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Interaction and micellar behavior of aqueous mixtures of surface active ionic liquid and cationic surfactant: experimental and theoretical studies

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Abstract

The interaction between an ionic liquid (1-dodecyl-3-methylimidazolium bromide or IL) and cationic surfactant (dodecyltrimethylammonium bromide (DTAB)) in aqueous solution has been investigated at various mole fractions and temperature 30 ˚C using experimental and theoretical methods. The critical micelle concentration (CMC) of pure components and their binary mixtures, mixed micellar composition at ideal state(X_1^{id} and X_2^{id}) and real state(X_1^m and X_2^m), interaction parameter (β^m), activity coefficients of components in mixed micelles (f_1^m and f_2^m), the standard Gibbs energy of micellization (ΔG^0_{mic}) values and the degree of counterion binding(α) have been calculated and discussed. It has been found for the DTAB/IL mixture that depending on the ionic liquid bulk concentration (y_1), repulsive or attractive interactions (positive or negative value of β^m) are produced in mixed micelle formation. The unique role of IL in changing behaviors of aqueous surfactant mixtures is described. In the theoretical section, the molecular interaction energy of the pure IL, pure DTAB, and mixed IL-DTAB have been estimated using density functional theory (DFT) calculations. The value of interaction energy parameter (β^m) has also been calculated at mole fraction of 0.5 and a good agreement with the experimental results was observed.

Keywords: Ionic liquid, DTAB, Micellization, DFT, Interaction energy.

1. Introduction

Ionic liquids (ILs) are a paticular class of molten organic salts that are liquids at or below 373 K. One of the most important properties of room temperature ionic liquids is their negligible vapor pressure that these compounds introduce as environmentally friendly green solvents [1-5]. Ionic liquids (ILs) are often composed of a bulky nonsymmetrical organic cation (such as alkylimidazolium, alkylpyridinium, and tetraalkylphosphonium) and a small inorganic anion (such as anions like halides (X^-), PF_6^- and BF_4^-)[6-8]. Ionic liquids are of much interest due to their many potential applications in a large number of areas such as in separation processes [9-10], catalytic reactions [11-12], solar cells [13], batteries [14] and nanomaterial synthesis [15].

Many applications of ILs would be closely related to their self-aggregate (or micellization) in aqueous

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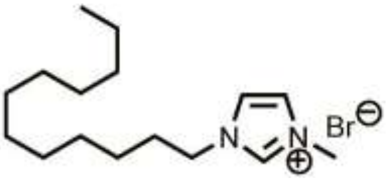
solution with surfactant-like manner [16]. Micellization behavior of 1-dodecyl-3-methylimidazolium bromide ($[C_{12}mim]Br$)(scheme 1) in aqueous solution studied by many researchers with a wide variety of methods, such as surface tension, vapor pressure osmometry (VPO), volumetric, conductivity and dynamic light scattering measurements [17-20]. The results showed that ($[C_{12}mim]Br$ act as long chain cationic surfactants in solution and form associates at higher concentration of the CMC value. The interfacial and micellization behavior of conventional surfactant mixtures have been widely investigated in solution, but these properties in the surfactant-ionic liquid mixtures are much less studied, and few reports can be found in the literature [21-23].



Scheme 1. Molecular model of 1-dodecyl-3-methylimidazolium bromide ($[C_{12}mim]Br$).

But no one has reported the mixed micellization of $[C_{12}mim]Br$ with cationic surfactant up to our knowledge except Sharma et al. [21] which reported the mixed micellization properties of 1-tetradecyl-3-methylimidazolium bromide ($C_{14}mimBr$) with tetradecyltrimethylammonium bromide (TTAB) and dimethylditetradecylammonium bromide (DTAB).

Ionic liquids and Dodecyltrimethylammonium bromide (DTAB, as cationic surfactant) mixed systems can form stable homogeneous solutions at various mole fractions with respect to the low mutual interactions between components. Mixing of two or more surfactants in an aqueous solution leads to the formation of mixed micelles.

In the present work, we investigated the interaction between $[C_{12}mim]Br$ and a cationic surfactant of dodecyltrimethylammonium bromide (DTAB) using the conductometric method in aqueous solutions at 303.15 K and density functional theory (DFT). In the first section, the conductivity measurements of surfactant-IL mixtures at different mole fractions were carried out to determine the critical micelle concentration (CMC) using the Carpena et al. method [24-26]. Then, the obtained results were used to calculate the micelle concentration (X_i^m), the interaction parameter between components (β^m) and activity coefficients (f_1^m and f_2^m) in the mixed micelles using regular solution theory [27-31].

In the second section, the molecular interaction energies, as well as interaction energy parameter between IL-DTAB in water solvent were calculated by DFT computations.

2. Experimental procedure

2.1. Materials

The 1-dodecyl-3-methylimidazolium bromide ionic liquid, IL (98 %) was purchased from Kimia Exir Chemical Co. (Tehran, Iran) and used without purification. Dodecyltrimethylammonium bromide, DTAB (≥98%) was procured from Merck Company and was recrystallized several times before use. All solutions (pure or mixture) were prepared with doubly distilled water.

