RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2014, **4**, 12275

Synthesis of two biofriendly anionic surfactants (*N*-*n*-decanoyl-L-valine and *N*-*n*-decanoyl-L-leucine) and their mixed micellization with nonionic surfactant Mega-10 in Tris-buffer medium at pH 9†

Sibani Das, Susmita Maiti and Soumen Ghosh*

Two biofriendly anionic amino acid surfactants (AAS), *N*-*n*-decanoyl-L-valine (C_{10}-val) and *N*-*n*-decanoyl-L-leucine (C_{10}-leu) were synthesized and mixed micellization of them with nonionic surfactant *N*-decanoyl-*N*-methyl-glucamine (Mega-10) was investigated by tensiometry and fluorimetry in 50 mM Tris-buffer (pH = 9) medium at 298 K. The critical micelle concentration (cmc), surface properties, *e.g.*, Gibbs surface excess (Γ_{max}), area of exclusion per surfactant monomer (A_{min}) and surface pressure at cmc (Π_{cmc}) were determined. Gibbs free energy of micellization (ΔG^0_m) and Gibbs free energy of adsorption (ΔG^0_{ads}) were also determined. Both the free energy values are negative indicating the spontaneity and stability of the mixed micelles. The size of the micelles was determined by dynamic light scattering (DLS) measurements. The deviation of mixed micelles from the ideal behavior was discussed on the basis of Clint, Motomura, Rubingh (regular solution theory), Rosen and Maeda's theory. Rubingh–Holland theory was applied on the ternary systems made by these three surfactants. The compositions of mixed micelle, the activity coefficients and the corresponding interaction parameters were evaluated from these theories. The interaction parameters (β) are negative, indicating attractive interaction between the ionic and nonionic surfactants. The micellar aggregation number (N_{agg}) and micropolarity were evaluated using steady state fluorescence measurements and the packing parameter (P) was determined on the basis of Israelachvili's theory. The standard free energy changes associated with the transfer of surfactant tail due to micellization of pure, binary and ternary combinations of surfactants were determined from Nagarajan's model. We report for the first time in detail the binary and ternary combinations using amino acid based surfactants.

Received 26th August 2013
Accepted 13th January 2014

DOI: 10.1039/c3ra44677h

www.rsc.org/advances

Introduction

Surfactants are widely used in everyday life on a large scale, which can affect aquatic environment. So, biodegradability and biocompatibility are important parts which require functionality of the desired surfactant. There is a pressing need for producing biofriendly surfactants. Amino acid surfactants are widely studied for this purpose as they mimic the structure of natural amphiphiles.[1–3] The spontaneous self-assembly of molecules into supramolecular architectures is a result of various noncovalent interactions such as hydrophobic, hydrogen-bonding, electrostatic, dipole–dipole, and van der Waals interactions. The geometry of the supramolecular aggregates is a result of a delicate balance of two opposing forces: attractive hydrophobic interaction between the tails and electrostatic repulsion between the head groups. Amino acid surfactants (AAS) find manifold applications in food, pharmaceutical, detergent and cosmetic industries as they are surface active, mild, nonirritating to human skin, low toxic and biocompatible.[4–7]

The solution properties of mixed surfactants are often more interesting than those of individual surfactants and have a wide range of applications in industrial preparation, pharmaceutical and medical formulations, enhanced oil recovery process, *etc.* Extensive investigations on binary mixtures of cationic–cationic,[8–11] cationic–anionic,[11–14] cationic–nonionic,[11,15–20] anionic–anionic,[11,21,22] anionic–nonionic[11,23–25] and nonionic–nonionic[11,20,26,27] surfactants have been reported and analyzed in the light of Clint,[28] Rubingh,[29] Rosen,[30] Motomura[31] and Maeda's[32] theories to understand the synergism and antagonism of binary compositions. A theoretical approach of a regular solution and molecular thermodynamic theory has been applied on a ternary mixture to determine the cmc and other micellar

---

Centre for Surface Science, Department of Chemistry, Jadavpur University, Kolkata-700 032, India. E-mail: gsoumen70@hotmail.com; Fax: +91 33 24146266

† Electronic supplementary information (ESI) available: Plots of composition dependent cmc and area minimum values for ternary systems and different surface and thermodynamic properties of binary combinations of surfactants. Different theoretical treatments and their corresponding data are also available in the ESI. See DOI: 10.1039/c3ra44677h

interaction parameters, shape and size of the mixed micelles. Such approach on ternary combinations is limited.[8,20,33]

AAS are widely used as low-molecular-mass organogelators (LMOG). The interfacial and bulk properties of the amino acid amphiphiles have been studied by many groups,[34–36] but their mixed micellar behavior has not been amply explored. Mega-10 is an alkylpolyglucoside. It has a hydrophilic sugar moiety and a hydrophobic alkanoyl chain. With increase in temperature, it cannot be clouded in aqueous solution. Mixed micellization of Mega-10 with cationic (alkyltrimethylammonium bromides, ATABs), anionic (sodium dodecylsulfate, SDS) and nonionic (poly(oxyethylene)alkyl ethers) have been reported earlier.[18,26,37,38]

Performance limitations of conventional surfactants have initiated an interest to alternate surfactant structures. From an environmental perspective, it is desirable to select biofriendly surfactants. We have therefore, synthesized two amino acid amphiphiles (C_{10}-val and C_{10}-leu) and for the first time performed tensiometric measurements on their various binary and ternary combinations with Mega-10 in Tris-buffer (50 mM) medium (pH = 9) to learn about the influence of amino acid surfactants on the micellization of nonionic surfactant, Mega-10. Detailed fundamental studies of multicomponent biocompatible surfactants are limited. The mutual interaction among the surfactants arises from the difference of the type and length of the amphiphile tail and the electrostatic and steric interactions between the head groups. In our study, the tails of all the surfactants are the same (constituting 10 carbon atoms in the linear chain), but they differ in the type and size of the head groups; there is a glucamide moiety (secondary amide linkage) in Mega-10; there are primary amide linkages at the juncture of the polar head and non-polar tail in both C_{10}-val and C_{10}-leu. We can systematically control the head group because surfactants derived from different amino acids have different head groups. Attempts have been taken to investigate the thermodynamics and interfacial adsorption parameters from tensiometric measurements, the aggregation number and polarity index of the micellar media from fluorimetry. In addition, the shape of the micelle can be predicted from the packing parameter and dynamic light scattering (DLS) measurements. The micellar compositions, critical micelle concentration (cmc) and interaction parameters for the binary systems were analyzed in the light of Clint's theory, Rubingh model based on the regular solution theory and Rosen and Motomura models. Stability and excess free energy of micellization of ionic–nonionic systems have been explained using Maeda's theory. The mixed micellar properties of the ternary system were analyzed on the basis of Rubingh–Holland theory. Nagarajan's model was applied to calculate the different contributions to the standard free energy due to micellization.

Experimental

Materials and methods

Thionyl chloride (purity, 98%), sodium hydroxide, sodium sulfate, triethylamine (purity, 98%), L-valine (purity, 99%) and L-leucine (purity, 99%) were purchased from SRL, India and solvents (methanol, chloroform, tetrahydrofuran, ethyl acetate and petroleum ether) were purchased from Merck, India. The solvents were freshly distilled before use. Decanoyl chloride (purity, 98%) and *N*-decanoyl-*N*-methyl-glucamine (Mega-10, 99.8%) are products of Aldrich. Tris(hydroxymethyl)aminomethane (Tris-buffer) was purchased from Merck. Cetylpyridinium chloride (CPC, purity = 99%) and pyrene were purchased from Aldrich. Pyrene was recrystallised before use.

