Figure 2.** Surface tension measurements against [Tween 20] at 298K

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interacting mixed system the ideal critical micelle concentrations can be predicted using Clint model:

\[
\frac{1}{\text{CMC}_{\text{ideal}}} = \frac{\alpha_1}{\text{CMC}_1} + \frac{(1-\alpha_1)}{\text{CMC}_2}
\]  

(CMC) \_1 and CMC \_2 are CMC values of the two pure surfactants; \(\alpha_1\) is Tween 20 mole ratio. CMC \_exp values of HDBAC and its mixtures at various initial mole fractions were calculated using conductivity measurements while CMC values for Tween 20 was extracted using surface tension measurements. The results show negative deviation from ideality where the CMC \_exp values is lower than CMC \_ideal calculated as in Fig 3, indicating that a mutual attractive interaction exists in micellization process of HDBAC - Tween 20 surfactants mixture. This is owing to the existence of cationic head groups in conjunction with bulky nonionic surfactant, which reduce the Columbic repulsion forces among them [Malik, 2019].

The Rubingh model is insolvable up to \(\alpha_1 = 0.3\) due to the large divergence in CMC magnitude of the two surfactants (13). From the data of table (2) one can prove that the micellar composition \(X_1^m\) rises with the mole fraction of Tween 20 increase from 0.1 to 0.3 indicating the enrichments in HDBAC molecules. This is owing to the higher hydrophobicity of Tween 20 nonionic surfactant than the cationic surfactant HDBAC and the contribution of the Tween 20 surfactant to the micelle formation is significant contrast to the cationic surfactant HDBAC. Positive (anti synergism) and negative (synergism) values of \(\beta\) were used to demonstrate mixed micelle formation, whereas a value close to zero corresponded to ideal action [Azum,2017; Rub,2017]. For all mole ratio studied, the values of \(\beta\) are negative meaning the interactions between HDBAC and Tween 20 in the micelle phase are more attractive than the interactions take place between the single surfactants. Also, the negative value of \(\beta\) for the mixed surfactants system reduces by growing the mole ratio of Tween 20 and this may inform about strong synergism in the forming of mixed micelles [Soheila, 2008; Renu, 2014]. The activity coefficients \(f_1\) and \(f_2\) which were obtained using the following equations, are the most powerful parameters for describing the degree of interaction between any surfactants present in the mixed micelles. The results of activity coefficients are given in table (2).

\[
f_1 = \exp (\beta (1 - X_1^m)^2)
\]  

\[
f_2 = \exp (\beta X_1^m)^2
\]  

\(f_1\) and \(f_2\) are substituted in equation (6) to estimate \(\Delta G_{ex}\) the excess Gibbs free energy of mixing) [Motomura, 1993], the results are given in table (2):

\[
\Delta G_{ex} = [X_1 \ln f_1 + (1-X_1)\ln f_2]RT
\]
The magnitude of activity coefficients, $f_1$ and $f_2$ obtained are $< 1$ which mean the non-ideal manner of the studied binary systems except for $\alpha_1$ system which shows a value greater than unity [Patel, 2015]. The table also shows the estimated $\Delta G_{\text{ex}}$ values are less than 0 which indicate that the micelles of mixed surfactants studied are more stable than the micelles of HDBAC and Tween 20 in individual forms and the maximum value are observed in case of $\alpha_1 = 0.3$ system at 298 K.

**Micellization Thermodynamic Functions**

As the CMC is temperature dependence, various thermodynamics parameters can be gained from the temperature dependent of surfactants CMC, such as, standard Gibbs free energy of micellization, $\Delta G^\circ_m$, enthalpy of micellization, $\Delta H^\circ_m$ and entropy of micellization, $\Delta S^\circ_m$. These functions help us understand the surfactant behavior and the related importance of the hydrophobic interactions, the contact of water-surfactant and the repulsion of head-group. The $\Delta G^\circ_m$ was calculated according to the following equation:

$$\Delta G^\circ_m = (2 - \alpha)RT \ln \chi_{\text{CMC}}$$  \hspace{1cm} (7)

Where $R$, $T$ and $\chi_{\text{CMC}}$ are gas constant, temperature and CMC in mole fraction. Also, $\Delta H^\circ_m$ was obtained by:

$$\Delta H^\circ_m = -(2 - \alpha)RT^2 \left( \frac{\partial \ln \chi_{\text{CMC}}}{\partial T} \right)$$  \hspace{1cm} (8)

Where $\left( \frac{\partial \ln \chi_{\text{CMC}}}{\partial T} \right)$ was estimated from the plot slope of $\ln \chi_{\text{CMC}}$ against $T$.

