Micellar interaction and thermodynamic behavior between double-chained surface active ionic liquid and conventional surfactants in aqueous solution

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Abstract−The mixed micellar properties of double-chained surface active ionic liquid (1, 3-didecyl-2-methylimidazolium chloride or TEGO) with two conventional cationic surfactants, dodecyltrimethylammonium bromide (DOTAB) and cetyltrimethylammonium bromide (CTAB) were investigated by using surface tension and conductivity experiments in aqueous solution at 303.15 K. TEGO is a special surface active agent with two specific critical micelle concentrations (CMC). To consider the effect of hydrophobic groups in synergism between components (surfactant and TEGO) in the mixed micelle, two cationic surfactants were selected that differed only in the length of the hydrocarbon chain (DOTAB: C12 and CTAB: C16). The experimental critical micelle concentration (CMC_{exp}), degree of micellar dissociation (g), the ideal critical micelle concentration (CMC_{id}), micellar mole fractions (X_1^m and X_2^m) and the interaction parameter (β^m) were determined by using Rubingh's model. The achieved β^m of the studied system is negative in the whole compositions denoting the synergistic interaction between components and their values increase with increasing chain lengths of surfactant from DOTAB to CTAB. The activity coefficients (f_1^m and f_2^m) are always less than unity in all mole fractions signifying non-ideality in the mixtures. Thermodynamic functions for mixed systems were estimated. The standard Gibbs energy of micellization (ΔG_{mic}^0) associated with transfer of surfactant monomers from the bulk phase to micelle phase was evaluated according to Zana's model in different situations and discussed with logical points in the new approach. The results show that the effect of hydrophobicity can regulate the synergism between cationic surfactants in the same electrical charges of head groups.

Keywords: Critical Micelle Concentration, TEGO, Interaction Parameter, Counter Ion Binding, Mixed Micelle
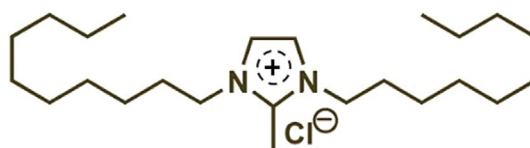
INTRODUCTION

Surface active agents (surfactants) are used in various applications, such as the petroleum industry (for enhanced oil recovery), food industry (as emulsifier; solubilizer, demulsifier, stabilizer and thickener), pharmaceuticals, agriculture, health and beauty products, and so on, where each product contains a blend of surface active agent (pure or mixed state) [1-6]. Surfactant mixtures with two or more surfactants often represent better performance than pure surfactants for industrial applications. The study of surfactant mixtures is useful from the environmental and economic viewpoints [7,8]. There is structural similarity (obviously) between conventional ionic surfactants and surface-active ionic liquid (SAIL), and hence, SAIL are also able to self-associate as micelles in aqueous media, like general ionic amphiphiles. The past two decades has seen much research on surface and micellar behaviors of imidazolium-based SAIL by different techniques such as fluorescence, interfacial tension, and conductometry [9-13]. The specific types of surface-active ionic liquid contain double hydrocarbon chains in their structures similar to gemini surfactants. This double-chained surface active ionic liquid (DSAIL), when properly designed, can show 2 or 3 orders of magnitude better interfacial activity and wetting properties than the similar ionic liquid with a single correspond-

ing long chain [9,14,15].

These new gemini ionic liquids have unique properties, such as higher thermal stability, lower CMC, and larger crystalline units than the homologous ionic liquid (IL) with a single hydrocarbon chain. Recently imidazolium-based ILs with structures resembling double-chain and bolaform surfactants have been investigated by different researchers who have reported good surface activity [17,18].

At the beginning of the 1990s, Metrohm Company began to commercialize its first ion selective electrode for concentration determination of anionic surfactants in household detergents by titration method. For this purpose, they introduced a new titrant called 1, 3-didecyl-2-methylimidazolium chloride from DSAIL class (with the brand name TEGOTrant A100) [19,20]. Scheme 1 shows the special structure of this compound (with the abbreviated name of TEGO).

This ionic liquid has a molecular framework intermediate between single-chained surfactant and a double-chained (or gemini) surfactant. For the first time comprehensively, the micellar behavior

Scheme 1. Molecular structure of 1, 3-didecyl-2-methylimidazolium chloride (TEGO).

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of 1, 3-didecyl-2-methylimidazolium chloride (TEGO) was studied by different techniques in aqueous media by González and coworkers. They reported that TEGO has two critical micelle concentrations (CMC's) in the concentration ranges 0.4-0.5 mM and 20-30 mM (depending on the probing method) with two different types of micelle [9].

Most of the surface active ILs (like TEGO) influence micellar and associative properties of surfactants in a way quite different from inorganic salts with formation of a network of three-dimensional hydrogen bond and hydrophobic-electrostatic interactions [21,22]. For this reason, when a surfactant is mixed with a ILs in an aqueous solution, its possible role as a secondary amphiphile should be investigated. Hence, these mixtures can be treated as typical binary surfactant systems in aqueous media, and the obtained CMC values for these mixtures were found to be highly dependent on the compositions of surfactant and IL [22,23].

In the present work, binary mixtures consisting of a special ionic liquid such as TEGO and two cationic surfactants with different hydrophobic tail (dodecyltrimethylammonium bromide (DOTAB) or cetyltrimethylammonium bromide (CTAB)) have been investigated by conductivity technique in aqueous solution. The goal in this study is to understand the effect of alkyl chain length of cationic surfactant on the mixed micelle formation and molecular interaction between components. In the literature survey, some studies are available on gemini surfactant-surfactant or SAIL-surfactant interactions *via* various techniques, but no considerable investigation has been designed to study the interaction between components similar to gemini ionic liquid (TEGO) and cationic surfactant in different mole ratios as new binary surfactant systems [24-27].