2.2. Specific conductivity measurements

A Consort conductometer (model C860) having a cell constant 1.01 cm^{-1} was used to measure the conductance of the samples after proper mixing. The conductivity cell was calibrated with KCl solution in the appropriate concentration range. All experiments were performed at 30 ˚C, and the temperature in all the measurements was maintained by circulating thermostatted water (EYELA NTT-1100, Japan) with a temperature stability of ±0.01 K. The stock solutions of the ($[C_{12}mim]Br$, DTAB and their mixtures were prepared in double-distilled water.

The conductivity was measured after every addition of pure components or binary mixtures with specific mole fractions in the aqueous solution (by Hamiltonian microliter syringe). When specific conductivity (κ) of the solution was plotted as a function of surfactant concentration, two straight lines with different slopes were obtained; and the intercept of these lines was considered as CMC.

2.3. Computational details

The geometries of the ionic liquid and cationic surfactant were optimized using the hybrid B3LYP functional. B3LYP is one of the most commonly used functionals of DFT and consists of a combination of B3 exchange functional [32] and LYP correlation functional [33]. A split valence triple zeta quality basis set (6-311G) was employed for all of the atoms. The frequency calculations were carried out on the all optimized geometries in order to confirm the real local minima on the potential energy surfaces as well as to consider zero point energy corrections. The effect of water solvent was considered using the self-consistent reaction field (SCRF) theory with Tomasi's Polarizable Continuum Model (PCM) [34]. In order to remove the basis set superposition error (BSSE), the Boys and Bernardi counterpoise correction method using ghost atom is also employed [35]. All DFT computations were performed using the Gaussian 09 program [36].

3. Results and discussion

3.1. Conductometric method

The specific conductance (*k*) versus surfactant concentration of Dodecyltrimethylammonium bromide (DTAB) and ([C_{12}mim]Br) plotted in Figs. 1 and 2, respectively. The specific conductance (*k*) increases with increasing the concentration of the surfactant in aqueous solution. Generally, this trend was nonlinear, with the change in conductivity caused by a given change in surfactant concentrations being larger at low concentrations than at high concentrations. This behavior is typically attributed to the distribution of surfactant molecules between the surface and the bulk of the liquid and the mobility of ions. These figures showed a moderate change in slope near a certain concentration known as the critical micelle concentration (CMC). The CMC is acquired from experimental plots, and often one finds that it is difficult to determine the exact break point providing the CMC value. To solve this problem, Carpena et al. proposed an efficient procedure to analyze the conductivity-concentration data of ionic surfactant solutions to determine parameters such as CMC and the degree of counterion binding (α) values [24].

The details of the Carpena model were described in our previous work [25]. Briefly, the procedure of CMC determination involves the fitting of experimental conductivity data, *k*, as a function of surfactant concentration, *C*, to the equation [24-25]:

$$\kappa_{(C)} = \kappa_{(0)} + A_1 C + \Delta C\,(A_2 - A_1)\ln\left(\frac{1+e^{(C-CMC)/\Delta C}}{1+e^{-CMC/\Delta C}}\right) \qquad (1)$$

where $k_{(0)}$ is the conductivity of deionized water, the independent variable (C) is the concentration of surfactant (pure or mixture), A_1 and A_2 are the slopes below and above CMC, respectively; and ΔC, is related to the surfactant concentration range where the sudden change of the conductivity occurs. The degree of counterion binding (α) is calculated from ($1-A_2/A_1$). Always, the post-slope being lower slope implies that the formed micelles have lower mobility in comparison to the free ions in solution. The data ($k_{(C)}$-C) were fitted with Eq. (1) using a nonlinear least squares method based on the Levenberg–Marquardt algorithm with four adjustable coefficients (A_1, A_2, CMC, and ΔC).

In this manuscript, the CMCs of pure components (DTAB and IL) and their binary mixtures at various mole fractions calculated by this analytical method. In Table 1, the adjustable parameters, A_1, A_2, CMC, ΔC and α for pure components are listed as well as the respective standard deviations of the fittings [24-26].

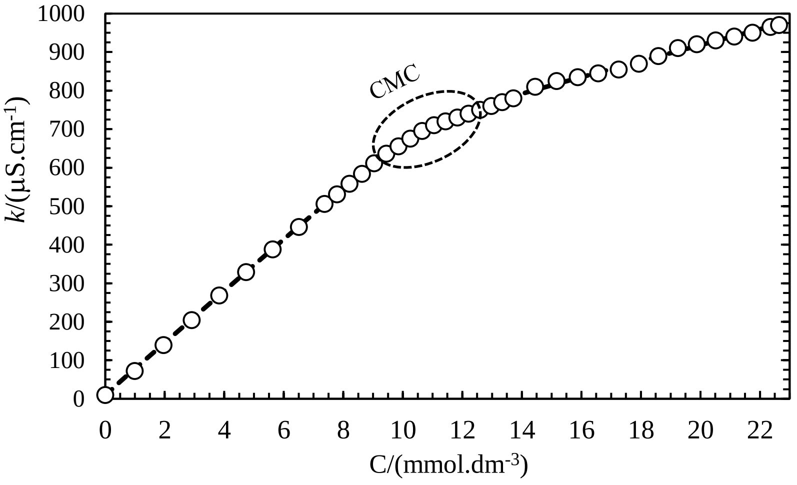


Fig. 1: Plot of specific conductivity against the concentration of IL ($[C_{12}mim]Br$). The symbols refer to the experimental data, and the dashed curves represent the correlation with Eq. (1).

