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ORIGINAL ARTICLE

Interactions in the mixed micelles of monomeric and gemini surfactants: Influence of some co-solvents as a function of temperature

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Abstract Mixed micellar behavior of a series of m-2-m cationic gemini surfactants (where $m = 10$, 12 and 14) with monomeric surfactants (dodecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide and cetyltrimethylammonium bromide) has been studied in aqueous and in aqueous n-propanol, n-butanol, tertiary butanol, propylene glycol and glycerol solutions using conductivity, surface tension, viscosity and dynamic light scattering techniques at 298.15, 308.15 and 318.15 K, respectively. In mixtures of 10–2–10 with monomeric surfactants, the synergistic interactions increase with the chain length of monomeric surfactants whereas the mixtures with 12–2–12 and 14–2–14 exhibit the opposite trends. However, the synergistic interactions decrease with the increase in temperature of all the mixtures. The thermodynamic and surface parameters have been evaluated and the influence of the variations in hydrophobic chain length of the surfactants and the type of the co-solvent on these parameters has been discussed. The hydrodynamic diameter increases with the chain length of the surfactants.

1. Introduction

In recent years, interfacial and micellar properties of mixed surfactant systems have attracted significant attention in the area of surface science and solution chemistry (Pan et al., 2012; Khan et al., 2014; Bielawska et al., 2014). Extensive investigations on binary mixtures of cationic–cationic, cationic–anionic, and cationic–nonionic systems have also been reported (Rosen and Hua, 1982; Moulik et al., 1996; Vora et al., 1999; Bakshi et al., 2002; Chakraborty et al., 2005; Svanedal et al., 2014), but nowadays studies involving gemini surfactant as one of the components in the mixed systems have attained special attention from both academic and industrial view points

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(Koya and Kabir-ud-Din, 2011; Martín et al., 2013; Khan et al., 2014; Fatma et al., 2015). Gemini surfactant is a family of surfactants possessing two polar/ionic head groups, covalently connected by a spacer group at the level of the head groups. Due to their enhanced self-assembling ability, these surfactants are superior to the conventional surfactants in characteristic features such as high surface activity, lower critical micelle concentration and Krafft temperature, unusual rheological properties and better wetting ability (Menger and Littau, 1993; Gull et al., 2009; Lu et al., 2012). In addition, the difference in the tail and the head groups of the gemini surfactants in the mixed systems may result in composition dependent micellar properties (Zana and Xia, 2004).

Many pharmaceutical formulations often require the addition of surfactants to regulate the physical properties of the product or improve its stability. The environmental factors such as temperature, pressure and the presence of co-solvents also affect the micellar, interfacial and thermodynamic parameters of these mixtures (Das and Ismail, 2008; Michele et al., 2011; Chakraborty et al., 2011). Thus, mixed surfactants serve as carrier of active ingredients and co-solvents help to improve this property by modifying the solvent characteristics which in turn influence the critical micellar concentration of these mixtures. It provides an opportunity to study the role of solvophobic effect in micellization. For instance, ethylene glycol is the most commonly used industrial co-solvent because it possesses high cohesive energy and dielectric constant and has many characteristics similar to that of water (Das and Das, 2009). Some studies have also been devoted on the mixed micellar properties of surfactants in the presence of ethylene glycol (Javadian et al., 2010; Tikariha et al., 2011; Koya and Kabir-ud-Din, 2011).

Further, short chain alcohols especially ethanol are also industrially important co-solvents because of their vital role in the preparation of microemulsions (Chavda and Bahadur, 2011; Kumar et al., 2012; Bielawska et al., 2013). But, to the best of our knowledge, the reports on the effect of presently used alcohols and glycols on the mixed micellar behavior of ionic gemini and monomeric surfactant mixtures are rare and limited only to conventional ionic/non-ionic surfactant mixtures (Gil and Lee, 2008; Park and Lee, 2012; Bielawska et al., 2014). The addition of alcohols can strongly influence the behavior of mixed micelles consisting of conventional monomeric/gemini ionic surfactants and increase or decrease micellar size depending upon the hydrophilic/hydrophobic character and thus can fine-tune the surfactant micelles template for the fabrication of nanomaterials (Kumar et al., 2012).

Therefore, we have investigated the effect of some short chain alcohols and glycols (2.5 and 5.0% v/v) on the mixed micellar and interfacial properties involving series of *m*-2-*m* gemini and alkyltrimethylammonium bromide (C_nTAB) monomeric surfactants using conductivity and viscosity measurements at 298.15, 308.15 and 318.15 K. These systems have also been evaluated by surface tension and dynamic light scattering techniques at 298.15 K. The monomeric surfactants used for this purpose are dodecyltrimethylammonium bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB) and cetyltrimethylammonium bromide (CTAB) whereas the co-solvents selected are n-propanol (PrOH), n-butanol (BuOH), tertiary butanol (tert BuOH), propylene glycol (PG) and glycerol (Gly). An attempt has been made to (i) find out the conditions for synergism in the bulk phase and at the air/water interface, (ii) evaluate the effect of various factors such as temperature, type of the co-solvent and chain length of monomeric or gemini surfactant on the interactions in the mixed micellar solutions and (iii) study the effect of alcohols and glycols on the variation in relative viscosity and the size of the mixed micelles.

2. Materials and methods

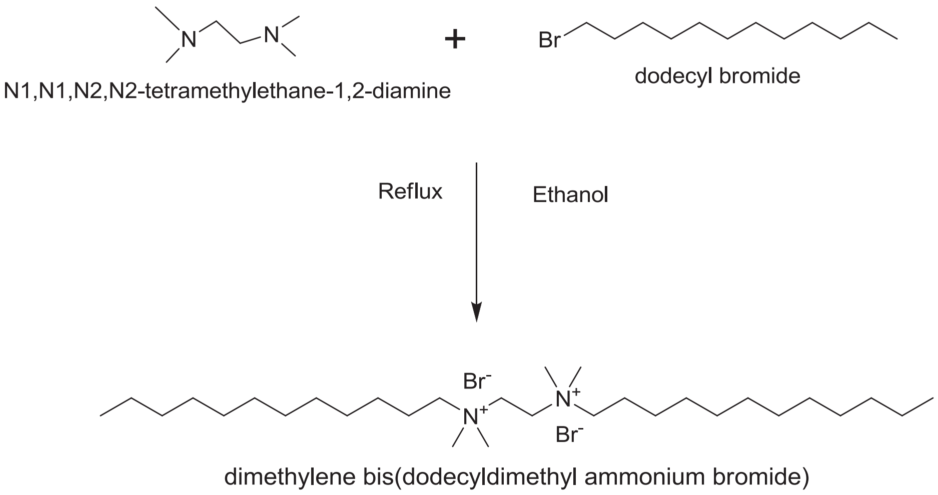
2.1. Materials

The dimethylene bis(alkyldimethyl ammonium bromide), denoted as ‘*m*-2-*m*’ (where *m* = 10, 12 and 14) gemini surfactants was synthesized by the reaction of N1,N1,N2,N2-tetramethylene-1,2-diamine with the corresponding alkyl bromides in extrapure alcohols by refluxing till the diamine present is completely consumed (Zana et al., 1991) as shown in Scheme 1. Once the reaction is complete, the solvent was removed by evaporation. The impure surfactants were recrystallized twice in 50:50 ethyl acetate/acetone mixtures. The final product thus recovered was then dried and kept in desiccator. All the other chemicals were more than 99% pure and used as such without further purification. The structure, sources and purity of the chemicals used are listed in Table 1. Double distilled and degassed water was used for the preparation of all the solutions.

2.2. Methods

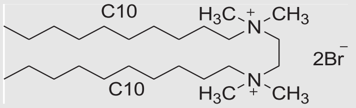
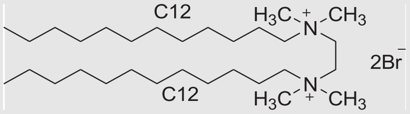
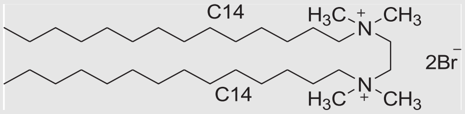
2.2.1. Conductivity measurements

The conductivity measurements were carried out with a digital conductivity meter (Systronics-306) using a dip-type cell with double walled glass jacket. The temperature of the conductivity cell was maintained within ±0.01 K using temperature bath (Model: MV 25F Julabo, Germany). The concentration



Scheme 1

Table 1 Name, structure and sources of chemicals used in the study.

S. no.	Compound	Structure	Source	Purity/grade
1.	DTAB		Lancaster Synthesis, UK	> 99%
2.	TTAB		Acros Organics, Germany	> 99%
3.	CTAB		Acros Organics, Germany	> 99%
4.	10–2–10		Synthesized in Laboratory	Characterized by ^{1}H NMR and Elemental analysis
5.	12–2–12		Synthesized in Laboratory	Characterized by ^{1}H NMR and Elemental analysis
6.	14–2–14		Synthesized in Laboratory	Characterized by ^{1}H NMR and Elemental analysis
7.	PrOH	$CH_3(CH_2)_2OH$	S.D. Fine, Mumbai	Extrapure AR
8.	BuOH	$CH_3(CH_2)_3OH$	S.D. Fine, Mumbai	Extrapure AR
9.	tert BuOH	$(CH_3)_3COH$	S.D. Fine, Mumbai	Extrapure AR
10.	PG	$CH_3CHOHCH_2OH$	S.D. Fine, Mumbai	Extrapure AR
11.	Gly	$CH_2OHCHOHCH_2OH$	S.D. Fine, Mumbai	Extrapure AR

of the solution was varied by aliquot addition of a stock surfactant solution of known concentration to a known volume of solvent in the vessel using a micropipette (Finnpipette Labsystems, Finland). The reproducibility in the measurement of critical micelle concentration (CMC) was calculated to be always within ±1%.