Different models based on thermodynamic equilibrium, such as Clint and Rubingh, were used to study the mixed micellization behavior between TEGO and cationic surfactants. In addition, various thermodynamic parameters of Gibbs free energy change as a function of component concentration were calculated and discussed in detail [28-31].

MATERIALS AND METHODS

1. Materials

1, 3-Didecyl-2-methylimidazolium chloride (TEGO) was purchased from Metrohm Company and used as received without further purification. Dodecyltrimethylammonium bromide (DOTAB), and cetyltrimethylammonium bromide (CTAB) were purchased from Merck Company. All the used materials with their chemical names, CAS number, molecular weight, purity and manufacturers are tabulated in Table 1.

2. Methods
2-1. Conductivity Measurements

The conductivity experiments were carried out with a digital conductivity meter (model C860, Consort, Belgium) and a dip-cell with a platinum electrode (cell constant=1.01 cm^{-1}). Before measurement, the conductometer probe was calibrated with potassium chloride (KCl) solutions of appropriate concentration range. A stock solution of surfactant was successively added to a known volume of water in a thermostat container using a micropipette and the conductivity of the solutions was measured after thorough mixing and thermal equilibration. Accuracy of measured conductivity was within ±0.5 μS·cm^{-1}. All the experiments were done at 303.15 K ±0.1 K. The temperature in all the experiments was controlled by circulating water through the outer jacket from a thermostat (EYELA NTT-1100, Japan).

2-2. Surface Tension Measurements

The surface tension of aqueous solutions of TEGO at different concentrations was measured with a du Nuoy ring tensiometer (KSV Sigma 701 tensiometer). The Platinum/Iridium ring was thoroughly cleaned and flamed before each experiment. Each measurement was repeated at least seven times until good reproducibility was obtained. In this method, the maximum force needed to pull the ring from the liquid interface was expressed as the surface tension of the solution in the static state. The maximum uncertainty of surface tension measurements is less than ±0.1 mN·m^{-1}.

RESULTS AND DISCUSSION

1. Micellar Properties of TEGO as Special Case

Several experimental methods can be used to estimate the micellar properties of surfactants. Measurement of conductance is broadly used to determine the CMC, aggregation number and the counterion dissociation degree of ionic micelles [12]. Conductivity measurements of TEGO in aqueous media are shown in Figs. 1-2, where the specific conductivity (κ) is plotted against the TEGO concentration.

This analysis was performed in two ranges of concentration: 0-3.29 mM and 0-52 mM. The obtained results show that TEGO produced two CMC values (one in the low concentration range, $CMC_1=$ 0.74 mM, and one in the high concentration range, $CMC_1=20.45$ mM). In the paper survey, one can obtain many examples that two critical micellar concentrations reported for amphiphiles in aqueous solution [32-34]. Surfactant molecules generally form spherical micelles at first CMC, but when surfactant concentration increases to a greater extent, the micelles are deformed and converted to other forms such as cylindrical micelle, disk- and lamellar-like micelles. This behavior of TEGO, was previously reported by Figueira-Gon-

Table 1. Source and purity of the used chemicals in this work

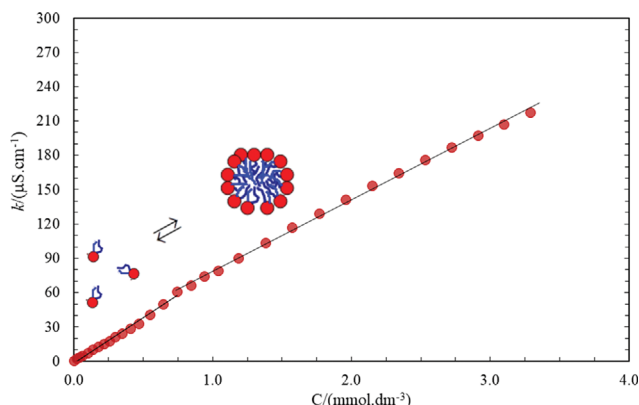| Compound	CAS number	Source	Molecular weight (g·mol^{-1})	Mass fraction purity
1, 3-Didecyl-2-methylimidazolium chloride (TEGO)	70862-65-6	Metrohom (Switzerland)	399.10	≥0.99
Dodecyltrimethylammonium bromide (DOTAB)	1119-94-4	Merck (Germany)	308.34	0.98
Cetyltrimethylammonium bromide (CTAB)	57-09-0	Merck (Germany)	364.45	≥0.98

Fig. 1. The plot of specific conductivity versus concentration of TEGO at 303.15 K: range of TEGO concentrations between 0 and 3.29 mM. The structural transition from a individual monomers to spherical micelles is shown for TEGO as an inset cartoon.
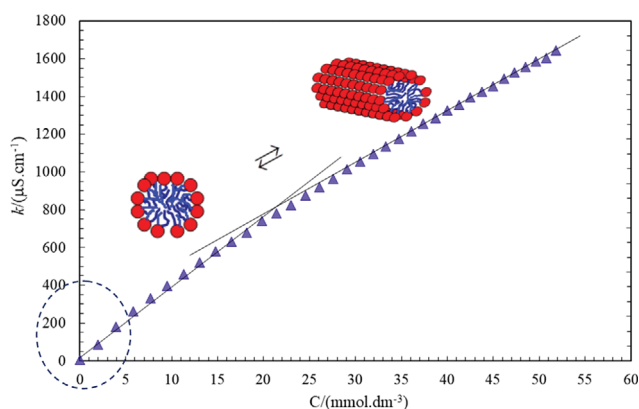

Fig. 2. The plot of specific conductivity versus concentration of TEGO at 303.15 K: range of TEGO concentrations between 0 and 52 mM. The structural transition from a spherical micelle to cylindrical ones is shown for TEGO as an inset cartoon.

zalez et al. with different techniques. They suggested that CMC_1 corresponds to the normal micelle with spherical structures, and CMC_2 typically demonstrates the transition from spherical to rod-like micelles (with cylindrical structures) [9].