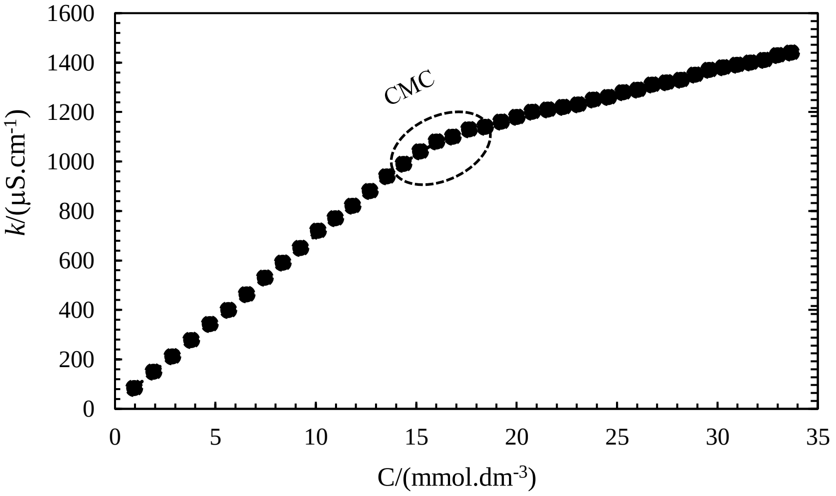


Fig. 2: Plot of specific conductivity against the concentration of dodecyltrimethylammonium bromide (DTAB). The symbols refer to the experimental data, and the dashed curves represent the correlation with Eq. (1).

Table 1. Adjustable coefficients of the Carpena model and the obtained values of α(the degree of counter-ion binding), R^2(correlation coefficient), S(standard deviation of the fitting for conductivity) and the Gibbs energy of micellization (ΔG^0_{mic}) for the pure surfactant at 303.15 K.

Component	A_1	A_2	CMC	ΔC	R^2	S	α	ΔG^0_{mic}
	$mS.cm^2.mol^{-1}$	$mS.cm^2.mol^{-1}$	$mmol.dm^{-3}$	$mmol.dm^{-3}$		$\mu S.cm^{-1}$		$kJ.mol^{-1}$
$[C_{12}mim]Br$	67338(±249)	20687(±322)	10.57(±0.065)	1.09(±0.08)	0.9997	4.32	0.692	-36.51
DTAB	68216(±137)	19311(±195)	15.78(±0.059)	0.85(±0.093)	0.9999	4.12	0.717	-35.34

Also, the standard deviations reported(S) in this Table 1 were calculated by applying the following equation:

$$S = \left[\sum_{i=1}^{M} \frac{(\kappa_{\exp.,i} - \kappa_{cal.,i})^2}{M - P} \right]^{1/2} \qquad (2)$$

where k stands for conductivity, M and P are the number of data points and the number of adjustable parameters used for fitting the experimental data with Eq. (1).

An evaluation of the surfactant tendency to form micelles is the standard Gibbs energy of micellization (ΔG^0_{mic}). The ΔG^0_{mic} can be used to estimate the spontaneity of a micellization process. A negative ΔG^0_{mic} demonstrates this process occurs spontaneous and is thermodynamically stable, whereas the positive ΔG^0_{mic} means the micellization is a disfavored nonspontaneous transfer. For the ionic surfactants, ΔG^0_{mic} was given by the following equation [25, 37]:

$$\Delta G^0_{mic} = (2 - {}^{p}\!/_{q})RT\ln(X_{CMC}) = (1+\alpha)RT\ln(X_{CMC}) \quad (3)$$

where q is the number of surfactant ions in the micelle, p is the number of counterions bound to the micelle (p/q is equal to $(1-\alpha)$) and X_{CMC} is the surfactant CMC in mole fraction units. The obtained results in Table 1 show that the values of $-\Delta G^0_{mic}$ increases from DTAB to IL. This indicates that the spontaneity of the process of micelle formation for IL is more than DTAB. The α value for DTAB is greater than the value for IL ($\alpha_{\mathrm{DTAB}} > \alpha_{\mathrm{IL}}$). This shows the DTAB micelle condensed more counterions and produced a more stable micelle (the easier micellization) and a higher aggregation number compared to the IL micelle. Figs. 3-4 show the variation of specific conductivity, *k*, as a function of the total surfactant concentration, C_{tot}, for IL(1)/DTAB(2) mixtures in mole fractions (y_1=0.3905, 0.8246 and 0.7098, 0.8924) at 303.15 K, typically.