Synthesis

Two amino acid amphiphiles, *N*-*n*-decanoyl-L-valine (C_{10}-val) and *N*-*n*-decanoyl-L-leucine (C_{10}-leu) were synthesized, purified and recrystallised by following the procedure reported by Miyagishi *et al.*[39,40] Scheme 1 for the synthesis is given below.

Preparation of L-amino acid methyl ester hydrochloride

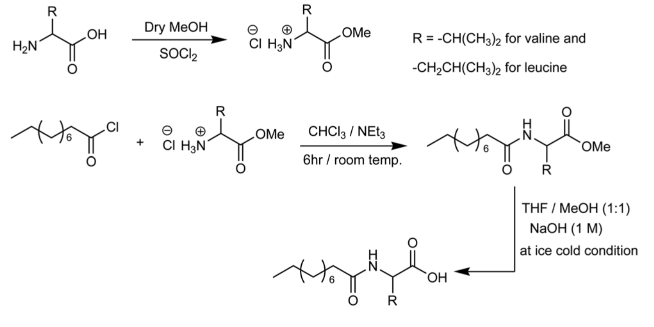
L-Amino acids (35 mmol) were added to 50 ml of ice cold methanol. Then thionyl chloride was added to it dropwise until the amino acid was completely dissolved and stirred for 24 h. The excess solvent was evaporated under reduced pressure and the white solid of L-amino acid methyl ester hydrochloride (31.85 mmol) was obtained.

Preparation of *N*-*n*-decanoyl-L-amino acid methyl ester

N-*n*-Decanoyl-L-amino acid methyl ester hydrochloride (17.91 mmol) was separately dispersed in 25 ml chloroform. 39.2 mmol NEt_3 was added dropwise to the ice cold solution and stirred. Then 10 ml chloroform solution of *n*-decanoyl chloride was added to it dropwise and the mixture was stirred at rt for 6 h. After completion of the reaction (checked from TLC), the reaction mixture was diluted with 50 ml chloroform and acidified with 1 (N) HCl. The organic layer was extracted with 0.5 (M) $NaHCO_3$ solution and finally with brine solution. The organic layer was taken on anhydrous Na_2SO_4 and shaken vigorously and filtered. Then the solvent was evaporated and the product was obtained as white powder.

Preparation of *N*-*n*-decanoyl-L-amino acid

N-*n*-Decanoyl-L-amino acid methyl ester (10.52 mmol) was dissolved in 15 ml THF–MeOH (1 : 1) and 1 (M) NaOH (10 ml) was added to it under ice cold conditions. The reaction mixture was stirred for 2 h and then acidified with 1 (N) HCl and extracted



Scheme 1 Synthetic path of amino acid amphiphiles.

with ethyl acetate. The organic layer was collected over anhydrous Na_2SO_4, shaken vigorously and filtered. Then the solvent was evaporated. White crystallized solid (7.57 mmol) was obtained after recrystallization of the crude product from ethyl acetate–petroleum ether (40 °C–60 °C).

Characterization

***N-n*-Decanoyl-L-valine.** Yield 2.1 g, 7.57 mmol, 72%; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm): 0.80–0.89 (t, terminal CH_3, 3H), 0.91–1.02 (t, CH_3, β to C_α, 6H), 1.25 (bs, $(CH_2)_6$, 12H), 1.55–1.70 (m, CH_2, β to –CONH, 2H), 2.17–2.3 (m, CH_2, α to –CONH, 2H and *CH*, attached to C_α, 1H), 4.56–4.65 (q, *CH*, –NHC*H*, 1H), 6.17–6.26 (d, –CON*H*, 1H), 9.4 (bs, –COOH, 1H). ^{13}C-NMR ($CDCl_3$, 300 MHz): δ (ppm): 14.05, 17.68, 18.94, 22.63, 25.78, 29.20, 29.23, 29.28, 29.42, 31.05, 31.83, 36.62, 57.06, 174.36, 175.17. IR (KBr): ν (cm^{-1}) = 3312.20, 2920.80, 2852.78, 1707.23, 1605.09, 1555.0.

***N-n*-Decanoyl-L-leucine.** Yield 2.08 g, 7.2 mmol, 70%; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm): 0.77–0.91 (t, terminal CH_3, 3H), 0.95–1.04 ((t, CH_3, β to C_α, 6H), 1.25 (bs, (CH_2)6, 12H), 1.54–1.77 (m, CH_2, β to –CONH, 2H, CH2 α to C_α, 2H and CH, β to C_α, 1H), 2.23–2.36 (t, CH_2, α to –CONH, 2H), 4.64–4.77 (q, CH, –NHCH, 1H), 6.27–6.33 (d, –CONH, 1H), 9.19 (bs, –COOH, 1H). ^{13}C-NMR ($CDCl_3$, 300 MHz): δ (ppm): 14.07, 21.84, 22.64, 22.81, 24.9, 25.69, 29.17, 29.24, 29.3, 29.43, 31.85, 36.34, 41.11, 51.0, 174.55, 176.26. IR (KBr): ν (cm^{-1}) = 3337.71, 2926.76, 2863.63, 1700.0, 1622.53, 1557.35.

Tensiometry. Tensiometric measurements were taken with a du Noüy tensiometer (Krüss, Germany) using the platinum ring detachment method. 5 ml of Tris-buffer solution (50 mM and pH = 9) was taken in a double-wall jacketed container and connected with a thermostated water bath (accuracy, ±0.1 K) at the requisite temperature of 298 K. Then individual and mixed surfactant solution of known concentration was added progressively. During such measurements, 15 min time interval for equilibration was allowed after the surfactant addition and thorough mixing. The cmc values were estimated from the break points in the surface tension-log [surfactant] plots. The determined surface tension (γ) values were accurate within ±0.1 mN m^{-1}.

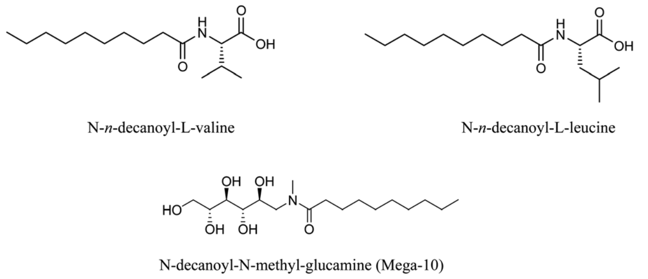
Fluorimetry. Fluorescence measurements were taken using Perkin Elmer LS55 fluorescence spectrophotometer. The temperature was kept at 298 K using a water-flow thermostat connected to the cell compartment. In all cases, the concentration of surfactant was used above the cmc. Pyrene was excited at 332 nm and its emission was recorded at 373 and 384 nm, which corresponded to the first and third vibrational peaks, respectively. The excitation and emission slits were 9 and 4 nm, respectively. A scan speed of 250 nm min^{-1} was used. The aggregation number (N_{agg}) was determined by a fluorescence quenching study of pyrene by cetylpyridinium chloride (CPC). The pyrene solution was added to the individual and mixed micellar solutions of surfactants. The probe concentration was kept low enough to avoid eximer formation. The quencher was added progressively and the intensity was recorded for data analysis.