Structural transitions in aggregate forms lead to changes in the slope of the plot of k against C. In the studied system, the conversion from TEGO monomers to spherical micelles happens at CMC_1 and can be seen in Fig. 1. The increase of electrical conductivity (k) in the pre-micellar zone is due to the presence of free counterions and TEGO monomers in the bulk solution. After micelle formation, the mobility of Cl^- decreases significantly in solution (due to counterion binding onto the micelles) and then the slope of the line (k-C) becomes less than before micellization. Inside Fig. 2, the region is shown as a dashed circle, which is plotted in Fig. 1 for comparison between two states.

Also, the formation of spherical micelle from individual monomers and cylindrical micelle from spherical micelle is shown as inset cartoons in Fig. 1 and Fig. 2, respectively. Cylindrical micelles
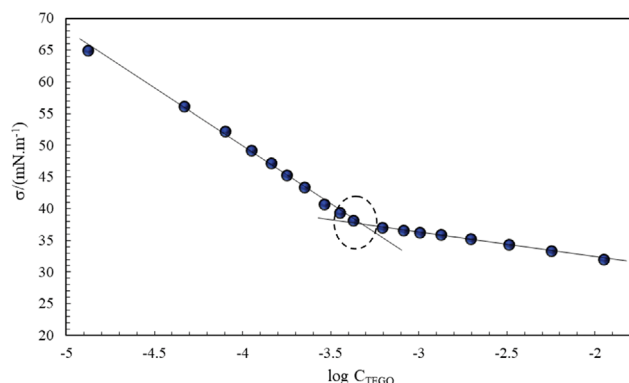

Fig. 3. Surface tension (σ) versus logarithmic concentration of TEGO (log[C_{TEGO}]) in range of TEGO concentrations between 0 and 11.2 mM.at 303.15 K.

appear in higher concentrations of the CMC_2 (20.45 mM), and this change in the micellar shape is related to the change in the slope of the k versus C in the solution.

To confirm our results obtained from conductivity data in the first point (CMC_1), a surface tension experiment was performed in the concentration range of 0-11.2 mM of aqueous solutions of TEGO.

Fig. 3 shows the results (the measurement values of the surface tension data as a function of $\log C_{TEGO}$). The break point in the plot, shown by a dashed circle, appears at 0.53 mM. This value is close to that observed from the conductometry method and ascribed to first CMC (or CMC_1) in this compound.

But, the CMC_1 value from conductivity data at 303.15 K is slightly higher in comparison to that gained from the surface tension method, due to the presence of non-surface-active material in premicellar associates of TEGO aqueous solutions [35,36].

Several interface parameters in the first point were calculated. Surface pressure at CMC_1 (Π_{CMC_1}) demonstrates the ability of decreasing surface tension by surfactant molecules in CMC_1. It can be calculated following Eq. (1) [1,27]:

$$\Pi_{CMC_1} = \sigma_0 - \sigma_{CMC_1} \tag{1}$$

where σ_0 is surface tension of pure water and σ_{CMC_1} is the surface tension of surfactant solution at CMC_1 point. The higher value of Π_{CMC_1} (≈ 34.5 mN·m^{-1}) in aqueous TEGO solution indicates greater ability to decrease surface tension in comparison to ordinary surfactants with one hydrocarbon chain.

The maximum coverage of the liquid -air interface by surfactant molecules can be calculated by the Gibbs surface excess at the CMC_1 point (Γ_{max}) which can be calculated from Eq. (2) [1,37,38]:

$$\Gamma_{max} = \frac{-1}{2.303nRT} \left(\frac{d\sigma}{d\log(C)} \right) \tag{2}$$

where R is the universal gas constant (8.314 J·mol^{-1}·K^{-1}), T is the absolute temperature in kelvin. The term of $\left(\dfrac{d\sigma}{d\log(C)} \right)$ is the maximum slope obtained of tangent of plot of σ against log[C] in the premicellar region, and n is the number of both positive and negative ions formed in solution per TEGO compound. Here, n is equal to 2.

Table 2. Surface properties of TEGO (or [C$_{10}$C$_{10}$mim]Cl) and [C$_{10}$mim]Cl

Amphiphile	σ_{CMC} (mN·m^{-1})	Π_{CMC_1} (mN·m^{-1})	pC$_{20}$	CMC$_1$/C$_{20}$	Γ_{max} (mmol·m^{-2})	A$_{min}$ (Å^2)
TEGO	37.5	34.5	2.43	0.15	3.81	43.6
[C$_{10}$mim]Br[a]	39.7	33.3	2.15	4.14	1.72	97

[a]Reported in Ref. [36]

The apparent minimum surface area occupied by each TEGO surfactant (A$_{min}$) at air-water surface can be calculated from this equation [1,37,38]:

$$A_{min} = \frac{10^{20}}{N_A \Gamma_{max}} \; (\text{Å}^2) \tag{3}$$

where N$_A$ is Avogadro's number.

pC$_{20}$ is surface parameter which is often used to evaluate the efficiency of surfactant adsorption at air-water surface, and Π_{CMC_1} is other surface parameter which indicates effectiveness of surface tension reduction at CMC. pC$_{20}$ is determined by using the Eq. (4) [1]:

$$pC_{20} = -\log(C_{20}) \tag{4}$$

where C$_{20}$ shows the bulk amphiphilic concentration needed to decrease the surface tension of pure solvent by 20 mN·m^{-1}.