The CMC values of IL/DTAB mixtures decrease with increasing the mole fraction of IL in the solution, and more IL molecules participate in the mixed micelle formation.

In the mixed micelle system, the surfactants may show either ideal or non-ideal behavior at the CMC. The ideal or non-ideal properties of mixed micelles of the IL with DTAB can be calculated by using a pseudo-phase model. The Clint model can be used to predict the CMC of mixed micelles in ideal behavior (CMC^{id}_{mix}) (the individual surfactants are non-interacting) [31, 38-40]:

$$CMC^{id}_{mix} = \frac{CMC_1 CMC_2}{y_1 CMC_2 + y_2 CMC_1} \quad (4)$$

where y_1 and y_2 represent the mole fraction of Ionic Liquid and DTAB, respectively, CMC_1 is the experimental CMC of pure IL and CMC_2 is the experimental CMC value of pure DTAB. The comparison between CMC^{id}_{mix} (from Clint model) and CMC_{mix} (from experimental data) can be easily predicted the non-ideal behavior of mixed micelles.

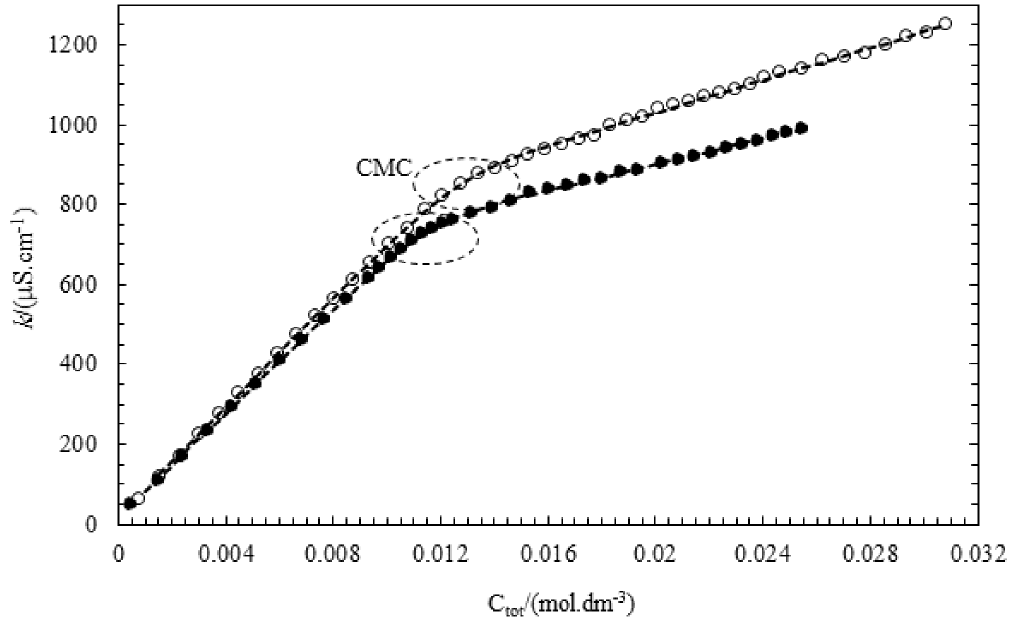


Fig. 3: Plot of specific conductivity against the concentration of IL(1)/DTAB(2) mixture at various mole fraction: (○) y_1=0.3905 and (●) y_1=0.8246. The symbols refer to the experimental data and the continuous dashed curves represent the correlation with Eq. (1).

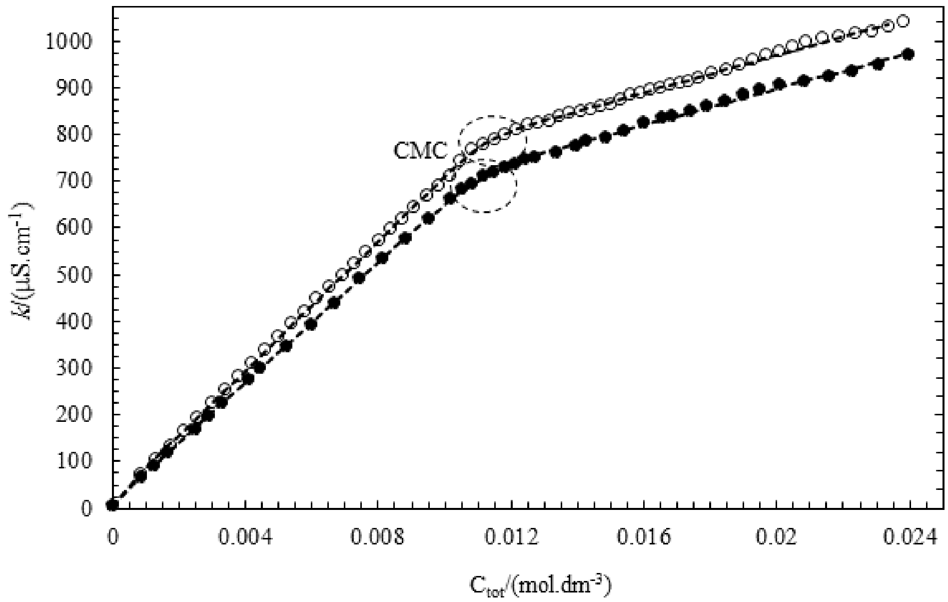


Fig. 4: Plot of specific conductivity against the concentration of IL(1)/DTAB(2) mixture at various mole fraction: (○) y_1=0.7098 and (●) y_1=0.8924. The symbols refer to the experimental data and the continuous dashed curve represents the correlation with Eq. (1).