Dynamic light scattering. DLS measurements were taken in a Malvern Zetasizers Nano-zs apparatus with a He-Ne laser (λ = 632 nm) at 298 K. Before the experiment, the surfactant solutions were filtered through cellulose acetate paper of pore size 0.45 μm.

Results and discussion

Critical micelle concentration (cmc)

In aqueous solution, the surfactants are preferentially adsorbed at the air–water interface and decrease the surface tension (γ) of water owing to their amphiphilic character. The surfactant monomers are aggregated with the help of attractive hydrophobic interaction in the tail after a threshold concentration of the surfactant. There is an equilibrium between the surfactant monomer and aggregates. These aggregates are called micelles and the corresponding threshold concentration is called critical micelle concentration (cmc). The corresponding surface tension is known as γ_{cmc}. Actually, γ_{cmc} is the measure of efficiency of the surfactant to populate the air–water interface. The cmc values of individual surfactants (structures of three surfactants are shown in Scheme 2) and different combinations of binary (C_{10}-val/Mega-10, C_{10}-leu/Mega-10 and C_{10}-val/C_{10}-leu) and ternary mixtures (C_{10}-val/C_{10}-leu/Mega-10) in the Tris-buffer medium (pH = 9) have been determined from the plot of γ *vs.* log[surfactant] (Fig. 1). The nonionic surfactant, Mega-10 has a smaller cmc value compared to the two ionic surfactants. The values are reported in Tables 1 and S1.† Mixed micellization processes of such binary and ternary combinations have not been reported earlier. In case of binary and ternary mixtures, the cmc values increase gradually with increasing composition of the ionic surfactants. These are similar to the reports on binary and ternary combinations of the following: sodium dodecylsulfate (SDS), polyoxyethylenesorbitan monolaurate (Tween-20) and polyoxyethylene lauryl ether (Brij-35);[33] cetylpyridinium chloride (CPC), polyoxyethylenesorbitan monopalmitate (Tween-40) and polyoxyethylene cetyl ether (Brij-56).[20] Tables 1A and S1† shows that the cmc values of the binaries lie between the individual values of the surfactants. From Table 1B, it was observed that the cmc values of the ternaries increase systematically with increasing proportion of C_{10}-val in the mixture. The dependence of cmc on the different combinations of the ternary mixture of C_{10}-val/C_{10}-leu/Mega-10 is illustrated in Fig. S1† in three dimensions. The base points of the prism



Scheme 2

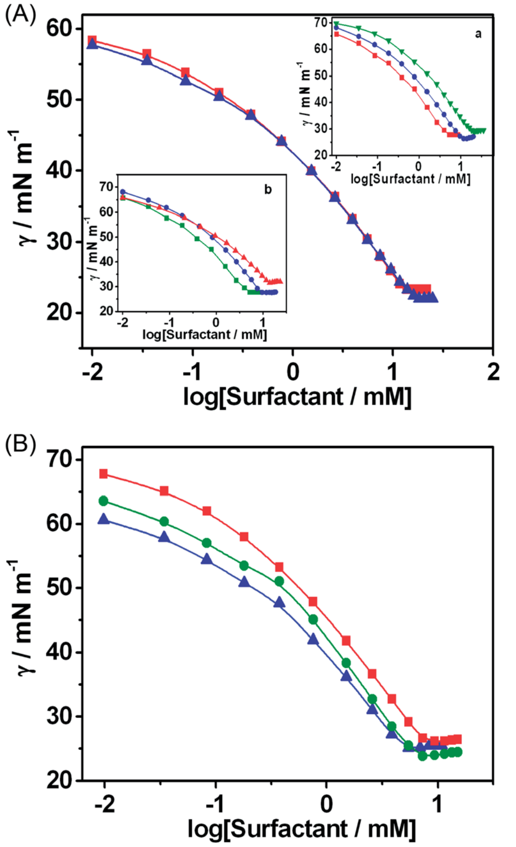


Fig. 1 (A) Determination of the cmc of binary combinations of C_{10}-val/C_{10}-leu at different mole fractions (■, $X_{C10\text{-val}} = 0.1$ and ▲, $X_{C10\text{-val}} = 0.9$) at 298 K. Inset: (a) C_{10}-val/Mega-10 (■, $X_{C10\text{-val}} = 0$, ●, $X_{C10\text{-val}} = 0.9$, ▲, $X_{C10\text{-val}} = 1$) and (B) C_{10}-leu/Mega-10 (■, $X_{C10\text{-leu}} = 0$, ●, $X_{C10\text{-leu}} = 0.9$, ▲, $X_{C10\text{-leu}} = 1$). (B) Determination of the cmc of ternary combinations of C_{10}-val/C_{10}-leu/Mega-10 at different mole fractions (▲, $X_{C10\text{-val/C10-leu/Mega-10}} = 0.125/0.25/0.625$, ●, 0.25/0.625/0.125 and ■, 0.625/0.125/0.25) at 298 K.

represent the compositions of the surfactants on triangular coordinates and the heights show the corresponding cmc values. A multifold profile is obtained; the trend of the molecular interaction dependent micellization process of the ternary mixture is complex and non-ideal in nature.

Adsorption at the air–water interface

Surfactants orient at the air–water interface and the interfacial adsorption per unit area of the surface at different concentrations can be evaluated using Gibbs adsorption equation. The efficiency of the surfactant molecule to populate the air–water interface in the form of monolayer can also be predicted from the Gibbs surface excess ($\Gamma_{\max}$).

$$\Gamma_{\max} = -\frac{1}{2.303\ nRT}\left[\frac{d\gamma}{d\log C}\right] \tag{1}$$

where R and T are the universal gas constant and absolute temperature, respectively, C is the concentration of surfactant taken and n is the effective number of species present in the solution. The C_{10}-val and C_{10}-leu produced two species each. The value of n in the binary mixtures of the surfactants was obtained from the following relation,

$$n = \sum pX_i \tag{2}$$

where X_i is the stoichiometric mole fraction and p is the number of species. Assuming complete monolayer formation at cmc, the minimum area per surfactant molecule at the air–water interface ($A_{\min}$) was calculated from the equation:

$$A_{\min} = \frac{10^{18}}{N_A \Gamma_{\max}} \tag{3}$$

where N_A is Avogadro's number. The $\Gamma_{\max}$ and $A_{\min}$ values for the binary and ternary combinations are presented in Tables 1A, B and S1,† respectively. For the binary mixtures, the $\Gamma_{\max}$ values gradually decrease with increasing concentration of ionic surfactants in the mixtures except for the C_{10}-val/C_{10}-leu combinations. In the latter case, the $\Gamma_{\max}$ value is almost constant. The $A_{\min}$ values of the mixtures are in the reverse order. The $A_{\min}$ of ionic surfactants are greater than that of Mega-10 due to the presence of electrostatic repulsion between the ionic head groups. The structural difference in the head group region affects the interaction between the surfactants. C_{10}-leu has an isobutyl group near the head group which requires a greater area of exclusion (0.95 nm^2 per molecule) than C_{10}-val (0.79 nm^2 per molecule), which contains an isopropyl group. The head group areas of the binary mixtures were in between those of pure components. The C_{10}-val/C_{10}-leu combinations have a higher area than that of other binary mixtures indicating an antagonistic or repulsive interaction between the head groups of the two anionic amphiphiles. For the ternary mixtures, both $\Gamma_{\max}$ and $A_{\min}$ are independent of the sample compositions. The dependence of $A_{\min}$ on the composition of the ternary system is displayed in 3-D form in Fig. S2.† The base points of the prism represent the compositions of the surfactants on triangular coordinates and the heights show the corresponding $A_{\min}$ values. Like in Fig. S1,† here a multifold profile has also been obtained. The surface pressure, Π_{cmc} was calculated from

$$\Pi_{\text{cmc}} = \gamma_{\text{sol}} - \gamma_{\text{cmc}} \tag{4}$$

where γ_{sol} and γ_{cmc} are the surface tension of the solvent without surfactant and the surface tension of the solvent including surfactant at the cmc respectively. All interfacial properties ($\Gamma_{\max}$, $A_{\min}$ and Π_{cmc}) are presented in Tables 1 and S1.†