2.2.2. Surface tension measurements

The CMC values of the surfactants were determined at 298.15 K by the surface tension (γ) measurements made by ring detachment method using Krüss Easy Dyne (K20) tensiometer (Krüss Gmbh, Hamburg, Germany) based upon duNoűy principle. For each set of experiments, the ring was washed thoroughly by double distilled water and then heated in alcohol flame. The readings were taken in triplicate to ensure the reproducibility in CMC measurements within ±2%.

2.2.3. Viscosity measurements

The relative viscosity of individual surfactants and their binary mixtures were determined by using an Ubbelohde type suspended level capillary viscometer. Water was circulated through the glass jacket surrounding the viscometer at constant temperature using thermostat. From the ratio of the efflux time of test solution, t, to that of the reference solvent, t_o, the relative viscosity (η_r) was calculated by ignoring the density correction factor in case of dilute solutions (Ozeki and Ikeda, 1980). For each measurement, 3–5 readings were taken and mean of three nearest values has been reported. The reproducibility in each reading is within ±2%.

2.2.4. Dynamic light scattering measurements

The size of the micelle has been obtained (Cai et al., 2013) by measuring the hydrodynamic diameter of the micelle (D_h) using Stokes–Einstein equation:

$$D_h = \frac{kT}{3\pi\eta D} \tag{1}$$

where k = Boltzmann constant, D = diffusion coefficient, T = Absolute temperature, and η = viscosity of the solution. The DLS measurements were performed using Malvern Zetasizer Nano ZS (Malvern, UK) apparatus with He-Ne laser (λ = 632 nm) at 298.15 K (Naskar et al., 2012). All the experimental solutions were passed through 0.2 µm filters (Whatman™, GE Healthcare, UK). The mean values of three measurements of each sample have been reported and the reproducibility in each reading is within ±3%.

3. Results and discussion

3.1. Conductivity studies

3.1.1. Mixed micellar interactions in aqueous solutions

The CMC values of the studied gemini and monomeric surfactants in aqueous solutions at different temperatures have been obtained by intersection of specific conductance (κ) versus concentration of the surfactant (C) plots in the pre-micellar and post-micellar regions as shown in Fig. 1 and were found to agree well with the literature (Bakshi et al., 2005; Modaressi et al., 2007; Das and Das, 2009; Akbas et al., 2012; Dubey, 2013). The CMC values of binary mixtures of these surfactants (C_m) over the whole mole fraction (α) range of monomeric

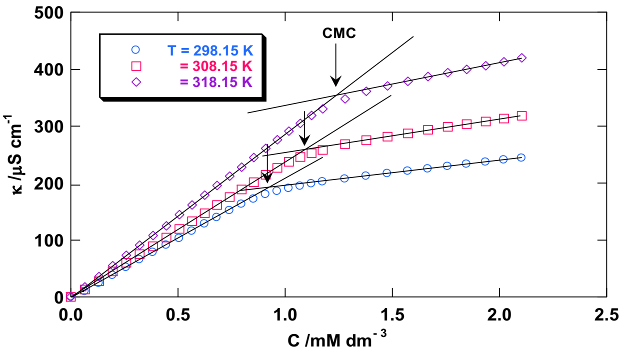


Figure 1 κ versus C plots for 12–2–12 in aqueous solutions at different temperatures.

surfactants have also been determined. The ideal CMC values of these mixtures (C_i) have been obtained from the Clint equation (Clint, 1975):

$$\frac{1}{C_i} = \frac{\alpha}{C_1} + \frac{1-\alpha}{C_2} \tag{2}$$

where C_1 and C_2 represent the CMC of monomeric and gemini surfactant respectively. The values of C_m and C_i thus determined for the mixtures of DTAB and gemini surfactants at 298.15 K in aqueous and in aqueous co-solvent solutions are given in Table 2. The remaining data at different temperatures have been provided in Tables S1–S3 (Supplementary Information). In case of 10–2–10 + DTAB mixtures, the C_m values are more than corresponding C_i values showing slight repulsive interactions between these two surfactants. But C_m becomes lower than C_i as the chain length of gemini surfactants is increased. It suggests that improved hydrophobic environment for the mixed micelle formation results in attractive interactions between the two surfactants. However, the difference between C_m and C_i values increases with temperature in 10–2–10 + DTAB mixture showing that the repulsive interactions increase whereas a decrease in the attractive interactions has been noticed in mixtures of 12–2–12/14–2–14 with DTAB. It is due to disruption of water structure surrounding the hydrophobic groups which delays the mixed micellization (Mehta et al., 2007; Yan et al., 2011; Moradi et al., 2013).

The degree of micellar dissociation (g) has also been calculated by taking the ratio of slopes of post-micellar region to those of pre-micellar region (Kumar et al., 2012). In 10–2–10 + DTAB mixture, the values of g remain almost constant (Table 2) throughout the whole mole fraction. However, in 12–2–12/14–2–14 + DTAB mixtures, the g values increase with α whereas a decrease in these values has been observed in mixtures with TTAB/CTAB (Tables S2–S3, Supplementary

Table 2 Experimental and ideal CMC (C_m, C_i), degree of dissociation (g), mixed micellar mole fractions (X_1, X_i), Excess free energy ($g^{M,E}$), interaction parameter (β), Standard Gibbs free energy, enthalpy and entropy (ΔG^o_m, ΔH^o_m, ΔS^o_m) of micellization for the mixtures of DTAB and gemini surfactants in aqueous solutions at 298.15 K using conductivity measurements at different mole fractions (α) of DTAB.

α	C_m (mmol dm^{-3})	C_i (mmol dm^{-3})	X_1	$g^{M,E}$ (kJ mol^{-1})	X_i	β	g	ΔG^o_m (kJ mol^{-1})	ΔH^o_m (kJ mol^{-1})	ΔS^o_m (J mol^{-1} K^{-1})
10–2–10 + DTAB										
0.000	6.33 (6.63)[a]	6.33					0.15	−60.35	−6.35	181.14
0.128	7.42	6.96	–	–	–	–	0.32	−52.05	−15.72	122.05
0.268	7.78	7.74	0.14	–	0.14	0.02	0.22	−56.09	−17.62	129.17
0.449	8.78	8.71	–	–	–	–	0.26	−53.81	−13.83	134.32
0.604	10.35	9.96	0.35	–	0.37	0.23	0.25	−53.15	−11.63	139.47
0.753	12.33	12.31	–	–	–	–	0.27	−51.39	−13.18	128.18
0.902	14.21	14.65	–	–	–	–	0.25	−51.47	−10.54	103.01
1.000	16.10 (16.00)[b]	16.10					0.27	−34.87	−5.17	99.89
12–2–12 + DTAB										
0.000	0.92 (0.90)[b]	0.92					0.20	−70.76	−28.60	141.46
0.128	0.85	1.01	0.15	−2.09	0.01	−3.50	0.30	−66.15	−41.52	80.25
0.268	1.06	1.21	0.13	−1.74	0.02	−2.48	0.31	−64.20	−44.10	65.35
0.449	1.21	1.51	0.18	−2.09	0.04	−2.49	0.29	−64.25	−29.56	112.14
0.604	1.57	2.01	0.21	−2.11	0.07	−2.05	0.42	−55.78	−28.60	88.47
0.753	1.93	3.58	0.36	−1.89	0.18	−3.22	0.61	−45.02	−15.81	95.61
0.902	2.98	6.11	0.34	−2.10	0.23	−2.64	0.63	−44.07	−17.62	89.24
1.000	16.10	16.10					0.27	−34.87	−5.17	99.89
14–2–14 + DTAB										
0.000	0.15 (0.16)[b]	0.15					0.24	−82.46	−36.21	148.25
0.128	0.16	0.17	0.06	−2.67	0.00	−4.12	0.27	−77.58	−57.02	67.62
0.268	0.18	0.21	0.12	−3.33	0.00	−4.61	0.41	−68.28	−49.06	62.25
0.449	0.23	0.27	0.12	−2.89	0.01	−3.78	0.36	−70.16	−39.95	98.31
0.604	0.28	0.37	0.16	−2.88	0.01	−3.83	0.45	−63.62	−47.96	49.47
0.753	0.46	0.71	0.24	−3.56	0.03	−4.02	0.56	−54.26	−19.69	112.21
0.902	0.44	0.77	0.23	−4.14	0.02	−4.04	0.57	−44.27	−14.53	103.41
1.000	16.10	16.10					0.27	−34.87	−5.17	99.89

[a] Akbas et al. (2012).

[b] Bakshi et al. (2005).

Information). Therefore, the degree of dissociation depends upon not only the head groups but also the chain lengths of the two surfactants. Moreover, the values of g increase with temperature for these mixtures due to electrostatic repulsions between the charged ion species leading to more dissociation at higher temperatures (Mehta and Kaur, 2013).