The values of σ_{CMC_1}, Π_{CMC_1}, pC$_{20}$, Γ_{max} and A$_{min}$ for TEGO are listed in Table 2 and these values were compared with those reported in the literature for conventional IL with same head group but with one alkyl chain (C$_{10}$) like 1-decyl-3-methylimidazolium bromide ([C$_{10}$mim]Br).

The σ_{CMC_1} value is smaller for TEGO suggesting stronger hydrophobic interactions for TEGO as compared to [C$_{10}$mim]Br.

Moreover, the larger value of pC$_{20}$ for TEGO shows the better performance of these molecules at water-air surface, and also shows that the surface tension value was reduced more efficiently with increasing hydrophobic chain from [C$_{10}$mim]Br to TEGO in pure system. The higher value of Π_{CMC_1} with increasing the number of hydrocarbon chains represents the greater effectiveness of the TEGO in surface and greater tendency of these molecules to migrate from bulk solution to the surface.

The values of Γ_{max} are 3.81 and 1.72 µmol·m^2 for TEGO in CMC$_1$ and [C$_{10}$mim]Br, respectively. Although in many cases the size of the polar head group is the predominant determinant for calculating the value of Γ_{max} [36], but in the same hydrophilic head groups of the compounds (TEGO and [C$_{10}$mim]Br), the hydrophobic interaction is a key factor and increases with the enhancement of the number of hydrocarbon chains. As a result, the IL molecules with two hydrophobic tails (i.e., TEGO) are easier to obtain better surface coverage, a larger Γ_{max} and a smaller A$_{min}$ than [C$_{10}$mim]Br molecules.

2. Interaction between the TEGO-surfactant Pairs

The specific conductance (k) of surfactant(1) and TEGO(2) mixtures determined at 303.15 K as a function of the total concentration, C$_{tot}$, are plotted in Figs. 4 and 5, typically. The k value increases with enhancing the surfactant concentration in mixtures. As can been seen from Figs. 4 and 5, these systems have a clear breakpoint
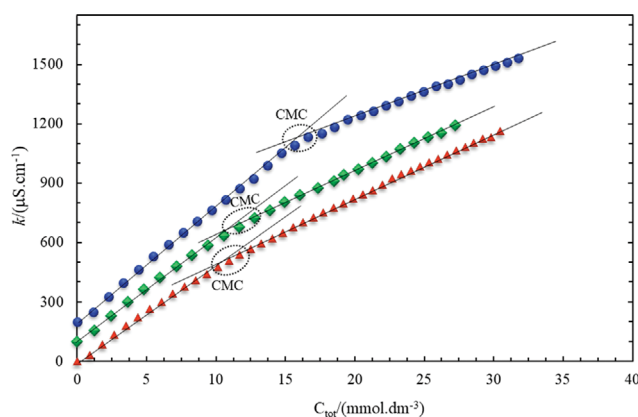

Fig. 4. Relationship between k and total concentration of DOTAB+ TEGO at various mole fractions of DOTAB (y$_1$) at 303.15 K: (▲) y$_1$=0.4474, (◆) y$_1$=0.6530 and (●) y$_1$=0.8773. The plots with signs (◆) and (●) have been moved by 100 and 200 scale units (mS·cm^{-1}), respectively.
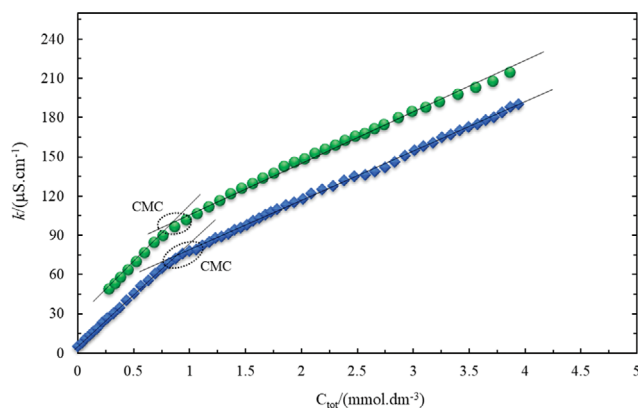

Fig. 5 Relationship between k and total concentration of CTAB+ TEGO at various mole fractions of CTAB (y$_1$) at 303.15 K: (●) y$_1$=0.7005 and (●) y$_1$=0.9013.

between the two slopes of the curve, and this point (i.e., CMC) can be determined by the intersection of two linear parts of the k vs. C$_{tot}$ plot.

The experimental CMC values of the mixed systems (CMC$_{mix}$) for DOTAB/TEGO and CTAB/TEGO are tabulated in Table 3.

Also, the CMC of the individual DOTAB was obtained 16.01 mM; that is not far from earlier results [39,40], and the CMC of the individual CTAB was evaluated as 0.972 mM at 303.15 K, which agrees with the previously reported of CMC for CTAB surfactant [39].