Thermodynamics of micellization and interfacial adsorption

The standard free energy of micellization per mole of monomer unit, ΔG_m^0 for the binary and ternary mixtures can be calculated from the regular solution theory using

$$\Delta G_m^0 = RT \ln X_{\text{cmc}} \tag{5}$$

where X_{cmc} is the cmc of the solutions in a mole fraction unit. The values of ΔG_m^0 obtained using the above equation is given in Tables 1 and S1.† The free energy of micellization (ΔG_m^0) is negative indicating the spontaneity of micelle formation and

Table 1 (A) Surface and thermodynamic properties of binary mixtures of C_{10}-val/Mega-10 in Tris-buffer medium (pH = 9) at 298 K. (B) Surface and thermodynamic properties of different ternary mixtures in Tris-buffer medium (pH = 9) at 298 K

A

$X_{C10\text{-val}}$/ $X_{C10\text{-leu}}$	cmc/(mM)	10^6 Γ_{max} mol^{-1} m^{-2}	A_{min} nm^{-2} per molecule	$A_{min}{}^{i}$ nm^{-2} per molecule	γ_{cmc} mN^{-1} m^{-1}	pC_{20}	$\frac{cmc}{C_{20}}$	Π_{cmc} mN^{-1} m^{-1}	$-\Delta G^0_m$ kJ^{-1} mol^{-1}	$-\Delta G^0_{ads}$ kJ^{-1} mol^{-1}
0	4.63	4.27	0.39	—	27.9	3.47	13.7	42.4	23.3	33.2
0.1	4.86	3.18	0.52	0.57	25.7	3.43	13.01	37.8	23.2	35.1
0.3	5.33	2.99	0.56	0.59	26.8	3.56	19.4	43.2	22.9	37.4
0.5	5.71	2.90	0.57	0.61	25.6	3.43	15.4	44.6	22.8	38.2
0.7	7.44	2.85	0.58	0.63	24.9	3.24	12.9	45.2	22.1	38.0
0.9	11.3	2.25	0.74	0.68	25.6	3.12	14.8	43.8	21.1	40.5
1	16.9	2.11	0.79	—	29.4	2.80	10.7	40.9	20.1	39.5

B

$X_{C10\text{-val}/C10\text{-leu/Mega-10}}$	cmc/(mM)	10^6 Γ_{max} mol^{-1} m^{-2}	A_{min} nm^{-2} per molecule	γ_{cmc} mN^{-1} m^{-1}	pC_{20}	$\frac{cmc}{C_{20}}$	Π_{cmc} mN^{-1} m^{-1}	$-\Delta G^0_m$ kJ^{-1} mol^{-1}	$-\Delta G^0_{ads}$ kJ^{-1} mol^{-1}
0.125/0.25/0.625	5.15	2.99	0.56	25.1	3.35	11.5	40.7	23.0	36.6
0.125/0.625/0.25	6.58	2.40	0.69	22.5	3.25	11.7	41.1	23.1	40.2
0.25/0.125/0.625	4.88	3.30	0.50	24.3	3.41	12.3	44.1	23.1	36.5
0.25/0.625/0.125	7.84	2.48	0.67	25.1	3.26	14.3	45.0	22.0	40.1
0.333/0.333/0.333	5.91	2.87	0.58	24.3	3.31	12.1	43.9	22.7	38.0
0.625/0.125/0.25	6.58	2.70	0.61	23.0	3.30	13.1	44.0	22.4	38.7
0.625/0.25/0.125	9.18	2.17	0.76	25.9	3.24	16.0	42.7	21.6	41.3

becomes less negative with increasing concentration of the ionic surfactant in the binary mixture except for that of C_{10}-val/C_{10}-leu mixtures where there are almost constant values of ΔG^0_m *i.e.*, equal spontaneity of micellization is obtained. The ΔG^0_m values of binary ionic mixtures are slightly lower than those of ionic/nonionic combinations. Ternary mixtures also show equal spontaneity of micellization. A similar type of observation is also obtained in previous works.[20]

The standard free energy of interfacial adsorption at the air–water interface was calculated from the following equation

$$\Delta G^0_{ads} = \Delta G^0_m - \frac{\Pi_{cmc}}{\Gamma_{max}} \tag{6}$$

The higher the negative value of ΔG^0_{ads}, the higher is the efficiency of the surfactant to be adsorbed at the surface. The results are presented in Table 1 and S1.† The magnitude of ΔG^0_{ads} is more negative than ΔG^0_m, indicating that adsorption at air–water interface is more spontaneous than micellization. C_{10}-leu is more surface-active than C_{10}-val. In the case of C_{10}-val/Mega-10 and C_{10}-leu/Mega-10 systems, ΔG^0_{ads} increase with increasing concentration of ionic surfactant in the mixture, whereas in the C_{10}-val/C_{10}-leu mixtures, equal values of ΔG^0_{ads} are obtained. The values of ΔG^0_m and ΔG^0_{ads} for ternary mixtures are comparable with binary systems.

Another physical parameter pC_{20} is defined as pC_{20} = −log C_{20}, where C_{20} is the molar concentration of the surfactant which is required to decrease the surface tension of the solvent by 20 mN m^{-1}. The parameter pC_{20} is the measure of surface activity of a surfactant. The higher the pC_{20} value, the more efficiently the surfactant can adsorb at the air–water interface and reduces the interfacial tension or the surface tension.[24] From Tables 1 and S1† we obtained the pC_{20} values of Mega-10, C_{10}-val and C_{10}-leu as 3.47, 2.80 and 3.03, respectively. The values indicate that Mega-10 is more surface-active than the ionic surfactants. Generally, the efficiency of adsorption of nonionic surfactant is much greater than in ionic surfactants with the same number of carbon atoms in the hydrophobic group. Because in the adsorption of ionic surfactants, the electrical repulsion between the ionic head groups of surfactant ions is already at the interface and the similarly charged oncoming surfactant ions increase the positive free energy of transfer of the hydrophilic head from the interior of the bulk phase to the interface. The $\frac{cmc}{C_{20}}$ ratio is considered as a measure of the tendency of the surfactant to adsorb at the interface relative to its micellization tendency. The values of pC_{20} and $\frac{cmc}{C_{20}}$ for the different binary and ternary compositions are close to each other and are shown in Tables 1 and S1.†

Aggregation number (N_{agg}) and micropolarity

The aggregation numbers of the individual surfactants and the binary and ternary mixtures (C_{10}-val/Mega-10, C_{10}-leu/Mega-10, C_{10}-val/C_{10}-leu and C_{10}-val/C_{10}-leu/Mega-10) were determined using the steady state fluorescence quenching method where pyrene was used as a fluorescence probe. This method is based on the quenching of the fluorescence probe by a known concentration of the quencher. The aggregation number of surfactants was determined using the equation

$$\ln\left(\frac{I_0}{I}\right) = \frac{N_{agg}[Q]}{[S] - cmc} \tag{7}$$

where I_0 and I are the fluorescence intensities of the surfactant in absence and presence of quencher, respectively. [S] and [Q]