A quantitative interpretation of the experimental results can be obtained by Rubingh's treatment, based on the regular solution theory (Rubingh, 1979). The micellar mole fraction of monomeric surfactant (X_1) as well as interaction parameter (β) can be calculated using the following equations:

$$\frac{X_1^2 \ \ln(C_m\alpha/C_1X_1)}{(1-X_1)^2 \ \ln\left[\frac{C_m(1-\alpha)}{C_2(1-X_1)}\right]} = 1 \qquad (3)$$

$$\beta = \frac{\ln(C_m\alpha/C_1X_1)}{(1-X_1)^2} \qquad (4)$$

The activity coefficients f_1 and f_2 of surfactants 1 and 2 are related to β as

$$f_1 = e^{\beta(1-x_1)^2} \qquad (5)$$

$$f_2 = e^{\beta x_1^2} \qquad (6)$$

The β values for the mixtures of 10–2–10 with DTAB at 298.15 K are slightly positive showing repulsive interactions (antagonism) between the two surfactants (Table 2). These values could not be calculated at certain α values and are shown as "–" in the tables. However, in 12–2–12 + DTAB mixtures, the negative β values show synergistic interactions between the two surfactants which increase with chain length of gemini surfactants as shown in Fig. 2a by the decrease in the average values of β (β_{avg}). It may be due to longer hydrophobic twin tails of gemini surfactant which interact more favorably with DTAB to form the core of mixed micelles. The negative β_{avg} decrease slightly with increase in temperature (Table S1, Supplementary Information) as a result of an increase in the C_m values due to disruption of water structure surrounding the hydrophobic groups as mentioned earlier.

Synergistic interactions have been observed gemini + TTAB mixtures at 298.15 and 308.15 K (Table S2, Supplementary Information). These interactions increase with hydrophobic chain length of the gemini surfactants (Fig. 2b) as expected. At 318.15 K, the mixtures of 10–2–10/12–2–12 + TTAB show antagonistic behavior although synergism is exhibited in mixture of 14–2–14. In mixtures of gemini + CTAB at 298.15 and 308.15 K (Table S3, Supplementary Information), the synergistic interactions become antagonistic with the increase in chain length of the gemini surfactants from 10 to 12 and with further increase in the chain length from 12 to 14, these interactions show synergistic effect (Fig. 2c). Similar synergistic effect in 14–2–14 + CTAB mixture has been reported by Mirgorodskaya et al. (2014). The study also shows that with the increase in spacer length of the gemini surfactant from 2 to 4, the mixture exhibits antagonistic effect and with further increase in spacer length to 6, the mixture behaves almost ideally. These comparisons indicate that mixed micellar behavior is not governed only by the hydrophobicity of side chains but also by the spacer length. Moreover, it has been noted that in mixtures of 10–2–10, the synergistic interactions increase with chain length of monomeric surfactants whereas in mixtures of 12–2–12/14–2–14, opposite is true. In the literature, an increase in the synergistic interactions in the mixtures of 10–2–10/12–2–12 with the hydrophobic chain length of a series of zwitterionic surfactants has been reported whereas no trend was followed in the mixtures with 14–2–14 (Bakshi and Singh, 2005).

The mole fraction of monomeric surfactant in the mixed micelles in the ideal state (X_i) has been obtained using Motomura theory (Motomura and Aratono, 1993) based on excess thermodynamic quantities from Eq. (7):

$$X_i = \frac{\alpha C_2}{\alpha C_2 + (1-\alpha)C_1} \qquad (7)$$

In 10–2–10 + DTAB mixtures at 298.15 K (Table 2), the calculated X_1 and X_i values are almost same at all α values. But with the increase in hydrophobic chain length of gemini surfactant, the X_1 values become more than X_i indicating that

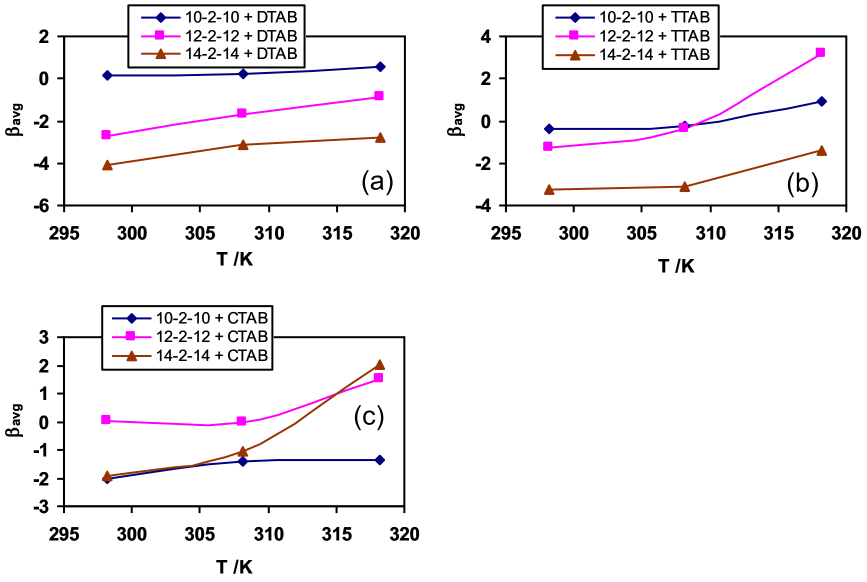


Figure 2 Variation in β_{avg} with temperature for different mixtures in aqueous solutions.

the contribution of DTAB in the mixed micelles increases. However, the difference between these two values decreases with the increase in temperature. For 10–2–10 + TTAB mixtures, the X_1 and X_i values are almost same at all α values (Fig. 3a). But, with the increase in chain length of gemini surfactant i.e. 12–2–12, the X_1 values are slightly more than X_i in 12–2–12 rich region ($\alpha < 0.268$) and become less in TTAB rich region as shown in Fig. 3b. However, in mixtures with 14–2–14, the X_1 values are always lower than X_i (Fig. 3c). This shows that the contribution of TTAB decreases with increase in chain length of gemini surfactant. Almost similar behavior is exhibited by the mixtures of CTAB with gemini surfactants (Table S3, Supplementary Information).

The excess free energy of micelle formation ($g^{M,E}$) describes the deviation from ideal mixing and has been calculated as follows based upon the Motomura theory (Motomura and Aratono, 1993):

$$g^{M,E} = RT(X_1^M \ln f_1^M + X_2^M \ln f_2^M) \tag{8}$$

where $f_1{}^M$ and $f_2{}^M$ are the activities of surfactant 1 (i.e. monomeric) and surfactant 2 (i.e. gemini). The values of $f_1{}^M$ and $f_2{}^M$ have been evaluated by

$$C_m X_1 = C_1 f_1^M X_1^M \tag{9}$$

$$C_m X_2 = C_2 f_2^M X_2^M \tag{10}$$

where $X_1{}^M$ and $X_2{}^M$ are the micelle mole fractions of monomeric and gemini surfactants, respectively. The values of $X_2{}^M$ are evaluated by

$$X_2^M = X_2 - (X_1 X_2 / C_m)(\partial C_m / \partial X_2)_{T,P} \tag{11}$$

The values of $g^{M,E}$ were found to be negative (Table 2) when the mixed micelles formed by the two surfactants show synergistic behavior whereas these values could not be determined when the two surfactants showed antagonistic behavior (Singh and Marangoni, 2007). The negative values of $g^{M,E}$ increase with the hydrophobic chain length of the surfactants and decrease with the increase in temperature. In general, these values follow almost similar trends as followed by β values.

3.1.2. Mixed micellar interactions in the presence of aqueous co-solvent solutions

Mixed micellar properties of m-2-m gemini surfactants with series of monomeric surfactants have also been studied in aqueous solutions containing 2.5 and 5.0% (v/v) of n-propanol (PrOH), n-butanol (BuOH), tertiary butanol (tert BuOH), propylene glycol (PG) and glycerol (Gly). The presence of various co-solvents modifies the dissociation of the surface groups as well as alters the hydrogen bonded structure of water (Ruiz, 1999). The addition of co-solvents results in the increase in the degree of dissociation (Tables S1–S3, Supplementary Information). It is due to reduction in ionic head group repulsions leading to decrease in surface charge density at the mixed micellar surface (Tiwari et al., 2014). For the present studied systems the increase in g is more in the presence of linear chain alcohols i.e. PrOH and BuOH as the incorporation of these alcohol molecules in the micelle is expected to cause a greater reduction among the charged groups at the micellar surface (Chavda and Bahadur, 2011). Further, the g values show a sharp increase at higher mole fractions of monomeric surfactant in the mixtures indicating that the presence of small amount of gemini surfactant in the micelles of monomeric surfactants tends to reduce the repulsions among the hydrophilic head groups to a greater extent than in pure gemini or monomeric surfactant solutions. This is because in pure surfactant solutions, the ability to bind counter ions is related to the charge density on the head group. But in surfactant mixtures, it is also related to the ability of the two different molecules to pack closely at the surface, thus making a compact micellar surface (Kabir-ud-Din et al., 2013).