The CMC_{mix}^{id} > CMC_{mix} indicates synergism (the attractive interaction) while CMC_{mix}^{id} < CMC_{mix} confirms antagonism (the repulsive interaction) in the mixed micelles. Fig. 5 shows that the CMC_{mix}^{id} values of DTAB/IL are greater than the CMC_{mix} suggesting synergistic between IL and DTAB molecules in mixed micelles, except in high concentration region of IL(y_1 > 0.8082), which CMC_{mix} value greater than CMC_{mix}^{id} (this conditions will be described later). The deviations from ideality in these mixtures must arise from structural dissimilarities of the hydrophilic groups in the components (with the same hydrophobic group).

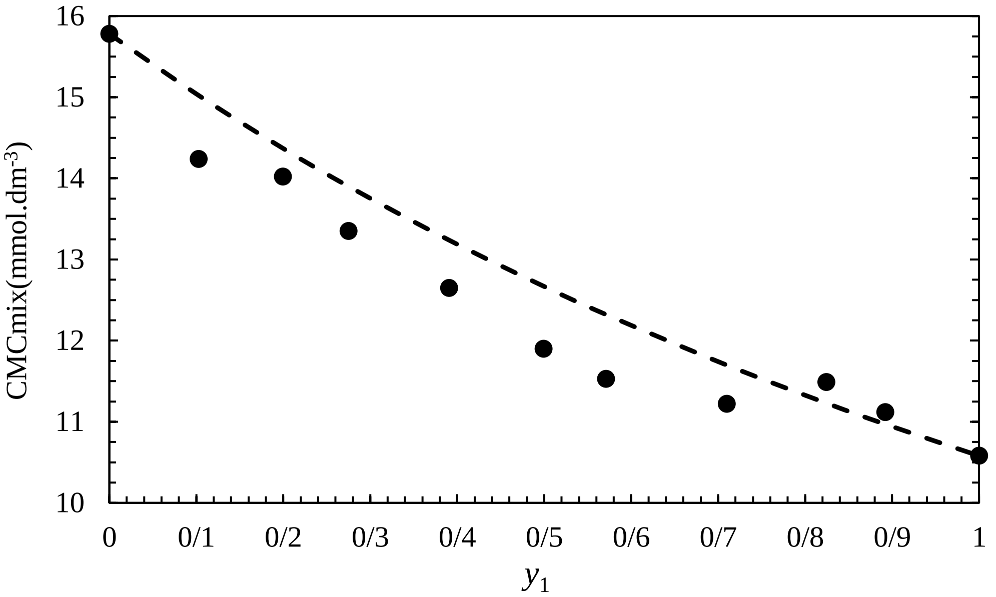


Fig. 5: Plot of critical micelle concentration, CMC, as a function of the bulk mole fraction of IL(y_1), in the mixtures of IL(1)/DTAB(2). The symbols refer to the experimental data, and the continuous dashed curve represents the calculated values with Clint's theory.