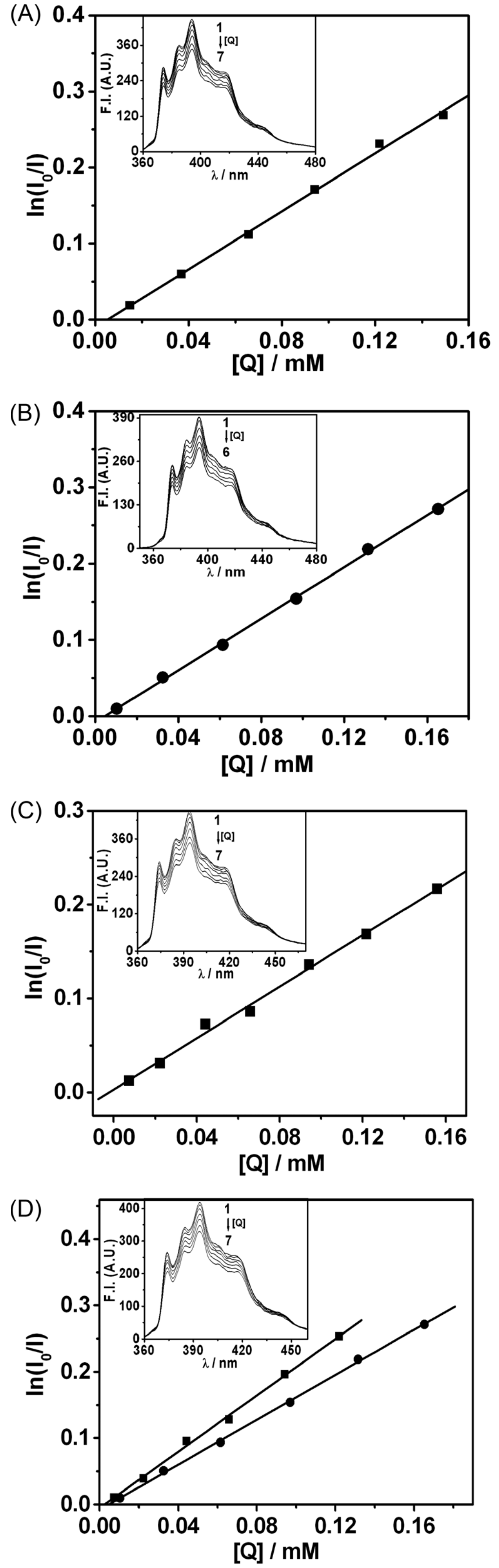


Fig. 2 (A) Plot of ln(I_0/I) *vs.* [Q] for C_{10}-val/Mega-10 ($X_{\text{C10-val}} = 0.5$). Inset: corresponding basic spectrum. (B) Plot of ln(I_0/I) *vs.* [Q] for C_{10}-leu/Mega-10 ($X_{\text{C10-leu}} = 0.7$). (C) Plot of ln(I_0/I) *vs.* [Q] for C_{10}-val/C_{10}-leu ($X_{\text{C10-val}} = 0.7$). Inset: corresponding basic spectrum. (D) Plot of ln(I_0/I) *vs.* [Q] for C_{10}-val/C_{10}-leu/Mega-10 (■, $X_{\text{C10-val/C10-leu/Mega-10}} = 0.125/0.625/0.25$ and ●, $X_{\text{C10-val/C10-leu/Mega-10}} = 0.625/0.125/0.25$). Inset: corresponding basic spectrum.

are the concentrations of the surfactant and quencher (CPC), respectively. The aggregation number, N_{agg}, is obtained from the fitting of fluorescence intensity data at various concentrations of a quencher. The aggregation numbers of C_{10}-val, C_{10}-leu and Mega-10 are 84, 52 and 91, respectively.

The Stern–Volmer equation was used to calculate the equilibrium constant (K_{SV}) for the interaction between fluorescence probe and quencher.

$$\frac{I_0}{I_Q} = 1 + K_{\text{SV}}[Q] \tag{8}$$

In the present study, a good linear plot (Fig. 2) was obtained and K_{SV} was found from the slope of the plot of (I_0/I_Q) *vs.* [Q]. The values of N_{agg} and K_{SV} were listed in Tables 2 and S2.† The aggregation number of the C_{10}-leu/Mega-10 and C_{10}-val/C_{10}-leu systems decreases with increasing concentration of C_{10}-leu and this is reasonable. The aggregation number of C_{10}-val/Mega-10 and ternary combinations is independent of the composition of amphiphiles. N_{agg} can be calculated by following the mixing rationale

$$N_{\text{agg}}^{\text{calcd}} = \sum X_i {N_{\text{agg}}}^i \tag{9}$$

where ${N_{\text{agg}}}^i$ is the individual aggregation number of the ionic and nonionic surfactants and X_i is the stoichiometric mole

Table 2 Values of aggregation number, Stern–Volmer constant, micropolarity, hydrodynamic diameter and diffusion coefficients of different (A) binary and (B) ternary mixtures in tris-buffer medium (pH = 9) at 298 K

$X_{\text{C10-val}}$/ $X_{\text{C10-leu}}$	$N_{\text{agg}}^{\text{obs}}$/ $N_{\text{agg}}^{\text{cal}}$	10^4 K_{SV}/L^{-1} mol^{-1}	I_1/I_3	D_{h}/nm (PDI)	$D_0 \times 10^{11}$ m^2 s^{-1}
0	91	2.35	0.84	6.30 (0.28)	7.78
0.1	93/87	2.43	0.82	3.60 (0.24)	13.6
0.3	76/79	2.05	0.79	2.90 (0.36)	16.9
0.5	69/71	1.53	0.77	2.70 (0.31)	18.2
0.7	63/64	1.73	0.77	2.70 (0.23)	18.2
0.9	60/56	1.72	0.73	2.70 (0.35)	18.2
1	52	1.67	0.72	2.60 (0.21)	18.9

$X_{\text{C10-val}}$/ $X_{\text{C10-leu}}$/ $X_{\text{Mega-10}}$	$N_{\text{agg}}^{\text{obs}}$/ $N_{\text{agg}}^{\text{cal}}$	10^4 K_{SV} L^{-1} mol^{-1}	I_1/I_3	D_{h}/nm (PDI)	$D_0 \times 10^{11}$ m^2 s^{-1}
0.125/0.25/0.625	79/80	2.07	0.79	2.32 (0.34)	21.1
0.125/0.625/0.25	77/66	2.07	0.76	2.38 (0.36)	20.6
0.25/0.125/0.625	78/84	2.04	0.80	2.33 (0.21)	21.1
0.25/0.625/0.125	77/65	2.17	0.77	2.38 (0.28)	20.6
0.333/0.333/0.333	82/76	2.21	0.76	2.67 (0.33)	18.7
0.625/0.125/0.25	90/82	2.42	0.78	2.33 (0.32)	21.1
0.625/0.25/0.125	67/77	1.95	0.77	2.34 (0.23)	21.1

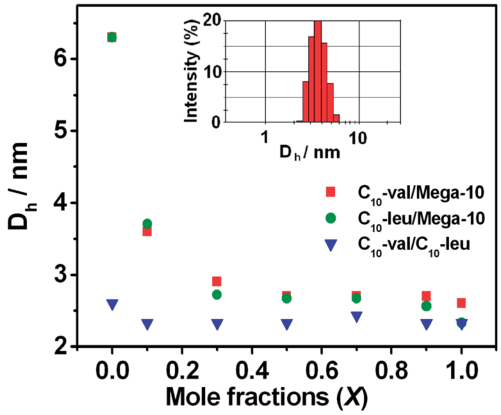


Fig. 3 Variation of the hydrodynamic diameter (D_h) with mole fractions of surfactants (X) Inset. Representative plot for the size distribution of C_{10}-leu/Mega-10 ($X_{C10\text{-leu}} = 0.3$).

fraction. Good agreement is found between the observed and calculated aggregation number (Tables 2 and S2†).