In order to compare the effect of various co-solvents on interactions between the studied surfactants, the β_{avg} values

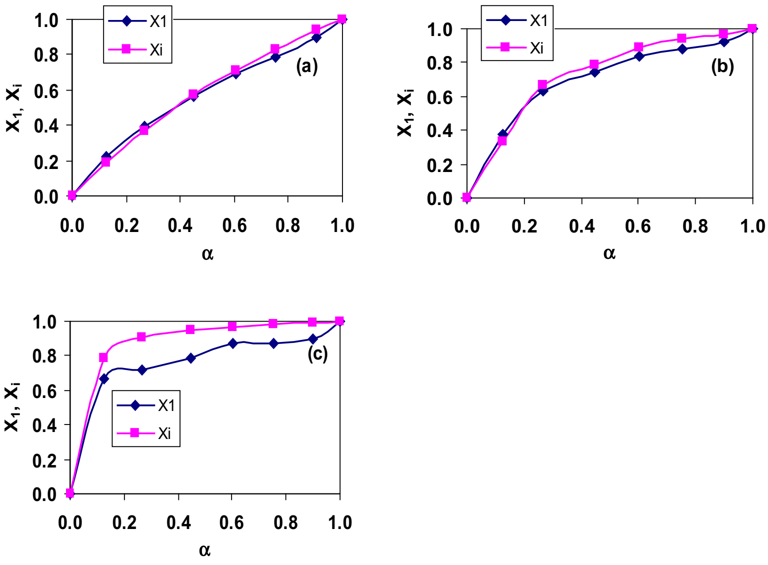


Figure 3 Plots of (♦) X_1 and (■) X_i versus α for the binary mixtures of TTAB with (a) 10–2–10 (b) 12–2–12 and (c) 14–2–14 in aqueous solutions at 298.15 K.

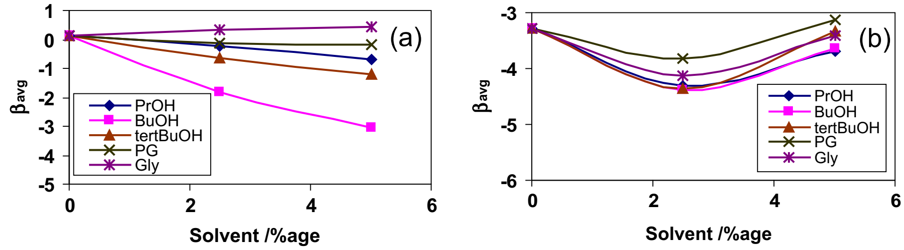


Figure 4 Variation of β_{avg} versus solvent composition for (a) 10–2–10 + DTAB, (b) 10–2–10 + TTAB, (c) 10–2–10 + CTAB, (d) 12–2–12 + DTAB, (e) 12–2–12 + TTAB, (f) 12–2–12 + CTAB, (g) 14–2–14 + DTAB, (h) 14–2–14 + TTAB and (i) 14–2–14 + CTAB mixtures at 298.15 K.

for some mixtures are given in Fig. 4 at 298.15 K. For the mixture of 10–2–10 + DTAB, β_{avg} values in the presence of all the co-solvents were negative (except with Gly) as compared to positive values in aqueous solutions, showing that the presence of all these co-solvents increases the hydrophobic interactions between these surfactants. The negative values of β_{avg} follow the sequence BuOH > tert BuOH > PrOH > PG. The influence of these co-solvents on the mixed micellar properties of surfactants can be explained on the basis of several different roles of alcohols (Kabir-ud-Din et al., 2007). On the one hand, the short chain alcohol molecules (up to three carbons) are miscible with water. They are located in the bulk phase of the micellar solution and replace water in the bulk solvent sphere that surrounds the hydrocarbon chain of surfactant and thus bind to the surfactant molecule. However, on the other hand, the alcohols with more than four carbon atoms are solubilized in such a way that their –OH group remains at the micellar surface whereas the hydrophobic part intercalates among the hydrophobic portions of the surfactants. The BuOH molecule is grouped with either short chain or long chain alcohols depending upon its solubility in the surfactant solution (Chavda et al., 2011; Dharaiya et al., 2013). Therefore, the locus of solubilization of BuOH is the most significant criteria in determining the physicochemical characteristics of the mixed micelles. In our case, the presence of both BuOH and tert BuOH increases the hydrophobic interactions more in comparison with those by PrOH and PG. It is due to higher octanol–water partition coefficient ($P_{o/w}$) of BuOH and tert BuOH (Chavda and Bahadur, 2011). This results in reduction of ionic repulsions among the positively charged head groups at the micellar surface as the average distance between the ionic head groups belonging to the different molecules increases and thus the micellar charge density decreases (Graciani et al., 2010). Moreover, the increase in hydrophobic interactions is smaller in the presence of tert BuOH as compared to BuOH since the polar –OH group in tert BuOH is located such that it divides nonpolar region into smaller regions which decrease $P_{o/w}$ or increase its solubility and thus it remains relatively more in the aqueous phase and thus incorporation in the mixed micelles is less. A comparison between the effect of PrOH and PG shows that the presence of additional –OH group in PG tends to decrease the number of ordered water molecules around the hydrophobic chain, thereby, decreasing the hydrophobic effect. Similar results have been obtained by Chavda and Bahadur (2011) for the effect of BuOH and 1,4 butadiene on the micellar behavior of 12–4–12 gemini surfactant using NMR studies. Gly, having three –OH groups, cannot penetrate into the micellar core and is located at the hydrophilic shell of the micelles. Moreover, $P_{o/w}$ value of Gly is the least (−2.55) among the studied co-solvents (Alexandridis and Yang, 2000) indicating strong affinity for water causing modification in solvent properties. Therefore, the solubility of surfactant tail increases resulting in higher C_m as compared to C_i values leading to positive β values.

In the presence of co-solvents too, the synergistic interactions increase with chain length of monomeric surfactants in mixtures with 10–2–10 and decrease in case of 12–2–12/14–2–14. Further, in certain mixtures, the synergistic interactions are more in 2.5% co-solvent solutions as compared to those in aqueous solutions and become less in 5% aqueous co-solvent solutions (Fig. 4b). It can be understood by considering that the distribution of the co-solvent between bulk phase and the pseudo micellar phase has two possible effects on C_m. Firstly, at low concentrations, it partitions more in micellar phase and the intercalation between surfactant molecules results in decrease in electrostatic repulsions leading to decrease in C_m and hence the synergism increases (Thimons et al., 1997). Secondly, at higher concentrations, water + co-solvent mixtures act like a better solvent for surfactant alkyl tail and hence increase the C_m which results in the decrease of synergetic interactions (Ruiz, 1999). The effect of temperature on these interactions in water + co-solvent system is similar to that in aqueous solutions.

At 298.15 K, the presence of BuOH and tert BuOH in 10–2–10 + DTAB mixtures shows higher X_1 than the corresponding X_i values whereas these two values remain almost same in aqueous solutions of the remaining co-solvents (Table S1, Supplementary Information). This indicates that the presence of longer chain alcohols increases the contribution of DTAB in the mixed micelles. However, the presence of these alcohols in 12–2–12/14–2–14 mixtures with DTAB has no affect on the X_1 and X_i values. Further, the relative difference between X_1 and X_i values remains almost same with the increase in co-solvent concentration and decreases with increase in temperature. The presence of alcohols in 10–2–10 + TTAB mixtures increases the contribution of TTAB in 10–2–10 rich region ($\alpha < 0.449$) although a decrease in TTAB contribution has been seen in TTAB rich region ($\alpha > 0.604$). However, the X_1 and X_i values remain almost same at all α values in the presence of PG and Gly. The presence of studied co-solvents in 12–2–12/14–2–14 + TTAB/CTAB mixtures exhibits almost similar variations in X_1 and X_i values as in aqueous solutions. From these observations it may be concluded that the presence of alcohols in short chain gemini and monomeric surfactant mixtures increases the contribution of monomeric surfactant whereas no significant variation is observed in mixtures of long chain surfactants. Similarly, the presence of glycols has no effect on the relative contribution of the two surfactants in all the mixtures. The effect of temperature on the *g* values of the mixtures depends upon the relative effect of the columbic and thermal forces (Zana, 1996). The former attracts surfactant head groups while the latter disperses the surfactant head groups. The thermal forces predominate the columbic forces and this leads to the separation between the counter ions and the head groups, hence increase the *g* values (Tables S1–S3, Supplementary Information).