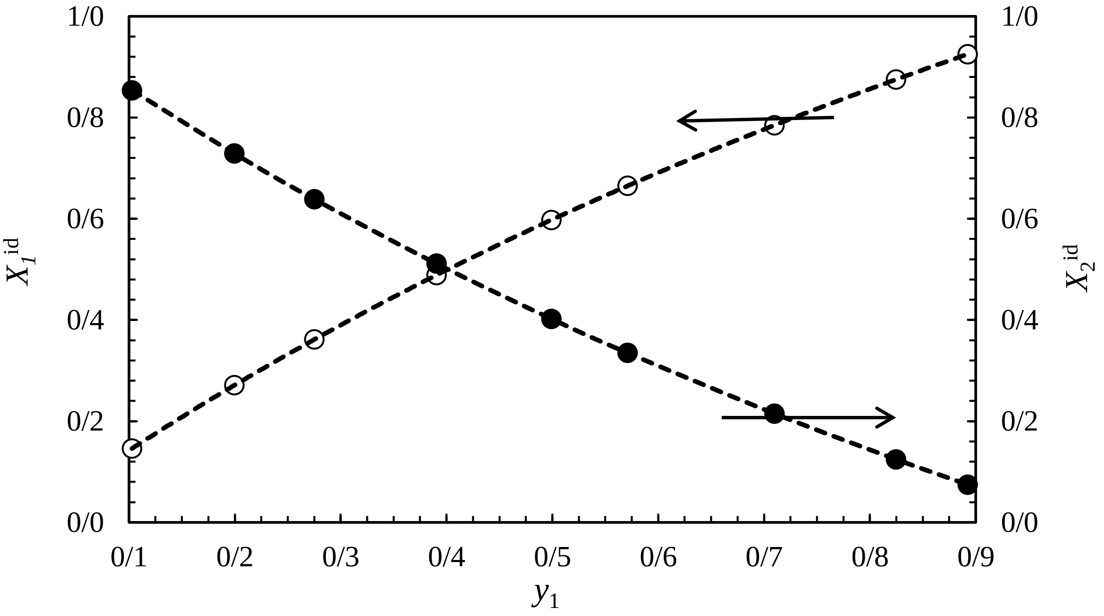


Fig. 6: Plot of the mole fractions of IL(X_1^{id}) and DTAB(X_2^{id}) as a function of the bulk mole fraction of IL (y_1), in the mixed micelles of IL(1)/DTAB(2). The symbols refer to the calculated data by the ideal state model, and the continuous dashed curve is a guide for the eyes.

The increase of X_1^{id} values indicates that the mixed micelle formation is favored as compared to micelle formation of DTAB component, and the mixed micellar phase is enriched with IL molecules at all mole fractions.

By using regular solution theory (RST) have been calculated micellar composition (X_i^m) and the interaction parameter (β^m) between surfactants in the mixed micelles [27-28]. Rubingh et al. pioneered the investigation on the non-ideality of the mixed micelles using this theory. The micelle mole fraction of IL (X_1^m), as well as interaction energy parameter (β^m), can be evaluated using the following relationships[27-28]:

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

and

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

where X_1^m is the mole fraction of IL in the mixed micelle; CMC_1, CMC_2, and CMC_{mix} are the critical micelle concentrations (*CMC*'s) for IL, DTAB, and their mixture, respectively, at the total mole fraction of IL in the mixture (y_1).

The β^m is an interaction energy parameter that expresses the degree interaction between dissimilar componds in the mixed micellar system. A negative value of β^m indicates that interactions in the mixed micelle are more attractive than the self-interaction of the surfactant-IL prior to mixing or less repulsive than before mixing. On the contrary, a positive value of β^m indicates that the attractive interaction of the surfactant-IL with each other in mixed micellar is weaker than the attractive interaction of the two surfactants prior to mixing. The results in Table 2 show a negative value of β^m in almost of the mole fractions (y_1<0.7), and a positive value in high mole fraction of IL (y_1>0.7).

In y_1<0.7: As can be seen from Table 2, the β^m values are negative in the region of mole fraction below 0.7 (y_1<0.7). Also, the mole fraction of IL at the mixed micelle (X_1^m) increases and the corresponding mole fraction of DTAB (X_2^m) decreases continuously as a function of y_1. This indicates that DTAB molecules present at the original micelle are continuously being displaced by IL molecules in the mixed state (enriched with ionic liquid monomers), which means that the surface activity of long-chain IL is superior to DTAB with the same alkyl chain length. The structure of IL and DTAB show that these surfactants having the same hydrophobic groups and different hydrophilic groups. When the mole fraction of IL increased in the mixed micelle, the interactions between IL and DTAB after mixing are less repulsive than before mixing (by a dilution effect). This is because the head group of imidazolium IL molecule (methylimidazolium head group) is more bulky and therefore less polar than trimethylammonium group which reduces the electrostatic repulsion between the ionic head groups and makes micelle formation energetically more favorable in this region of mole fraction.

In y_1>0.7: As can be seen from Table 2 and Fig. 5, with increasing y_1, CMC_{mix} values became higher than CMC_{mix}^{id} and positive β^m values were obtained as a measure of the repulsive interaction between the IL and surfactant. These results seem to demonstrate a close correspondence between the CMC value and the interaction parameter β^m in this range of high y_1.

To describe the change in behavior from attractive to repulsive interaction between the compounds with increasing y_1, the first consideration is due to the high concentration of the IL in mixed micelle in this region (in the other words, the IL concentration in the mixed micelle is very predominant (almost over 90%)). At these y_1 values, the insertion of DTAB monomers between IL molecules is very low in the mixed micelles, and probably produces an increase in the electrostatic repulsion between the head group of imidazolium of IL molecules leading to mixed micelle formation at higher CMC than expected, giving rise to positive β^m.

From another point of view, CMC and the y_1 values changed on a range of several orders of magnitude. As can be observed, the variation from attractive to repulsive interaction depends on the y_1 value. In the binary mixture of IL/DTAB, attractive interaction occurs when y_1 < 0.7. For higher values of y_1, repulsive interactions between IL and DTAB in the mixed micelle are generated given the higher CMC_{mix} values with respect to the CMC_{mix}^{id}. As the results shown in Table 2, an increase or decrease in the CMC_{mix} (positive or negative values of β^m) can be achieved via the adjustment of the bulk mole fraction of components in the solution. Thus, a special application for IL/surfactant mixtures can be obtained by controlling the mole fraction of components in the experimental conditions [3, 43].