The microstructures of the micelles are often explained by the important micro environmental property, called micropolarity. It is obtained from the ratio of first and third vibronic peak of pyrene (I_1/I_3). The micropolarity values range from ≈1.9 in polar solvent to ≈0.6 in hydrocarbon. The experimentally obtained values of micropolarity are within 0.72 to 0.84 which is close to 0.6; *i.e.*, pyrene is preferentially solubilized in the hydrophobic region.[41] Thus, the polarity sensed by the probe could give information on the polarity in this micellar region. From Tables 2 and S2,† it is observed that the polarity index decreases with increasing concentration of ionic surfactant in the mixture of C_{10}-val/Mega-10 and C_{10}-leu/Mega-10, indicating that pyrene senses more hydrophobic environment. The decrease of micellar diameter is more prominent than the decrease of aggregation number from Mega-10 to ionic surfactants. As a result, more compact micelles are formed with increasing concentration of ionic surfactant, that is, hydrophobicity increases. Penetration of solvent in Mega-10 micelle is easier than the micelle of ionic surfactants. So, pyrene senses more hydrophobicity in ionic surfactants than in Mega-10 and the polarity decreases with increasing concentration of ionic surfactants.

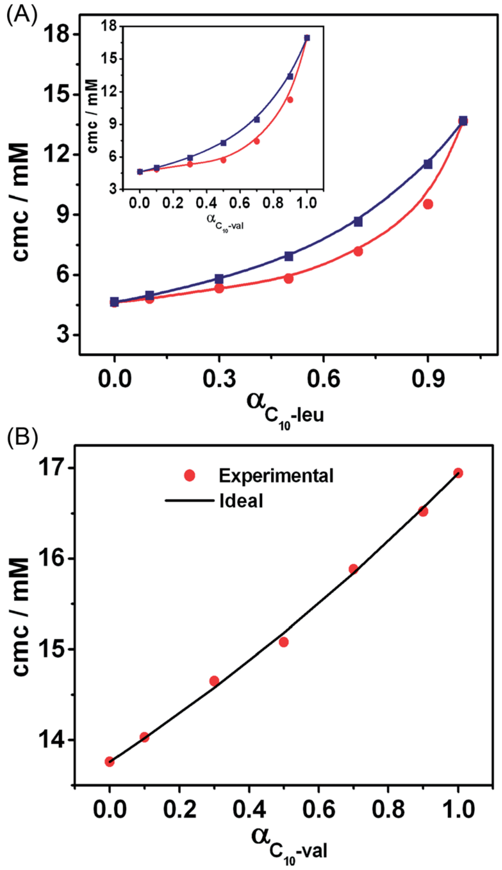


Fig. 4 (A) Variation of the ideal and experimental cmc with mole fraction for C_{10}-leu/Mega-10 binary mixture. Inset: variation of the ideal and experimental cmc with mole fraction for C_{10}-val/Mega-10 binary mixture. (B) Variation of the ideal and experimental cmc with mole fraction for C_{10}-val/C_{10}-leu binary mixture.

Hydrodynamic diameter (D_h) and diffusion coefficient (D_0)

The hydrodynamic diameters of all binary and ternary systems were determined using DLS measurement. The instrument measures the diffusion coefficient (D_0) of micellar systems and evaluates the hydrodynamic diameter (D_h) in term of the Stoke–Einstein equation

$$D_0 = \frac{kT}{6\pi\eta R_h} \tag{10}$$

where k is the Boltzmann constant, T is the absolute temperature, η is the viscosity of solution and R_h (= D_h/2) is the hydrodynamic radius. The D_0 values are reported in Tables 2 and S2.† For binary mixtures, an increasing tendency of D_0 with increasing the mole fractions of ionic surfactant is observed; although in a few cases, constant values of D_0 are also obtained. For ternary mixtures, constant values of D_0 are obtained. The hydrodynamic diameter of the micelle of Mega-10 is quite higher (6.30 nm) than that obtained from two ionic surfactants (2.33 nm for C_{10}-val and 2.6 nm for C_{10}-leu). The corresponding polydispersity index (PDI) values (in the parenthesis) are also reported in Tables 2 and S2.† The hydrodynamic diameters of all binary and ternary compositions are close to each other. The hydrodynamic diameter of pure and mixed surfactants indicates a spherical shape of the micelle. The low PDI value for all combinations indicates monodispersity of the solution. The variations of the

Table 3 Micellar compositions ($X_M/X_R/X_I^{\sigma}$), interaction parameters (β_R/β^{σ}), activity coefficients (f_R) and cmc's of binary mixtures at 298 K by Motomura, Rubingh and Rosen methods at different stoichiometric compositions (X_i) of C_{10}-val/Mega-10

$X_{C10\text{-val}}$	$X_M/X_R/X_I^{\sigma}$	β_R/β^{σ}	$f_R^{C10\text{-val}}$	$f_R^{Mega\text{-}10}$	cmc/mM obsd/Clint
0.1	0.02/0.05/0.46	−0.69/−9.39	0.54	1.00	4.86/4.99
0.3	0.22/0.17/0.51	−0.88/−6.94	0.54	0.97	5.33/5.92
0.5	0.23/0.31/0.55	−1.25/−5.85	0.55	0.89	5.71/7.27
0.7	0.27/0.43/0.61	−0.98/−4.40	0.73	0.83	7.44/9.42
0.9	0.78/0.66/0.73	−0.80/−2.61	0.91	0.70	11.3/13.4

hydrodynamic diameter with the mole fraction of surfactant for three binary combinations are shown in Fig. 3.

Mutual interaction of surfactants in micelles

Mixed micelles can be both ideal and nonideal. The ideal behavior of the mixed micelles can be explained by the equation[28]

$$\frac{1}{C_\mathrm{m}} = \sum_{i=1}^{n} \frac{X_i}{f_i C_i} \tag{11}$$

where C_i and C_m denote the critical micellar concentrations of the ith component and the mixture, respectively; X_i is the stoichiometric mole fraction of the ith component in solution and f_i is the activity coefficient. For ideal mixed micelle, $f_i = 1$ and eqn (11) becomes Clint's equation and it is

$$\frac{1}{C_\mathrm{m}} = \sum_{i=1}^{n} \frac{X_i}{C_i} \tag{12}$$

In the case of eqn (11), the value of f_i is necessary to determine cmc, but eqn (12) is straightforward for evaluating the cmc. The cmc of the binary and ternary mixtures can be predicted from the knowledge of cmc of the individual surfactants. This is useful for a comparison between ideal and nonideal mixtures. The ideal cmc values of the binary mixtures using eqn (12) were reported in Tables 3 and S3.† The calculated values for the binary systems, C_{10}-val/Mega-10 and C_{10}-leu/Mega-10 are higher than that obtained experimentally (Fig. 4A). There is more deviation of cmc observed at a higher ionic mole fraction indicating the presence of non-ideality due to mutual interaction of amphiphiles in the micelle. But the experimental cmc values for the system C_{10}-val/C_{10}-leu are very close to the ideal cmc value (Fig. 4B).