3.1.3. Thermodynamics of Micellization

The standard Gibbs free energy of micellization (ΔG_m^o) can be calculated on the basis of phase separation model for ionic surfactants using Eqs. (12) and (13):

$$\Delta G_m^o = (2-g)RT\ln X_{\mathrm{CMC}} \quad \text{for ionic monomeric surfactants} \tag{12}$$

$$\Delta G_m^o = (3-2g)RT\ln X_{\mathrm{CMC}} \quad \text{for gemini surfactants and their mixtures} \tag{13}$$

From the temperature dependence of CMC, the standard enthalpy change for the mixed micellization process, ΔH_m^o can be obtained as

$$\Delta H_m^o = -(2-g)RT^2\frac{d(\ln X_{\mathrm{CMC}})}{dT} \quad \text{for ionic monomeric surfactants} \tag{14}$$

$$\Delta H_m^o = -(3-2g)RT^2\frac{d(\ln X_{\mathrm{CMC}})}{dT} \quad \text{for gemini surfactants and their mixtures} \tag{15}$$

The entropy change associated with the micellization process ΔS_m^o is obtained by using the following relationship:

$$\Delta S_m^o = \frac{\Delta H_m^o - \Delta G_m^o}{T} \tag{16}$$

The process of mixed micellization becomes less spontaneous with the increase in co-solvent concentration and temperature as indicated by decrease in ΔG_m^o values (Tables S1–S3, Supplementary Information). However, among the studied co-solvents, the process is more spontaneous in mixtures containing alcohols than glycols. The negative values of ΔH_m^o in all the mixtures indicate that the process is exothermic in nature and becomes more so with the increase in temperature and chain length. It is due to possible interactions between surfactant–solvent and solvent–solvent molecules and change in the hydration of head groups of cationic amphiphiles with temperature (Batigöç et al., 2011; Koya et al., 2013). These values decrease with the increase in additive concentration because of decrease in energy required to break up the iceberg structure surrounding the hydrophobic part of the mixture (Tikariha et al., 2012). The more negative values of ΔH_m^o in the mixtures than those in case of pure components further show that the mixed micellization is enthalpically more favorable. ΔS_m^o values decrease with increase in temperature as the aggregation becomes poor at higher temperatures due to enhanced molecular motions (Banipal et al., 2011; Sood et al., 2012). These values roughly show a decrease with increase in percentage of additives implying that the ordering of the randomly oriented cationic surfactants from the solvated form to the micellar structure is more pronounced than the destruction of the water structure. As the enthalpy of micellization is negative and becomes more negative with the rise in temperature accordingly positive entropy becomes less positive and therefore there is entropy–enthalpy compensation in all the studied systems (Mehta et al., 2007).

3.2. Surface tension studies

The CMC values for the mixtures of gemini and monomeric surfactants in aqueous and aqueous co-solvent solutions at 298.15 K were obtained from the break in surface tension (γ) versus concentration plots as shown in Fig. 5. Since there is not much change in the γ values for $0 < \alpha < 0.48$, therefore only representative data (at $\alpha = 0.356$) have been plotted. Moreover, the considerable decrease in the CMC from $\alpha = 1.000$ to 0.903 is due to the incorporation of gemini in the micelles of monomeric surfactants causing enhancement in the hydrophobic interactions (Azum et al., 2008). These CMC values (C'_m) for DTAB + gemini surfactant mixtures, along with their ideal values (C'_i), calculated by Clint Eq. (1), are given in Table 3 whereas C'_m and C'_i values for the remaining mixtures are included in Table S4 (Supplementary Information).

Regular solution theory (Rubingh, 1979) has been used to obtain interaction parameter (β') and mole fraction of monomeric surfactant (X'_1) as explained in the previous section. The average values of β'(β'_{avg}) are negative for all the mixtures (except 10–2–10 + DTAB) as shown in Fig. 6a. Moreover, β'_{avg} values for 10–2–10 + monomeric surfactant mixtures decrease with increase in chain length (*m*) of monomeric surfactants although an increase in these values has been seen in mixtures with 12–2–12/14–2–14. These results agree well with those obtained by conductivity measurements although β'_{avg} were slightly more negative than β_{avg}. The micellar mole fraction of monomeric surfactant (X^{γ}_1) and interaction parameter (β^{γ}) at the mixed adsorbed monolayer has also been obtained from Rosen Model (Rosen and Zhou, 2001) using the following equations:

$$\frac{(X_1^{\gamma})^2\ln(C_{12}\alpha/C_1^oX_1^{\gamma})}{(1-X_1^{\gamma})^2\ln(C_{12}(1-\alpha)/C_2^o(1-X_1^{\gamma}))} = 1 \tag{17}$$

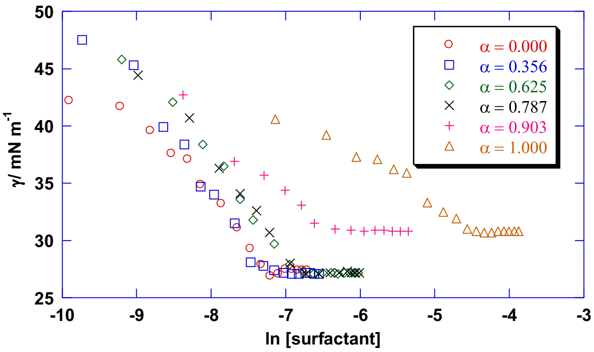


Figure 5 Plot of surface tension (γ) versus total concentration for 12–2–12 and DTAB mixtures in aqueous solutions at different mole fractions of DTAB (α) at 298.15 K.

Table 3 Experimental and ideal CMC (C'_m, C'_i), mixed micellar mole fractions (X'_1, X^{γ}_1, X'_i), interaction parameters (β', β^{γ}) for the mixtures of DTAB and gemini surfactant systems in aqueous solutions at 298.15 K using surface tension measurements at different mole fractions of DTAB (α).

α	C'_m (mmol dm^{-3})	C'_i (mmol dm^{-3})	X'_1	X^{γ}_1	X'_i	β'	β^{γ}
10–2–10 + DTAB							
0.000	5.86	5.86					
0.156	6.90	6.26	–	–	–	–	–
0.356	7.46	7.12	–	0.14	–	–	0.63
0.480	7.99	7.47	0.22	0.19	0.26	0.41	0.59
0.625	8.96	8.25	0.35	0.36	0.39	0.47	0.24
0.787	10.25	9.43	0.56	0.52	0.58	0.68	0.99
0.903	12.66	10.62	0.75	0.62	0.78	3.49	0.87
1.000	13.94	13.94					
12–2–12 + DTAB							
0.000	0.80	0.80					
0.156	0.60	0.91	0.20	0.21	0.01	−5.34	−5.54
0.356	0.71	1.11	0.22	0.22	0.01	−3.84	−4.65
0.480	0.79	1.33	0.26	0.26	0.04	−4.04	−3.88
0.625	1.21	1.72	0.25	0.31	0.08	−2.56	−3.98
0.787	1.21	2.58	0.36	0.38	0.16	−3.83	−4.43
0.903	1.32	4.61	0.46	0.46	0.34	−5.30	−5.40
1.000	13.94	13.94					
14–2–14 + DTAB							
0.000	0.15	0.15					
0.156	0.08	0.17	0.23	0.25	0.00	−9.24	−10.02
0.356	0.11	0.21	0.24	0.26	0.01	−7.24	−8.56
0.480	0.14	0.24	0.23	0.29	0.01	−6.61	−8.97
0.625	0.20	0.33	0.23	0.29	0.01	−5.36	−7.45
0.787	0.32	0.54	0.25	0.32	0.03	−4.50	−6.93
0.903	0.38	1.02	0.37	0.39	0.07	−5.75	−8.85
1.000	13.94	13.94					

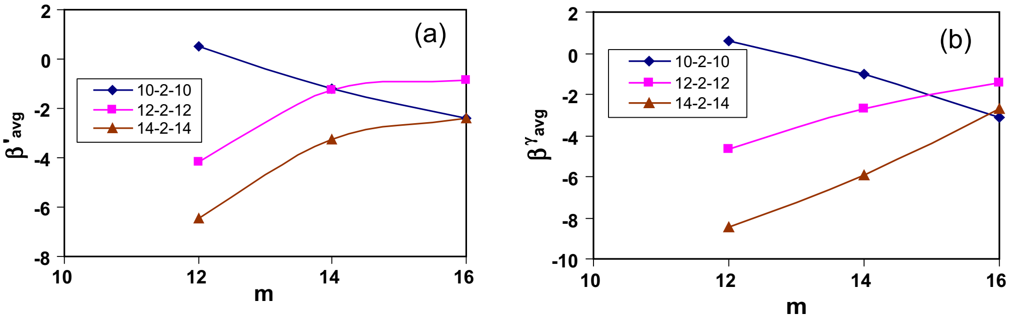


Figure 6 Variations of β'_{avg} and $\beta^{\gamma}_{\text{avg}}$ for the mixtures of gemini surfactants with chain length (m) of monomeric surfactants in aqueous solutions at 298.15 K.

where C^o_1, C^o_2 and C_{12} are the molar concentrations in the solution phase of surfactant 1 (monomeric), surfactant 2 (gemini) and their mixtures, respectively. The values of X^{γ}_1 can be used to calculate the interfacial molecular interaction parameter (β^{γ}) as

$$\beta^{\gamma} = \frac{\ln(C_{12}\alpha / C^o_1 X^{\gamma}_1)}{(1 - X^{\gamma}_1)^2} \tag{18}$$

The synergistic interactions in the surfactant mixtures are not governed only by the β values but also by the relevant properties of the individual surfactant in the mixture (Rosen and Zhou, 2001). The conditions for synergism in a mixture of two surfactants are as follows:

(i) β must be negative
(ii) $|\beta| > |\ln (C_1/C_2)|$
(iii) $|\beta^{\gamma} - \beta| > [|\ln(C^o_1/C^o_2)| - |\ln(C_1/C_2)|]$

The calculations based upon the data shown in Tables 2 and 3 reveal that the mixtures of 12–2–12/14–2–14 with DTAB satisfy all the three conditions and thus exhibit synergism whereas 10–2–10 + DTAB mixture does not follow these conditions and show antagonism.

Similar to the mixed micelle formation, the conditions for synergism in mixed monolayer formation are as follows:

(i) β^{γ} must be negative
(ii) $|\beta^{\gamma}| > |\ln(C_1^o/C_2^o)|$

It can be seen from the data in Table 3 that both these conditions are fulfilled by the mixtures of 12–2–12/14–2–14 whereas the mixture of 10–2–10 with DTAB does not obey these conditions.