In the ideal state, when $f_1^m = f_2^m = 1$ there is no net interaction between the IL and DTAB in the mixed micelle, but for the non-ideal mixture, the activity coefficients (f_1^m and f_2^m) are calculated using X_1^m and β^m values as follows [27-28]:

$$f_1^m = \exp[\beta^m (1 - X_1^m)^2] \tag{8}$$

$$f_2^m = \exp[\beta^m (X_1^m)^2] \tag{9}$$

The activity coefficients (f_1^m and f_2^m), are obtained to be below one for the studied mixtures(up to $y_1 < 0.7$) that point out the occurrence of nonideal behavior IL–DTAB mixtures, and shows the attractive interactions between the compounds in the mixed micelles (Table 2).

Table 2. The critical micelle concentration in mixed micelle(CMC_{mix}), *CMC* and the mole fraction of ionic liquid in the ideal mixed micelle (CMC_{mix}^{id} and X_1^{id}), the Gibbs energy of micellization(ΔG_{mic}^0), the degrees of counter-ion binding (*α*), the interaction parameters(X_1^m and β^m) and activity coefficients (f_1^m and f_2^m) according to Rubingh's model of IL(1)/DTAB(2) mixed systems at 303.15 K.

y_1	CMC_{mix}	CMC_{mix}^{id}	α	ΔG_{mic}^0	X_1^{id}	X_1^m	β^m	f_1^m	f_2^m
	mM	mM		kJ.mol^{-1}					
0.1028	14.24	15.02	0.7204	-35.85	0.1460	0.1801	-0.3922	0.7683	0.9874
0.1996	14.02	14.37	0.7179	-35.87	0.2711	0.2818	-0.1228	0.9386	0.9903
0.2752	13.35	13.90	0.7121	-35.96	0.3616	0.3718	-0.1731	0.9340	0.9764
0.3905	12.65	13.24	0.7015	-35.96	0.4886	0.4896	-0.1822	0.9536	0.9573
0.4992	11.89	12.67	0.6588	-35.32	0.5979	0.5783	-0.1660	0.9709	0.9460
0.5711	11.53	12.32	0.6760	-35.82	0.6651	0.6458	-0.2944	0.9637	0.8844
0.7098	11.22	11.70	0.7120	-36.70	0.7849	0.7629	-0.2386	0.9867	0.8704
0.8246	11.49	11.23	0.7500	-37.42	0.8752	0.8933	0.2185	1.0025	1.1905
0.8924	11.12	10.97	0.6994	-36.47	0.9252	0.9372	0.2022	1.0008	1.1944

3. 2. DFT Results

The interaction energy parameter (β^m) could be calculated according to the following equation [27-28, 44-45].

$$\beta^m = [W_{AB} - (W_{AA} + W_{BB})/2]/RT$$

(10)

In this equation (according RST model), where W_{AA}(J.mol^{-1}) is the molar interaction energy of the first surfactant(DTAB- DTAB), W_{BB} is the molar self-interaction energy of the second surfactant(IL-IL), W_{AB} is the molar interaction energy of IL-DTAB, R is the molar gas constant, T is the absolute temperature. In order to calculate the molecular interaction energies, we first optimized the structures of IL and DTAB separately in water solvent using B3LYP functional and 6-311G basis set. Then we optimized two molecules of IL-IL, DTAB-DTAB, and IL-DTAB at the same level of theory and basis set in the water solvent. The optimized structures were reported in Fig. 7(a-c). The molecular interaction energies (W_{ij}) were calculated using the equation 11:

$$W_{ij} = E_{ij} - E_i - E_j \tag{11}$$

In this equation, E_{ij} is the energy of optimized *i-j* molecules together, E_i and E_j are the energy of optimized i and j molecules, respectively. The values of W_{AA}, W_{BB}, and W_{AB} are obtained 3.0407, 2.9304, and 2.5707 kJ.mol^{-1}, respectively. The positive values of *W* indicate that repulsive interactions are dominated in IL, DTAB, and IL-DTAB. The value of β^m is obtained -0.1674 which is in good agreement with the experimental value of -0.1660 obtained at mole fraction of 0.5. The negative value of β^m indicates that IL-DTAB mixture experience either greater attraction or less repulsion compare to the pure IL and DTAB.