Table 3 The values of experimental critical micelle concentration and ideal critical micelle concentration (CMC_{mix}^{exp} and CMC_{mix}^{id}) from the conductivity measurements, the micellar mole fractions of component 1 (X_1^m), interaction parameter (β^m), activity coefficients (f_1^m and f_2^m) according to Rubingh and the degree of micellar dissociation (g) for surfactant(1)/TEGO(2) mixed systems in aqueous solutions at various mole fraction (y_1) at 303.15 K[a]

y_1	CMC_{mix}^{exp} (mM)	CMC_{mix}^{id} (mM)	g	X_1^m	β^m	f_1^m	f_2^m
			DOTAB(1)/TEGO(2)				
0.1273	16.71	19.75	0.83	0.2421	−1.04	0.5491	0.9407
0.2105	14.72	19.32	0.863	0.3393	−1.28	0.5708	0.8625
0.3496	11.43	18.64	0.81	0.4526	−1.98	0.5518	0.6660
0.4474	10.21	18.19	0.68	0.5036	−2.30	0.5669	0.5576
0.5489	10.39	17.74	0.70	0.5526	−2.19	0.6450	0.5123
0.6530	10.76	17.31	0.61	0.6065	−2.09	0.7241	0.4644
0.7649	11.58	16.86	0.49	0.6771	−1.93	0.8176	0.4125
0.8773	16.03	16.44	0.40	0.8821	−0.27	0.9962	0.8097
			CTAB(1)/TEGO(2)				
0.2998	1.05	2.92	0.74	0.6454	−5.50	0.5007	0.1011
0.7005	0.94	1.36	0.55	0.7989	−4.20	0.8437	0.0685
0.8011	0.90	1.20	0.46	0.8329	−4.24	0.8887	0.0528
0.9013	0.86	1.07	0.47	0.8673	−4.57	0.9224	0.0317

[a]Relative standard uncertainties (u_r) limits is u_r (CMC)=±2.5%, Relative standard uncertainties (u_r) are, u_r (X_1^m)≈±3% and u_r (β)≈±4% and u_r (f_1^m, f_2^m)≈±4%

The ideal or non-ideal behavior of surfactant mixtures by considering mutual interactions can be evaluated in terms of Clint's model [30,41,42]:

$$CMC_{mix}^{id} = \frac{CMC_1 CMC_2}{y_1 CMC_2 + (1-y_1) CMC_1} \quad (5)$$

where CMC_1, CMC_2, and CMC_{mix}^{id} are the critical micellar concentrations of surfactant 1 (DOTAB or CTAB), amphiphile 2 (TEGO in the second CMC), and the mixed system of compounds 1 and 2 in the ideal condition, respectively, and y_1 is stoichiometric mole fraction of amphiphile 1 in the bulk mixture.

The difference between CMC's ($\Delta(CMC_{mix})=(CMC_{mix}^{id}-CMC_{mix}^{exp})$ ≠0), positive or negative deviation, proposes attractive interaction ($\Delta(CMC_{mix})>0$) or repulsive interaction ($\Delta(CMC_{mix})<0$) in the mixed micelle, which can be due to the intermolecular interaction between the surfactant pairs. As can been seen in Table 3, the experimental CMC values (CMC_{mix}^{exp}) are less than those calculated by the client theory (CMC_{mix}^{id}). So, the systems show nonideal effects with attractive interactions among the surfactants at the mixed micelles [3].

Rubingh's model (according to the regular solution theory (RST)) was used to determine the composition of components at mixed micelle (X_1^m) along with the interaction parameter (β^m) at the mixed micelle through the following fundamental relationships [28,29]:

$$(X_1^m)^2 \ln\left(\frac{y_1 CMC_{mix}^{exp}}{(X_1^m)CMC_1}\right) = (1-X_1^m)^2 \ln\left(\frac{(1-y_1)CMC_{mix}^{exp}}{(1-X_1^m)CMC_2}\right) \quad (6)$$

$$\beta^m = \frac{1}{(1-X_1^m)^2} \ln \frac{y_1 CMC_{mix}^{exp}}{(X_1^m)CMC_1} \quad (7)$$

where X_1^m is the micellar mole fraction of component 1 in the mixed micelle, y_1 is its bulk mole fraction. Eq. (6) is repeatedly solved to
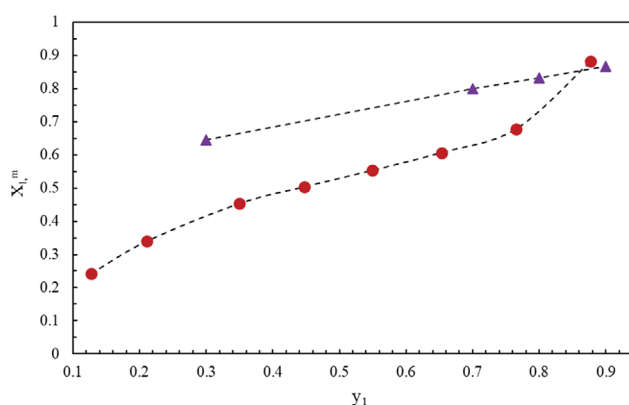

Fig. 6. Variation of the micellar mole fraction (X_1^m) with the stoichiometric mole fraction of surfactant (y_1) in the mixtures of surfactant(1)/TEGO(2). The symbols indicate the determined results by RST: (●) DOTAB and (▲) CTAB, and the continuous dashed curves are calculated by fitting a third order polynomial equation.

compute the X_1^m value, then this parameter (X_1^m) is used in Eq. (7) to calculate β^m.