Motomura theory (Motomura and Aratono, 1993) has been used to calculate the mole fraction of the monomeric surfactant (X'_i) in ideal state. The $X^{\gamma}{}_1$ values are in general smaller than X'_i (Table S4, Supplementary Information) showing that contribution of monomeric surfactant is more in mixed micelle formation than in mixed monolayer. Further, $X^{\gamma}{}_1$ values increase with the chain length of ionic surfactants. The average values of β^{γ} ($\beta^{\gamma}{}_{\mathrm{avg}}$) are more negative than those of β'_{avg} in most of the mixtures which indicate stronger interactions at the air–solution interface (Fig. 6b). The negative magnitude of β^{γ} values increases in the presence of alcohols because the intercalation of these alcohols in the mixed micelles causes screening of electrostatic repulsions between head groups of the two types of surfactants and increases hydrophobic interactions (Mohammad et al., 2011).

The maximum excess concentration ($\Gamma_{\max}$) and minimum area per surfactant molecule ($A_{\min}$) at the air–water interface can be obtained from Eqs. (19) and (20), respectively:

$$\Gamma_{\max} = \frac{-1}{nRT}\left(\frac{d\gamma}{d\ln[\text{surfactant}]}\right) \tag{19}$$

$$A_{\min} = \frac{10^{20}}{N_A \Gamma_{\max}} \tag{20}$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}), T is temperature in Kelvin, [surfactant] is the concentration of the surfactant in solution and N_A is the Avogadro number (6.023×10^{23} molecules mol^{-1}). The constant n (prefactor) has been taken as 2 for these surfactants and their mixtures (Mohammad et al., 2011). The $\Gamma_{\max}$ and $A_{\min}$ values for the studied gemini surfactants and DTAB mixtures are given in Table 4 whereas data for the remaining mixtures are summarized in Table S5 (Supplementary Information). The lower $\Gamma_{\max}$ values in case of pure gemini as compared to monomeric surfactants are due to the fact that these molecules, having two hydrophobic head groups covalently bonded with the help of a spacer and thus occupy more area. Moreover, with the increase in chain length of these surfactants, the surface area occupied by each molecule increases further and hence $\Gamma_{\max}$ decreases (Table S5, Supplementary Information). In 2.5% alcohol solutions, these $\Gamma_{\max}$ values increase whereas $A_{\min}$ decrease due to intercalation of alcohol molecules between aqueous and micellar phase which results in decrease in polar head group repul-

Table 4 Maximum surface excess concentration ($\Gamma_{\max}$), experimental and ideal values of minimum area per molecule ($A_{\min}$, $A^{id}{}_{\min}$), CMC and surface concentration ratio (C'_m/C_{20}) and surface pressure at CMC (Π_{CMC}), Standard free energies of micellization, adsorption and at the air–water interface ($\Delta G'^{o}_{m}$, ΔG^{o}_{ad}, $G^{(s)}{}_{\min}$) and packing parameter (P^*) for the mixtures of DTAB and gemini surfactants in aqueous solutions at 298.15 K using surface tension measurements at different mole fractions of DTAB (α).

α	$\Gamma_{\max} \cdot 10^6$ (mol m^{-2})	$A_{\min}$ (Å^2 molecule^{-1})	$A^{id}{}_{\min}$ (Å^2 molecule^{-1})	C'_m/C_{20}	Π_{CMC} (mN m^{-1})	$G^{(s)}{}_{\min}$ (kJ mol^{-1})	$\Delta G'^{o}_{m}$ (kJ mol^{-1})	ΔG^{o}_{ad} (kJ mol^{-1})	P^*
10–2–10 + DTAB									
0.000	1.30	127.59		3.76	44.48	23.90	−22.69	−61.46	0.32
0.156	0.78	213.16	–	3.65	45.08	34.56	−22.29	−80.16	-
0.356	0.89	196.32	148.23	3.14	44.15	28.24	−21.59	−72.12	0.23
0.480	1.09	151.70	155.45	2.86	44.15	25.26	−21.92	−62.26	0.20
0.625	0.94	176.70	165.06	2.51	43.80	29.16	−21.64	−68.26	0.26
0.787	0.73	225.28	174.10	3.36	42.21	39.74	−21.31	−78.58	0.35
0.903	0.66	250.51	144.72	2.61	40.60	46.77	−20.78	−82.04	0.44
1.000	1.57	105.81		2.54	40.67	37.24	−20.93	−70.22	0.20
12–2–12 + DTAB									
0.000	1.19	139.55		4.42	45.39	20.28	−27.63	−62.50	0.30
0.156	1.11	149.43	143.01	6.67	44.38	24.41	−28.34	−68.28	0.34
0.356	1.24	136.35	144.24	6.64	45.01	21.28	−28.01	65.41	0.39
0.480	1.34	123.78	146.70	6.10	45.11	20.04	−27.65	−61.28	0.44
0.625	1.52	108.82	150.38	6.71	44.76	17.78	−26.61	−55.94	0.40
0.787	1.16	143.10	155.54	4.84	44.88	23.20	−26.60	−65.28	0.39
0.903	1.61	103.11	161.43	5.81	43.65	17.48	−26.39	−53.50	0.37
1.000	1.57	105.81		2.54	40.67	37.24	−20.93	−70.22	0.20
14–2–14 + DTAB									
0.000	1.15	144.50		10.06	29.98	33.59	−31.76	−55.82	0.29
0.156	0.79	210.68	150.21	4.96	44.68	34.41	−33.20	−89.90	0.24
0.356	0.91	171.25	150.94	5.73	44.59	28.56	−32.41	−80.46	0.33
0.480	1.10	150.31	152.93	6.13	45.11	24.34	−31.93	−72.77	0.25
0.625	0.84	197.55	152.93	4.86	44.76	32.29	−31.02	−84.27	0.25
0.787	0.90	183.87	154.97	6.15	44.88	29.81	−29.85	−79.55	0.26
0.903	1.10	150.45	159.73	5.39	43.65	25.51	−29.45	−69.01	0.34
1.000	1.57	105.81		2.54	40.67	37.24	−20.93	−70.22	0.20

P^* stands for P or P_{eff}.

sions leading to tight packing (Khan et al., 2014). The increase in $\Gamma_{\max}$ is more in case of gemini than monomeric surfactants. However, the $\Gamma_{\max}$ values decrease with further increase in alcohol percentage (5.0%) as these alcohols act as better co-solvents at higher concentrations (Ruiz, 1999). In case of glycol solutions, $\Gamma_{\max}$ decreases ($A_{\min}$ increases) with the increase in glycol concentration because glycols are more soluble in the aqueous phase and therefore, tend to keep the surfactant molecules far apart from any association, resulting in decrease in compactness (Sohrabi et al., 2010). Moreover, in case of gemini surfactants, the increase in $A_{\min}$ is more in comparison with that in monomeric surfactants because the spacer gets extended and thus the distance between the head groups increases in the presence of glycols (Batigöç et al., 2011).

The value of surface pressure at the CMC (Π_{CMC}) is obtained from the equation $\Pi_{\mathrm{CMC}} = \gamma_o - \gamma_{\mathrm{CMC}}$, where γ_o is the surface tension of aqueous solution of co-solvent and γ_{CMC} is the surface tension at CMC. The γ_o values among the studied co-solvents follow the sequence of PG > PrOH > tert BuOH > Gly > BuOH. Moreover, Π_{CMC} values in the presence of studied co-solvents are much lower than those in aqueous solutions and decrease with increase in concentration of co-solvent. Π_{CMC} values are the least in the presence of Gly among these co-solvents (Table S5, Supplementary Information) indicating significant reduction in the effectiveness of the surfactants in lowering the surface tension.

The standard Gibbs free energies of micellization and adsorption ($\Delta G'^{o}_{m}$, ΔG^{o}_{ad}) have been calculated as per the following equations:

$$\Delta G'^{o}_{m} = RT \ln X'_{\mathrm{CMC}} \tag{21}$$

$$\Delta G^{o}_{ad} = \Delta G'^{o}_{m} - \frac{\pi_{\mathrm{CMC}}}{\Gamma_{\max}} \tag{22}$$

where X' is the CMC in mole fraction units obtained from surface tension studies. The more negative values of ΔG^{o}_{ad} than $\Delta G'^{o}_{m}$ (Tables 4 and S5, Supplementary Information) confirm that micellization is secondary in nature as compared to surface adsorption; therefore, work has to be done to transfer the molecules from the monomeric form to the micelle form (Khan et al., 2012). The magnitude of both $\Delta G'^{o}_{m}$ and ΔG^{o}_{ad} increases with the chain length of ionic surfactant and the effect is more in case of gemini surfactants. $\Delta G'^{o}_{m}$ values were more negative in the presence of PrOH and BuOH than in aqueous solution whereas no significant variation is observed in case of remaining studied co-solvents. However, the magnitude of ΔG^{o}_{ad} values is smaller in the presence of co-solvents than in aqueous solutions. It shows that the second term ($\Pi_{\mathrm{CMC}}/\Gamma_{\max}$) in Eq. (22) plays a significant role in determining the adsorption tendency.