$\Delta S^\circ_m$ was determined from the next relation between free energy of micellization and the enthalpy of micellization:

$$\Delta S^\circ_m = \frac{\Delta H^\circ_m - \Delta G^\circ_m}{T}$$  \hspace{1cm} (9)

Table 3. Thermodynamic parameters for individual and different mole fraction of HDBAC-Tween20 surfactants mixture

<table>
<thead>
<tr>
<th>Thermodynamic parameters</th>
<th>Surfactant mole fraction</th>
<th>Temp./ K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HDBAC 0.9 HDBAC 0.7 HDBAC 0.5 HDBAC 0.3 HDBAC 0.1 HDBAC</td>
<td></td>
</tr>
<tr>
<td>$\Delta G^\circ_m$ kJ/mole</td>
<td>-12.083 -10.401 -11.321 -10.752 -9.632 -7.532</td>
<td>288</td>
</tr>
<tr>
<td>$\Delta H^\circ_m$ kJ/mole</td>
<td>-5.403 -3.912 -2.786 -4.476 -3.882 -3.880</td>
<td></td>
</tr>
<tr>
<td>$\Delta H^\circ_m$ kJ/mole</td>
<td>-5.785 -4.189 -2.983 -4.793 -4.157 -4.155</td>
<td></td>
</tr>
<tr>
<td>$\Delta H^\circ_m$ kJ/mole</td>
<td>-6.180 -4.474 -3.186 -5.119 -4.440 -4.438</td>
<td></td>
</tr>
<tr>
<td>$\Delta G^\circ_m$ kJ/mole</td>
<td>-9.504 -4.726 -7.236 -3.627 -3.863 -4.274</td>
<td>318</td>
</tr>
<tr>
<td>$\Delta H^\circ_m$ kJ/mole</td>
<td>-6.588 -4.770 -3.396 -5.457 -4.733 -4.731</td>
<td></td>
</tr>
<tr>
<td>$\Delta S^\circ_m$ J/mole.K</td>
<td>20.440 11.336 12.711 6.052 4.811 0.198</td>
<td></td>
</tr>
</tbody>
</table>

The results of thermodynamic parameters were given in Table 3 which shows the $\Delta G^\circ_m$ values are negative for both single and mixture of HDBAC-Tween20 surfactants indicating the indicating the spontaneity of the micelle formation. Also, the values of $\Delta G^\circ_m$ become more negative with
increasing temperature for HDBAC and mixture, while its negative values decreasing with decreasing initial mole fraction of HDBAC. The results of Table 3 show the process of micellization of HDBAC and Tween 20 is spontaneous and there is decreasing in $\Delta G_m^o$ with rise in temperature which belongs to the desolvation of the hydrophilic groups of these surfactants [Wu, 2013].

The lowering of $\Delta G_m^o$ with lowering HDBAC mole ratio shows the forming of mixed micelles is decreased. This behavior can be owing to the electrostatic attractions among the charge of head groups so the mixed micelle became unstable [Ren, 2014].

The values of $\Delta H_m^o$ are negative and increased negatively with increasing in temperature, suggesting the forming of mixed micelle was more proper and micellization process of individual and mixture surfactants is exothermic.

The entropy of micellization $\Delta S_m^o$ for HDBAC and its mixtures with Tween 20 of all mole fraction ratios are positive, implying that entropy gain promotes the micellization process [Islam, 2003]. Also, the entropy of micellization values decrease with increasing temperature because of increased water structure in its presence as a result of intermolecular hydrogen bonding [Homendra, 2006].

Conclusions

In this work, we present a focused study on mixed micelles formation and thermodynamic of micellization parameters of dual mixture for cationic surfactant HDBAC and nonionic surfactant Tween 20. The values of CMC of mixtures rise with decreasing in the initial mole ratio of HDBAC, and with an increasing in temperature. The whole CMC<sub>Exp</sub> values are less than CMC<sub>ideal</sub> values which indicate the presence of attractive interactions resulting in a nonideal behavior. This result is confirmed by the negative values of $\beta$ parameter over the various mole ratios. This negative variation signals that there are many attractive interactions between the implying strong synergism in the formation of mixed micelles. $\Delta G_m^o$ values display the micellization of the studied mixtures are spontaneous. $\Delta G_m^e$ values obtained suggest that the micelles of studied mixtures are most stable than the micelles of HDBAC and Tween 20 in individual forms.

References

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