The estimated values of X_1^m and β^m of both mixtures are collected in Table 3.

The values of X_1^m related to surfactant in mixed micelle (DOTAB or CTAB) evaluated based on Rubingh's model increased with increasing y_1 for two systems (see Fig. 6). These results show that the participation of component 1 (DOTAB or CTAB) in the mixed micelle formation increases with the increase of y_1.

Up to a range of around $y_1<0.54$ (for DOTAB/TEGO) and $y_1>$ 0.9 (for CTAB/TEGO), the values of X_1^m were obtained to be more than the y_1, but after these concentrations, the trend was reversed

(*i.e.*, $y_1 > X_1^m$).

This phenomenon is due to the type of intermolecular interaction between components (electrostatic and nonpolar interactions). This change behavior is observed at higher values of y_1 in a system containing surfactant with longer alkyl chain length (meaning CTAB/TEGO), suggesting that the micellization process is more affected by hydrophobic interactions between components.

The β^m values have three possibilities: (a) $\beta^m = 0$ for an ideal mixed micelle, which specifies no interaction between the mixture components, (b) $\beta^m > 0$ for antagonistic effects, whereas (c) $\beta^m < 0$ denotes the synergistic effects or attractive interactions.

The β^m values obtained were negative in both systems at different y_1, indicating the presence of attractive interactions or synergism at the mixed micelle (Table 3). The negative value of β^m in surfactant-TEGO mixture is due to the increase of attractive interaction between the nonpolar tails of molecules and the decrease of the repulsive interaction between the polar groups with positive charge in the surfactant molecules after mixing.

The mean β^m values for DOTAB/TEGO and CTAB/TEGO are -1.64 and -4.63, indicating that the synergistic effect is greater for CTAB/TEGO compared to DOTAB/TEGO. Also, this result exhibits that the β^m values with increasing hydrocarbon chain length from DOTAB to CTAB are more remarkable and higher in absolute value. From the molecular point of view, β^m can be divided into two parts: (a) the value obtained from interaction between the hydrophobic sections of surfactants 1 and 2 in the micelle core (β_{core}^m), (b) the value obtained from electrostatic interaction between the charged head groups of components 1 and 2 in micelle surface ($\beta_{elec.}^m$) [43]:

$$\beta^m = \beta_{core}^m + \beta_{elec.}^m \qquad (8)$$

The electrostatic repulsion between cationic surfactants (DOTAB or CTAB) and TEGO is similar due to the existence of a positive charge on the quaternary cation of the nitrogen atom and the imidazolium ring. Hence the value of the $\beta_{elec.}^m$ parameter in both systems is almost identical.

Two surfactants have quaternary ammonium head groups, but the difference is in the hydrocarbon chain length ($C_{12}H_{25}$- for DOTAB and $C_{16}H_{33}$- for CTAB); therefore, van der Waals bonds or overlapping of chains between the nonpolar tails will be different in the two systems and the synergistic effect is mostly controlled by these interactions (i.e., β_{core}^m), indicating more interaction between CTAB and TEGO than DOTAB and TEGO in mixed micelles. This expectation is being confirmed by average β^m values.

3. The Activity Coefficient Values and Thermodynamic Parameters

In the non-ideal binary systems of surfactants, the activity coefficients of components in the mixed micelles (f_i^m) on the basis of the regular solution theory (RST) can be determined by using the values of β^m and X_1^m [28,29,44,45]:

$$f_1^m = \exp[\beta^m (1 - X_1^m)^2] \qquad (9)$$

$$f_2^m = \exp[\beta^m (X_1^m)^2] \qquad (10)$$

The values of these parameters are tabulated in the seventh and eighth columns in Table 3. The values of f_1^m and f_2^m are found to be

less than unity, indicating the non-ideality with synergistic effects between the mixed components. As is obvious from results, f_2^m values related to TEGO in mixed micellar systems are in the order of CTAB/TEGO<DOTAB/TEGO, which is in conformity with their β^m values. The results also show that the activity coefficients of TEGO decrease with increasing the bulk mole fraction of component 1 (surfactant) in the mixture, signifying that the system becomes more non-ideal (due to increasing the attractive hydrophobic interaction between the tail groups of CTAB and TEGO).

In addition, the molecular thermodynamic theory for mixed surfactants was used to measure the thermodynamic functions of the studied systems. The standard Gibbs energy of micellization (ΔG_{mic}^0) is the Gibbs free energy of transfer of one mole of amphiphile from the bulk solution to the micelle phase.

According to the Zana model, ΔG_{mic}^0 is calculated for many general states of ionic amphiphiles by using the Eq. (11) [46]:

$$\Delta G_{mic}^0 = RT\left(\frac{1}{j} + \alpha \frac{i}{j}\left|\frac{Z_s}{Z_c}\right|\right)\ln(CMC) + RT\left(\alpha \frac{i}{j}\left|\frac{Z_s}{Z_c}\right|\ln\frac{i}{j}\left|\frac{Z_s}{Z_c}\right| - \frac{\ln j}{j}\right) \quad (11)$$

where i charged groups of surfactant with valency z_s (total charge iz_s), z_c is the valency of the counterion, and j alkyl chains connected by some spacer groups. α is the degree of counterion binding to micelles ($\alpha = 1 - S_2/S_1$), where S_2/S_1 is the slope of the post-CMC and the pre-CMC in the conductance *vs.* concentration plots, respectively. The second term on the right hand side of Eq. (11) can be neglected with respect to the first term, and this equation reduces to (with a good approximation):

$$\Delta G_{mic}^0 \approx RT\left(\frac{1}{j} + \alpha \frac{i}{j}\left|\frac{Z_s}{Z_c}\right|\right)\ln(CMC) \qquad (12)$$