The C'_m/C_{20} ratio measures reduction in the surface tension of water by the presence of additional surfactant or co-solvents. It has been observed that the ratio decreases in the presence of co-solvents and increases with the chain length of monomeric/gemini surfactants (Table S5, Supplementary Information). The decrease in the ratio is more in case of alcohols as compared to glycols. Sugihara et al. (2003) have proposed a thermodynamic quantity, and the minimum free energy at the air–solution interface, $G^{(s)}_{\min}$, for evaluating synergism in mixing and is given as

$$G^{(s)}_{\min} = A_{\min}\gamma_{\mathrm{CMC}}N_A \tag{23}$$

$G^{(s)}_{\min}$ is regarded as the work needed to make an interface per mole or the free energy change accompanied by the transition from the bulk phase to the interface of the components in the solution. In other words, the lower the value of $G^{(s)}_{\min}$, the more thermodynamically stable surface is formed. It can be seen from Table S5 (Supplementary Information), that the $G^{(s)}_{\min}$ values are lower in the presence of alcohols at lower concentrations (2.5%) in comparison with those in aqueous solutions and become higher in 5.0% alcohol solutions. However, these values decrease with the increase in the amount of glycols (PG and Gly) in the solution.

According to Israelachvili et al. (1976), the nature of amphiphile packing in micelles and their structural geometry can be predicted by packing parameter (P) defined by the relation,

$$P = \frac{V}{A\, l_c} \tag{24}$$

where V is the volume of the micelle which can be considered as fluid and incompressible, A is the surface area of the head group and l_c is the maximum effective length of the hydrophobic chain of the monomer.

The critical or effective length for a saturated hydrocarbon chain with C_n number of carbon atoms can be obtained from Tanford formula (Tanford, 1980):

$$l_c \leqslant l_{\max} \approx (0.154 + 0.1265C_n)\ \mathrm{nm} \tag{25}$$

where $l_{\max}$ is the maximum length of the chain. The volume of the micelle can be obtained from

$$V = (0.0274 + 0.0269C_n)\ \mathrm{nm}^3 \tag{26}$$

Since the exact determination of the head group area A is comparatively difficult, therefore $A_{\min}$ values have been used instead of A in the above calculations (Kabir-ud-Din et al., 2010; Rodríguez et al., 2008; Ray et al., 2007). In the mixed micelles, the aggregation can be evaluated in terms of the effective packing parameter (P_{eff}) as (Ray et al., 2007)

$$P_{eff} = \frac{\sum V_i x_i^{\mathrm{mic}}}{(\sum A_i x_i^{\mathrm{mic}}) l_c} \tag{27}$$

where x_i^{mic} and A_i are the micellar mole fraction and area of the ith component in the mixed micelles, respectively. The shape and type of amphiphile aggregates can be predicted from the magnitude of P or P_{eff} so that, for spherical assemblies, $P \leqslant 0.333$; for non spherical shape, $0.333 < P < 0.5$; for vesicles and bilayer, $0.5 < P < 1$ and for inverted structures $P > 1$. Thus all the studied ionic surfactants produce spherical or non spherical micelles in aqueous solutions as shown in Tables 4 and S5 (Supplementary Information). The values of P_{eff}, in general, are more in mixed micellar solutions than pure monomeric surfactant solutions which indicate transformations to vesicles and bilayers. It is because, in case of mixed systems, the presence of gemini surfactant with spacer group weakens the strong electrostatic effect between the head groups which decreases the area per molecule ($A_{\min}$) significantly, thereby increasing P_{eff} values, leading to the formation of vesicles (Shang et al., 2007). In addition, as the mole fraction of the gemini component increases in the mixtures, the net surface charge increases along with the hydrophobicity. This net charge discourages the aggregation but on the other hand, the stronger hydrophobicity promotes the aggregation and makes them come close to each other to form micelles. The values of P_{eff} increase in the presence of co-solvents and are more in alcohols than in glycols. With the increase in hydrophobic chain length of the gemini surfactant and alcohols, the hydrophobic volume V increases, causing increase in P_{eff}, leading to changes in the micellar shapes.

3.3. Viscosity studies

3.3.1. Relative viscosity in aqueous solutions

The relative viscosity (η_r) of the studied mixed micellar systems has been calculated at different temperatures and the data are summarized in Table S6 (Supplementary Information). The η_r values increase with the chain length of both types of surfactants but the effect is more in case of gemini as compared to monomeric surfactants. It can be explained by considering that in aqueous solutions of monomeric surfactants, the head groups are randomly distributed on the surface separating the aqueous and the micellar hydrophobic core. Due to the opposite forces involved in micellization, the distribution of distance between the head groups is more at thermodynamic equilibrium distance (Zana, 2002). In contrast, the distribution of distance between head groups in gemini surfactants is bimodal. This bimodal distribution of head group distances and the effect of chemical linkage between head groups on packing of the surfactant alkyl chains in the micellar core affect the curvature of the surfactant layers and thus the micellar shape which influences the properties in the solutions.

In mixtures of 10–2–10 + monomeric surfactants, the η_r values decrease with the increase in mole fraction (α) of monomeric surfactants (Fig. 7a) although an increase in η_r has been seen with the hydrophobic chain length of monomeric surfactants. It can be explained by considering two opposing factors (Kabir-ud-Din et al., 1996; Patel et al., 2009) which are responsible for the variation in the η_r values; one is the electrostatic repulsion term originating from intermicellar and intramicellar columbic interactions which result in micelle formation with higher surface area per head group i.e. spherical micelles and the other is due to hydrophobic interactions between the hydrocarbon part of the micelles/monomers which tries to achieve aggregates with tightly packed chains i.e. rods or disks. Therefore, the increased hydrophobic interactions in case of longer chain monomeric surfactants are mainly responsible for the pronounced micellar growth and a distinct rise in viscosity (Wang et al., 2008). Similar results have been observed with the increase in chain length of gemini surfactants as shown in Fig. 7b. A sudden increase in η_r at $\alpha = 0.356$ for the mixture of 12–2–12 + DTAB may be due to breakdown of 12–2–12 micelles to incorporate similar hydrophobic chain length DTAB resulting in increase in η_r (Bakshi et al., 2006). The η_r values decrease with the increase in α in mixture of 1 2–2–12/14–2–14 with TTAB/CTAB (Table S6, Supplementary Information). Moreover, the η_r values in all the studied mixtures decrease with increase in temperature. It is because at higher temperatures, the hydrophobic interactions among the

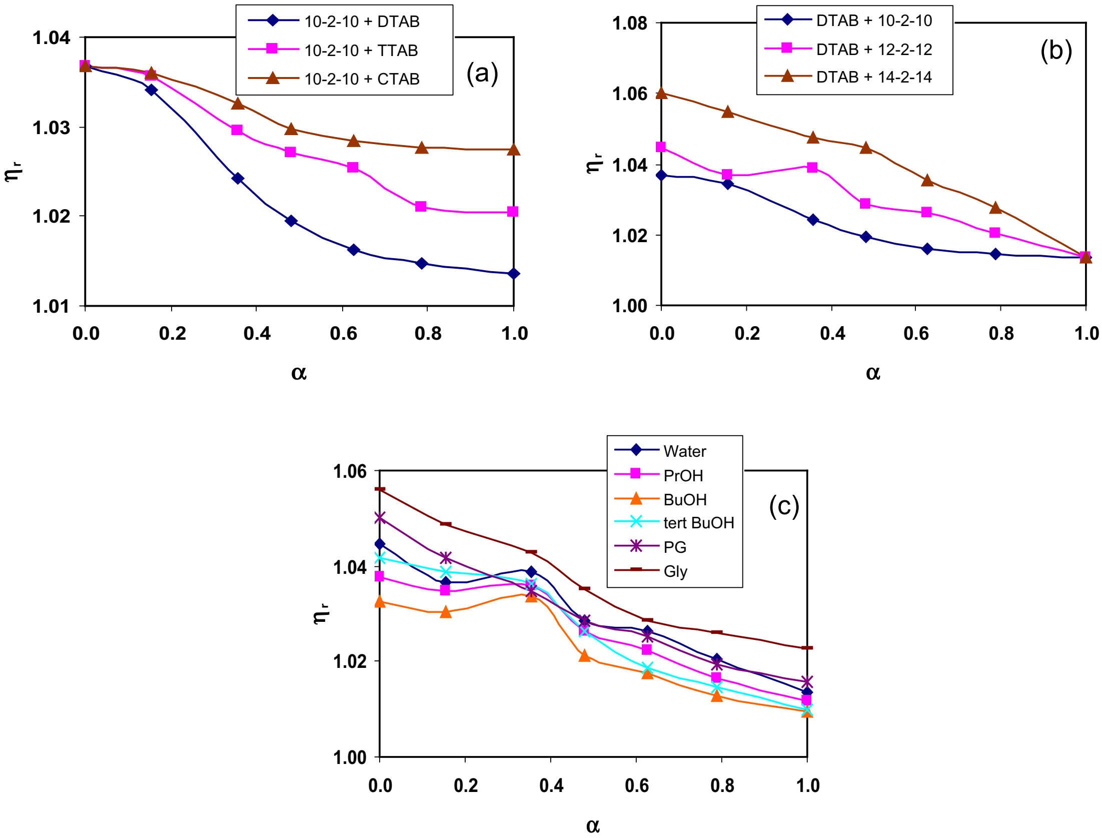


Figure 7 Effect of hydrophobic chain length of (a) monomeric (b) gemini surfactants on the variation of η_r with α in mixed micellar aqueous solutions; (c) variation of η_r with α for the mixture of 12–2–12 + DTAB in the presence 2.5% of different co-solvents at 298.15 K.

surfactant molecules decrease resulting in the decrease in the size of the micellar aggregates (Patel et al., 2009).