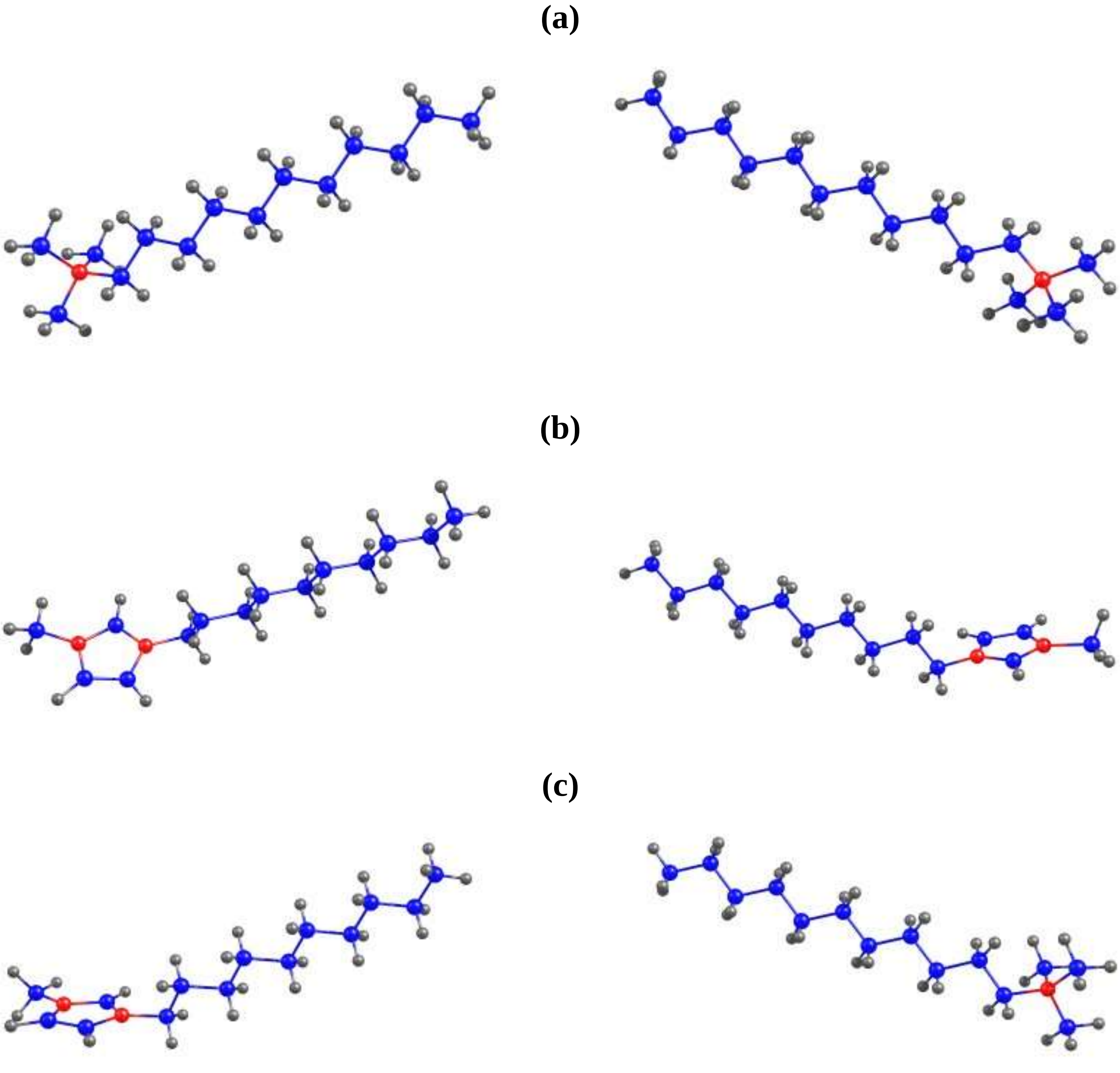


Fig. 7. The optimized structures of (a) DTAB-DTAB, (b) IL-IL, and (c) IL-DTAB at the B3LYP level of theory in water solvent. Carbon, hydrogen, and nitrogen atoms are presented in blue, gray, and red colors respectively

4. Conclusion

The experimental and theoretical studies of the mixed micelle of surface active ionic liquid (IL) and cationic surfactant (DTAB) has been examined in this paper. The differences between the CMC_{mix} (experimental) and CMC_{mix}^{id} (calculated from Clint model) values confirm that interaction between IL and surfactant occurs. The result obtained has been shown a change from attractive to repulsive interaction for this system (this phenomenon is depended to the mole fraction of IL (y_1)). At $y_1 < 0.7$, CMC_{mix} values are lower than the ideal state (CMC_{mix}^{id}), indicating positive synergism in mixed-micelle formation (or attractive interactions between components), and for high IL mole fractions ($y_1 > 0.7$), CMC_{mix} values are higher than the ideal state (CMC_{mix}^{id}), indicating negative synergism in mixed-micelle formation (or repulsive interactions between components). Also, the interaction parameter or β^m changed from a negative value at $y_1<0.7$ to a positive value in high mole fraction of IL at $y_1>0.7$. The Gibbs energy of micellization (ΔG_{mic}^0) in mixed micelles are also negative indicating the process of micelization to be spontaneous and the magnitude increases with the increase IL mole fraction.

DFT computations through B3LYP functional and 6-311G basis set were employed to calculate the molecular interaction energies in pure IL, pure DTAB, and IL-DTAB mixture. The interaction energy parameter (β^m) for IL-DTAB mixture was also estimated using DFT results and good agreement with the experimental results (Rubingh model) was observed at mole fraction of 0.5.

Acknowledgments

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