For the two studied systems, both values of z_s and z_c are the same (equal to 1) for surfactant (DOTAB and CTAB) and TEGO. Also, z_s and z_c in pure and mixed states are not different from each other, but the value of j in different types of amphiphiles is different ($j_{DOTAB} = j_{CTAB} = 1$ and $j_{TEGO} = 2$). In the pure state for conventional surfactants (DOTAB and CTAB), $i = j = |z_s| = |z_c| = 1$ and Eq. (12) reduce to:

$$\Delta G_{mic}^0 \approx RT(1 + \alpha)\ln(CMC) \qquad (13)$$

And in pure state, each TEGO molecule has a one polar head group attached to two hydrocarbon chains. In this case, $i = |z_s| = |z_c| = 1$, $j = 2$ and Eq. (12) reduce to:

$$\Delta G_{mic}^0 \approx RT(0.5 + \alpha/2)\ln(CMC) \qquad (14)$$

After mixing, micelles are composed of surfactants with various structures (mixed micelles). In many articles, the magnitude of the structure effect of each surfactant in mixtures is not considered in the calculation of j.

In the new approach, instead of a constant value of j in surfactant mixtures, this value can be replaced with j_{mix}, which may be calculated from a simple mixing rule:

$$j_{mix} = X_1^m j_1 + (1 - X_1^m) j_2 \qquad (15)$$

where X_1^m is related to the micellar mole fraction of component 1, and j_1 and j_2 indicate the number of the alkyl chain in amphiphile molecules. Therefore, by combining Eqs. (12) and (15),

Table 4. The values of thermodynamic parameters for surfactant (1)TEGO(2) mixtures at different mole fractions of ionic liquid and 303.15 K

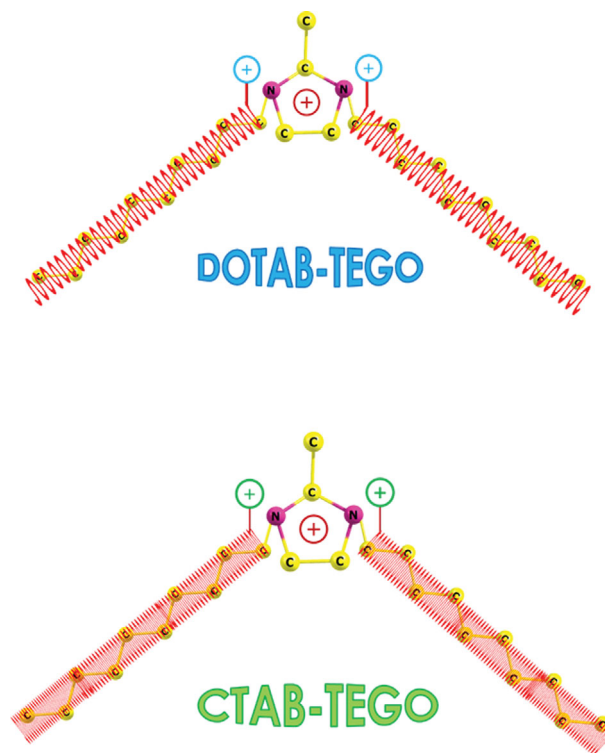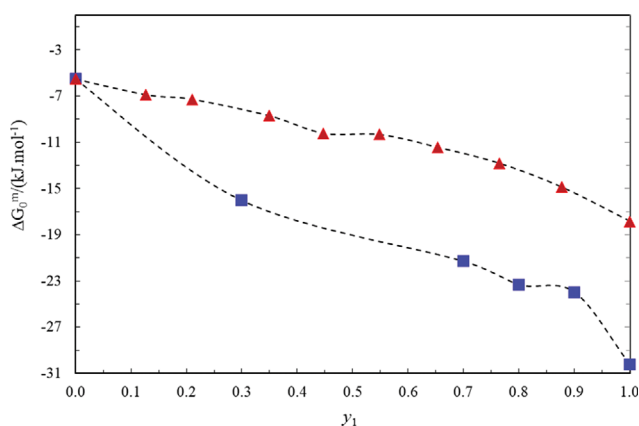| y_1	ΔG_{mic}^0	ΔG_{ex}
	kJ·mol^{-1}	kJ·mol^{-1}
DOTAB(1)/TEGO(2)		
0	−5.52	
0.1273	−6.88	−0.48
0.2105	−7.28	−0.73
0.3496	−8.70	−1.24
0.4474	−10.22	−1.45
0.5489	−10.33	−1.36
0.6530	−11.43	−1.25
0.7649	−12.82	−1.06
0.8773	−14.89	−0.07
1	−17.85[*]	
CTAB(1)/TEGO(2)		
0	−5.52	
0.2998	−16.02	−3.17
0.7005	−21.28	−1.70
0.8011	−23.31	−1.49
0.9013	−23.96	−1.33
1	−30.24[*]	

*This values for DOTAB and CTAB are less negative than the reported values in the previous papers because of using CMC instead of X_{CMC} in Eq. (13) [39,40].

$$\Delta G_{mic}^0 \approx RT\left(\frac{1}{j_{mix}} + \frac{\alpha}{j_{mix}}\right)\ln(CMC) \qquad (16)$$

In this situation, ΔG_{mic}^0 becomes dependent on the micellar mole fraction in mixed micelles, which is closer to reality and different from previous studies.