3.3.2. *Effect of co-solvents on relative viscosity*

The presence of studied alcohols and glycols (at low concentrations) has marginal affect on the mixed micellar solutions of gemini and monomeric surfactants. For instance, the η_r values are slightly lower in case of PrOH and BuOH whereas slightly higher values have been observed in PG and Gly solutions as compared to those in aqueous solutions (Fig. 7c). The lower values of η_r in the presence of short chain alcohols are due to higher solubility in water and consequently lower solubility in the micelles (Siddiqui et al., 2012). However, an increase in the η_r values has also been reported in case of medium chain length alcohols (C_6-, C_7- and C_8OH) due to their tendency to be embedded among the monomers forming micelles resulting in the significant change in the shape of the micelles (Ansari et al., 2012). Moreover, it has been suggested by Mukerjee (1979) that a solvent is mainly solubilized at the micellar surface. This increases the effective volume V of the hydrophobic chain in Eq. (25) leading to increase in P. It leads to micellar growth and increase in η_r. The sudden rise in η_r for 12–2–12 + DTAB mixture at $\alpha = 0.356$ in the presence of the studied alcohols is more as compared to that in Gly solutions as shown in Fig. 7c. It is due to partitioning of alcohols among the similar hydrophobic chain length monomer units of mixed micelles which leads to reduction in electrostatic repulsions and hence promotes micellar growth.

3.4. *Dynamic light scattering measurements*

DLS measurements have been carried out to obtain further information on the physicochemical properties of the mixed surfactant systems. The size of the micelles formed in aqueous and aqueous co-solvent solutions has been determined by measuring hydrodynamic diameter (D_h) of the micelle using Stokes–Einstein Eq. (1). The D_h values for the studied mixtures at different α values are summarized in Table S7 (Supplementary Information). These D_h values increase with the hydrophobic chain length of the surfactants as shown in Fig. 8a due to the decrease in aggregation number which results in the formation of loose micelles (Varade et al., 2004; Kamboj et al., 2014). These trends are supported by the variation in η_r values with chain length of these surfactants. Moreover, it is evident from the literature that the decrease in electrostatic repulsions between polar head groups of surfactant molecules favors the micellar growth (Li et al., 2010). In aqueous solutions of 10–2–10 + DTAB, D_h values decrease with increase in mole fraction of DTAB. When the hydrophobic chain length of the gemini is increased from 10 to 12, D_h values increase up to $\alpha \approx 0.480$ and then decrease with further increase in α (Fig. 8a). Similar effect on η_r values has been seen from viscosity studies at $\alpha \approx 0.356$. This shows that there are structural transitions of the micelles at these α values which are further supported by the P_{eff} values. A slight rise in D_h values has been seen in mixtures of gemini surfactants with TTAB at $\alpha \approx 0.625$ (Fig. 8b). Similarly, in gemini + CTAB mixtures,

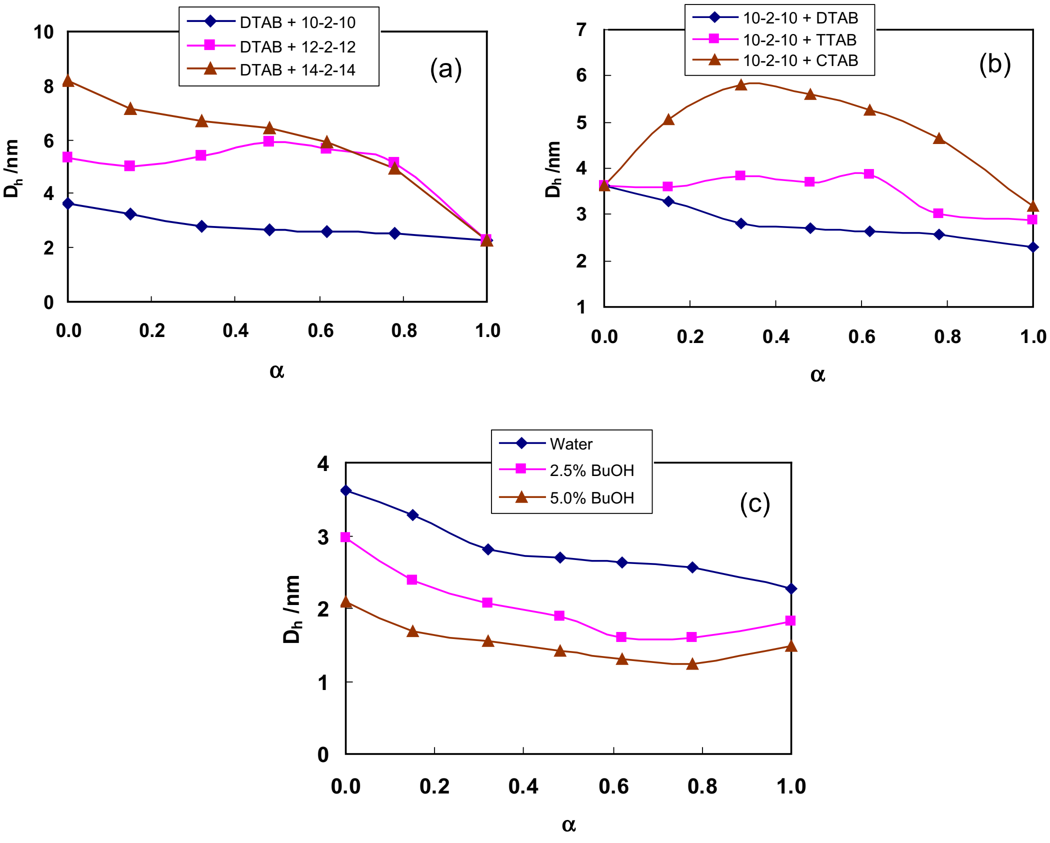


Figure 8 Effect of hydrophobic chain length of (a) gemini and (b) monomeric surfactants on the variation of D_h with α in aqueous mixed micellar solutions; (c) n-butanol (BuOH) on the D_h on the mixed micellar solutions of 10–2–10 + DTAB at 298.15 K.

the D_h values increase initially with α and then decrease with further increase in α (Table S7, Supplementary Information).

The presence of alcohols decreases the D_h values for the mixtures (Fig. 8c) whereas glycols have the opposite effects. These observations are well supported by the variation in the η_r values. The decrease in D_h values in the presence of alcohols is due to penetration of alcohol molecules in the micellar system which results in small mixed aggregates (Tomi et al., 2009; Kuperkar et al., 2011). Further, the decrease is more in case of longer chain alcohol i.e. BuOH which is in accordance with the results obtained from conductivity and surface tension studies. In case of tert BuOH, the polar –OH group is positioned so that it divides the nonpolar organic region into smaller regions that increase its solubility in water i.e. it remains relatively more in aqueous bulk phase and incorporation with micelles is less. D_h values of surfactant mixtures decrease with increase in alcohol percentage (Table S7, Supplementary Information) and are more significant in mixtures with smaller chain length surfactants. Moreover, the relative variation in the D_h with α in the presence of co-solvents follows the similar trends as in aqueous solutions.

In case of glycols, the additional hydroxyl groups tend to decrease number of ordered water molecules around surfactant hydrophobic chain thereby decreasing the hydrophobic effect and hence D_h increases. These observations are further supported by the difference in the partition coefficients of glycols in comparison with that of alcohols as reported by Mullally et al. (2004). Further, the presence of these glycols in the palisade layer of micelles decreases the entropy and the results are in good agreement with those from the conductivity studies. Apart from this, the alkyl chain between the two hydroxyl groups may not be of sufficient length for a favorable interaction with the hydrophobic core of mixed micelles. Hence, the presence of either PG or Gly causes an increase in the D_h values of the studied surfactants and their mixtures.

4. Conclusions

The studies on the mixed micellar characteristics of a series of monomeric and gemini surfactants in aqueous solutions show that in the mixtures of 10–2–10 with monomeric surfactants, the synergistic interactions increase with chain length of monomeric surfactants whereas the mixtures with 12–2–12 and 14–2–14 follow the opposite trend. However, these synergistic interactions decrease with increase in temperature due to disruption of water structure surrounding the hydrophobic groups. Further, the contribution of monomeric surfactant in the mixed micelles decreases with increase in chain length of gemini surfactants as well as temperature.

In 2.5% co-solvents, the synergistic interactions increase and are strongest in case of BuOH among the studied co-solvents. However, in certain mixtures, the synergistic interactions decrease at higher (5.0%) concentration of these co-solvents. The presence of alcohols in mixtures of short chain gemini and monomeric surfactants increases the contribution of monomeric surfactant in the mixed micelles whereas no significant effect is seen in mixtures consisting of longer chain surfactant mixtures. The presence of short chain linear alcohols (PrOH and BuOH) decreases the η_r values of the mixed micelles whereas slight increase in the η_r values has been observed in case of glycols (PG and Gly). The hydrodynamic diameter (D_h) increases with chain length of these surfactants. The alcohols decrease the D_h values of the surfactant mixtures whereas glycols show the opposite effect. The DLS results support the observations from the viscosity studies.

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Appendix A. Supplementary material

Tables containing mixed micellar, surface, thermodynamic, relative viscosity and hydrodynamic diameter data of the mixtures in aqueous and aqueous co-solvent solutions are included. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.arabjc.2015.12.009.

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