Different theoretical treatments of Motomura, Rubingh, Rosen and Maeda have been used to explain the molecular interactions in mixed micelles of binary combinations. According to Motomura, the mixed micelles are considered as macroscopic bulk phase. The related energetic parameters can be obtained from the excess thermodynamic quantities. The micellar mole fraction of a surfactant in the mixed micelle (X_M) can be calculated from the following equation

$$X_\mathrm{M} = \hat{X}_1 - \left(\hat{X}_1 \hat{X}_2 / \hat{C}_\mathrm{m}\right) \left(\frac{\partial \hat{C}_\mathrm{m}}{\partial \hat{X}_1}\right)_{P,T} \tag{13}$$

The values of X_M for binary mixtures are presented in Tables 3 and S3.† For all binary combinations, the X_M values are lower than the stoichiometric mole fractions; similar types of observation are reported for CPC/Bj-56 (ref. 20) and CTAB/Bj-56.[42] Motomura's model does not depend on the nature of the surfactants and their counterions. It helps to predict the micellar composition only.

The experimental results were interpreted on the basis of Rubingh's theory based on the regular solution theory. The micelle mole fraction of the surfactants (X_R) and interaction parameters of the mixed micelles (β_R) are calculated iteratively using the equations:[29]

$$\frac{{X_\mathrm{R}}^2 \;\ln[C_\mathrm{m} X_1 / C_1 X_\mathrm{R}]}{(1 - X_\mathrm{R})^2 \ln[C_\mathrm{m}(1 - X_1)/C_2(1 - X_\mathrm{R})]} = 1 \tag{14}$$

where C_1 and C_2 are the critical micelle concentrations of surfactants 1 and 2, respectively, and C_m is the cmc of the mixed micelle.

The interaction parameter (β) can be calculated from the following equation

$$\beta_\mathrm{R} = \frac{\ln(C_\mathrm{m} X_1 / C_1 X_\mathrm{R})}{(1 - X_\mathrm{R})^2} \tag{15}$$

β is an indicator of the degree of interaction between two surfactants in mixed micelles relative to the self-interaction of two surfactants under two similar conditions before mixing and accounts for deviation from ideality.

The activity coefficients of components ${f_\mathrm{R}}^1$ and ${f_\mathrm{R}}^2$ in a mixed micelle can be calculated from the following equations

$${f_\mathrm{R}}^1 = \exp[\beta_\mathrm{R}(1 - X_\mathrm{R})]^2 \tag{16}$$

$${f_\mathrm{R}}^2 = \exp\left[\beta_\mathrm{R} {X_\mathrm{R}}^2\right] \tag{17}$$

The values of X_R, β_R and activity coefficients (f_R) for the binary mixtures are listed in Tables 3 and S3.† The values of X_R are lower than the stoichiometric mole fraction. The activity coefficients of Mega-10 are higher than the ionic surfactants (except at $X_{\mathrm{C10\text{-}val}}$ and $X_{\mathrm{C10\text{-}leu}} = 0.9$), *i.e.*, adsorption of nonionic surfactant at the interface is higher than the nonionic surfactants. The values of $f_\mathrm{R}^{\mathrm{C_{10}\text{-}val}}$ and $f_\mathrm{R}^{\mathrm{C_{10}\text{-}leu}}$ in a binary combination of C_{10}-val/C_{10}-leu are almost equal and close to unity, indicating that both surfactants have nearly the same surface activity. Here different molecular activity characteristics have been manifested in the ionic/nonionic and ionic/ionic mixed micelles containing surfactants with similar tails but dissimilar head groups. The β_R values are negative for both C_{10}-val/Mega-10 and C_{10}-leu/Mega-10 systems, indicating an attractive interaction between the surfactants, the more negative the β_R value, the greater will be the attraction. The phenomenon of attractive interaction in a mixed micelle is called synergism. For the system C_{10}-val/C_{10}-leu, some of the β_R values are positive (small value), indicating low repulsive interaction between the surfactants. Such behavior has also been observed for CPC–CTAB systems.[42]

The interaction parameters (β^σ) at the air–water interface for the mixed monolayer formation and mole fraction of the surfactants (${X_1}^\sigma$) can be calculated from Rosen's model.[30,43] The equation is given below

$$\frac{\left({X_1}^\sigma\right)^2 \ln\left(X_1 \ln\left[(1 - X_1) C_\mathrm{m}^0 / {X_1}^\sigma C_1^0\right]\right)}{\left(1 - {X_1}^\sigma\right)^2 \ln\left[(1 - X_1) C_\mathrm{m}^0 / \left(1 - {X_1}^\sigma\right) C_2^0\right]} = 1 \tag{18}$$

where X_1 is the stoichiometric mole fraction of the ionic surfactant 1 and C_1^0, C_2^0 and C_m^0 are the molar concentrations of surfactants 1, 2 and their mixtures in the solution phase, respectively, at a constant γ value. The values of X_1^{σ} for all the binary systems are higher than that obtained from Rubingh and Motomura's models except for $X_1 = 0.9$ indicating the higher surface activity toward micellization. Using the value of X_1^{σ}, the interaction parameter (β^{σ}) was calculated from the following equation

$$\beta^{\sigma} = \frac{\ln\left(X_1 C_{\mathrm{m}}^0 / X_1^{\sigma} C_1^0\right)}{\left(1 - X_1^{\sigma}\right)^2}. \tag{19}$$

The β^{σ} values obtained from Rosen's model for all binary compositions are negative, indicating an attractive interaction between the surfactants. The β^{σ} values are highly negative, particularly at a lower mole fraction of ionic surfactants, probably due to the synergistic electrostatic interaction between the hydrophilic groups of the anionic amphiphilic molecule and the glucamide molecule. The values of β^{σ} are more negative than β_{R}, indicating a greater tendency toward population of the surface than towards micellization. The ideal area minimum ($A_{\min}{}^{i}$) values for binary combinations are calculated with the help of the micellar mole fractions (X_1^{σ}) obtained from Rosen's model and $A_{\min}$ values for pure surfactants, using the following equation

$$A_{\min}{}^{i} = X_1^{\sigma} A_{\min}{}^{1} + (1 - X_1^{\sigma}) A_{\min}{}^{2} \tag{20}$$

The $A_{\min}$ values of ionic/nonionic combinations are very close to the ideal area minimum ($A_{\min}{}^{i}$) values. The divergence is maximum for the mixture containing fewer ionic surfactants.