The values of ΔG_{mic}^0 listed in Table 4 are negative for pure and mixed amphiphiles.

The negative values indicate that the micellization process occurred spontaneously in the aqueous solution. The negative values of ΔG_{mic}^0 increased with the increase of hydrocarbon chain length (from DOTAB to CTAB). This shows that the role of hydrophobic sections is very significant for easier formation of micelles in pure surfactant or their binary systems with TEGO. In the surfactant(1)/TEGO(2) system, the values of X_1^m were obtained to be more than the stoichiometric mole fraction (y_1). It confirms that higher surfactant molecules are placed in the mixed micelles. Also, the longer hydrophobic tails of CTAB molecules in CTAB/TEGO system have more flexible chain segment, which is more intertwined with TEGO molecules during the aggregation process, thus increasing the hydrophobic interactions and forming a closely packed structure (more stable). The effect of hydrocarbon chain length, chain flexibility, the interweaving of alkyl chains with each other and strength of attractive interaction between molecules in two systems as a comparison is shown schematically in Fig. 7. CTAB molecules are placed around TEGO chains like a tighter spring in compared to DOTAB (stronger hydrophobic interaction

Fig. 7. The hydrophobic interactions between surfactant (DOTAB or CTAB) and TEGO in two systems.

Fig. 8. Plot of the Gibbs energy of micellization (ΔG_m^0) as a function of the bulk mole fraction of surfactant (y_1), in the mixed micelles of surfactant (1)/TEGO(2). The symbols refer to the calculated data by Eq. (16): (▲) DOTAB and (■) CTAB, and the continuous dashed curve is a guide for visualization.

and more spontaneous processes).

Also, the results exhibit a continuous increase of ΔG_{mic}^0 with the increase of the mole fraction of surfactant (DOTAB and CTAB) in the two investigated systems (see Fig. 8). The interaction between the hydrocarbon chains of species is the important factor for achieving a negative value of ΔG_{mic}^0 in the systems with the same electrical charges. In the system containing species with longer chains, the process of micelle formation is more spontaneous than the other system with shorter chains, and the $\lfloor \Delta G_{mic}^0 \rfloor$ values increase

with increasing of mole fractions of y_1 (due to hydrophobicity of the molecules increases and their tendency to form mixed micelles also increases).

The mole fractions of surfactants in mixed micelle (X_1^m and X_2^m) and activity coefficient of surfactants (f_1^m/f_2^m) based on RST were used to evaluate the values of excess Gibbs free energy of mixtures (ΔG_{ex}). The magnitude of ΔG_{ex} is an estimation of the difference between ideality and non-ideality of mixtures, which can be expressed as [47-50]:

$$\Delta G_{ex} = \Delta G_{mix}^{non-ideal} - \Delta G_{mix}^{ideal} \tag{17}$$

$$\Delta G_{ex} = RT[X_1^m \ln(X_1^m f_1^m) + X_2^m \ln(X_2^m f_2^m)] \\ - RT[X_1^m \ln X_1^m + X_2^m \ln X_2^m] \tag{18}$$

After simplification, Eq. (18) reduces to:

$$\Delta G_{ex} = RT[X_1^m \ln f_1^m + X_2^m \ln f_2^m] \tag{19}$$

Table 4 demonstrates the values of ΔG_{ex} for two investigated mixtures. The values of $\Delta G_{ex} < 0$ for systems at all y_1 show that $\Delta G_{mix}^{non-ideal}$ is more negative than ΔG_{mix}^{ideal}. These values again confirm the non-ideal interactions between components.

For the CTAB/TEGO mixture (compared to DOTAB/TEGO mixture), the evaluated values of the ΔG_{ex} are more negative, denoting that the mixed micellar system between TEGO and long chain amphiphile is thermodynamically more stable than TEGO and short chain surfactant (in agreement with the obtained results of synergism behavior and interaction parameter in above section).

CONCLUSIONS

To clarify the effect of hydrophobicity interactions in the mixed micellar system between single and double-chain surfactants, the binary mixtures of surfactants (DOTAB+TEGO and CTAB+TEGO) with similar hydrophilicity interactions were selected and investigated using conductivity technique at various compositions (in 303.15 K). The outcomes of this work show that empirical CMC values of two systems are less than the ideal one; this suggests the presence of mutual interactions with a deviation from the ideal mixture-behavior.

Micellar mole fraction (X_1^m) values in accordance Rubingh's model were obtained to be significantly more than the used bulk mole fraction of surfactant (y_1), denoting the participation of surfactant in large value in micellar mixtures of surfactant-TEGO. Also, the obtained results show that the activity coefficients of amphiphiles were found to be less than 1 ($f_i^m \ll 1$) and interaction parameter (β^m) values are negative in whole compositions, confirming synergism in DOTAB+TEGO and CTAB+TEGO mixed systems. In the same hydrophilic interactions between components in mixtures, the mean value of $|\beta^m|$ for CTAB-TEGO system is more than DOTAB-TEGO system, signifying that the hydrophobic interaction between the CTAB and TEGO after mixing is stronger than DOTAB and TEGO. The free energy of mixed micellization (ΔG_{mic}^0) was determined according to the Zana equation, and the results show that ΔG_{mic}^0 were very dependent on the hydrocarbon chain length and the number of hydrocarbon tails in surfactants. The negative ΔG_{mic}^0 values show that mixed micellar structure of

the surfactant and TEGO were more stable than micelles obtained by pure components, and this process becomes more negative with increasing hydrophobic properties from DOTAB to CTAB.

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