Maeda's model[32] is applicable for ionic/nonionic mixed micelles where the ionic head group repulsion decreases in the presence of nonionic surfactant in the mixture. This model is applicable for solutions with a moderately high ionic strength. The proposed equation for the standard free energy change due to the micellization process as a polynomial function of the ionic mole fraction in the micellar phase, X_{I}, is

$$\Delta G_{\mathrm{m}}^0 = RT(B_0 + B_1 X_{\mathrm{I}} + B_2 X_{\mathrm{I}}^2) \tag{21}$$

where

$$B_0 = \ln X_{\mathrm{CN}} \tag{22}$$

$$B_1 + B_2 = \ln\left(\frac{X_{\mathrm{C_I}}}{X_{\mathrm{C_N}}}\right) \tag{23}$$

$$B_2 = -\beta \tag{24}$$

X_{CN} and X_{CI} are the cmc values of nonionic and ionic surfactants, respectively, in mole fraction units. B_1 is related to the standard free energy change associated with the introduction of ionic species into a nonionic micelle coupled with the release of nonionic species from the micelle. B_2 $(-\beta)$ is the interaction parameter in the micellar phase. The interaction parameter can be obtained from Rubingh model. R and T have their usual meanings. The values of ΔG_{m}^0, B_0, B_1 and B_2 are given in Table 4. Here, the B_0 value is constant. For both systems, B_1 and B_2 values show opposite trend with increasing mole fraction of ionic surfactant. The positive value of B_1 denotes the major role of the attractive interaction in the stability of the mixed micelle. The ΔG_{m}^0 values obtained from Maeda's model are very close to those obtained from Gibbs adsorption equation which are almost constant.

The excess free energy of the ionic–nonionic mixed micelle (g^{ex}) was calculated from another theoretical model of Maeda,[44] based on Gibbs–Duhem equation considered by Hall.[45] The equation is

$$g^{\mathrm{ex}} = X_{\mathrm{mI}} \ln f_{\mathrm{I}} + (1 - X_{\mathrm{mI}}) \ln f_{\mathrm{N}} \tag{25}$$

The detailed calculation of X_{mI}, f_{I} and f_{N} was given in the ESI.† β can be calculated from

$$\beta = \frac{g^{\mathrm{ex}}}{X_{\mathrm{m_I}}(1 - X_{\mathrm{m_I}})} \tag{26}$$

Table 4 shows that micellar mole fractions of both systems are lower than the corresponding stoichiometric mole fractions. The values of the activity coefficients of ionic and nonionic

Table 4 Free energy and interaction parameters from Maeda's model

$X_{\mathrm{C10\text{-}val}}/X_{\mathrm{C10\text{-}leu}}$	$-B_0$	B_1	B_2	$-\Delta G_{\mathrm{m}}^0$ kJ^{-1} mol^{-1}	d ln C_{m}/d X_1	X_{m1}	f_1	f_{N}	g^{ex}	β
C$_{10}$-val/Mega-10										
0.1	9.39	0.61	0.69	23.1	0.46	0.06	0.48	1.00	−0.04	−0.71
0.3		0.42	0.88	22.8	0.40	0.21	0.45	1.02	−0.15	−0.90
0.5		0.05	1.25	22.4	0.83	0.29	0.58	0.87	−0.25	−1.21
0.7		0.32	0.98	21.5	1.70	0.34	0.90	0.73	−0.24	−1.07
0.9		0.50	0.80	20.6	2.07	0.71	0.84	0.89	−0.16	−0.78
C$_{10}$-leu/Mega-10										
0.1	9.39	0.39	0.70	23.2	0.52	0.05	0.70	0.98	−0.04	−0.84
0.3		0.46	0.63	22.8	0.48	0.2	0.58	1.01	−0.10	−0.63
0.5		0.34	0.75	22.4	0.74	0.31	0.68	0.91	−0.18	−0.84
0.7		0.24	0.85	21.8	1.23	0.44	0.83	0.83	−0.19	−0.77
0.9		0.17	0.92	21.0	1.41	0.77	0.81	0.89	−0.19	−1.07

Table 5 Micellar compositions (X^{RH}), activity coefficients (f^{RH}) and cmc_{RH} in ternary mixtures of C_{10}-val/C_{10}-leu/Mega-10 at 298 K by Rubingh–Holland (RH) method at different stoichiometric compositions (X_i)

$X_{C10\text{-val}}/X_{C10\text{-leu}}/X_{Mega\text{-}10}$	$X^{RH}_{C_{10}\text{-val}}/X^{RH}_{C_{10}\text{-leu}}/X^{RH}_{Mega\text{-}10}$	$f^{RH}_{C_{10}\text{-val}}/f^{RH}_{C_{10}\text{-leu}}/f^{RH}_{Mega\text{-}10}$	cmc/mM RH/obs/Clint
0.125/0.25/0.625	0.071/0.156/0.772	0.566/0.636/0.959	5.48/5.15/5.77
0.125/0.625/0.25	0.074/0.422/0.504	0.765/0.827/0.822	7.68/6.58/8.60
0.25/0.125/0.625	0.144/0.079/0.778	0.567/0.637/0.958	5.52/4.88/5.87
0.25/0.625/0.125	0.164/0.476/0.360	0.863/0.913/0.718	9.57/7.84/10.6
0.333/0.333/0.333	0.194/0.219/0.586	0.714/0.780/0.866	7.06/5.91/8.17
0.625/0.125/0.25	0.385/0.088/0.527	0.768/0.829/0.820	8.01/6.58/9.65
0.625/0.25/0.125	0.425/0.198/0.377	0.866/0.915/0.714	9.97/9.18/11.8

amphiphiles follow the same trend in the case of both C_{10}-val/Mega-10 and C_{10}-leu/Mega-10 systems. For C_{10}-val/Mega-10 combination, g^{ex} and β values follow the same trend, but this is not true in the case of other systems. In both systems, negative values of β signify synergism. The activity coefficients of nonionic surfactant (f_I) is higher than the ionic surfactants (f_N).

Theoretical evaluation of cmc of multicomponent surfactant mixture is limited. Rubingh–Holland theory is applicable for evaluating the micellar composition, activity coefficient and cmc of the ternary surfactant mixture.

According to the Rubingh–Holland[46] (RH) method for a multicomponent system, the activity coefficients f_i, f_j, f_k, … of

Table 6 Parameters obtained from the models of Nagarajan and Israelachvili

Surf/$X_{C10\text{-val}}/X_{C10\text{-leu}}$	a_e (Å)^2	P	k^{-1}/Å	$-\left(\frac{\Delta\mu_g^0}{kT}\right)_T$	$\left(\frac{\Delta\mu_g^0}{kT}\right)_I$	$\left(\frac{\Delta\mu_g^0}{kT}\right)_H$	$\left(\frac{\Delta\mu_g^0}{kT}\right)_P$	$-\Delta G_m^0$ kJ^{-1} mol^{-1}	cmc/(mM)
Pure surfactants									
Mega-10	57.4	0.36	13.0	16.6	7.01	—	0.057	23.5	4.28
C_{10}-val	55.8	0.38	11.7	21.8	6.83	6.80	0.057	20.0	17.7
C_{10}-leu	56.2	0.37	12.0	22.0	6.88	6.88	0.057	20.4	14.8
C_{10}-val/Mega-10									
0.1	57.3	0.37	13.0	16.8	7.00	0.34	0.057	23.3	4.56
0.3	57.1	0.37	13.0	17.4	6.98	1.17	0.057	22.9	5.46
0.5	56.9	0.37	12.8	18.2	6.96	2.13	0.057	22.3	6.76
0.7	56.7	0.37	12.7	18.8	6.94	2.96	0.057	21.9	8.08
0.9	56.3	0.37	12.3	20.0	6.90	4.54	0.057	21.0	11.4
C_{10}-leu/Mega-10									
0.1	57.4	0.37	13.0	16.9	7.01	0.41	0.057	23.3	4.58
0.3	57.2	0.37	12.9	17.5	6.99	1.24	0.057	22.9	5.32
0.5	57.0	0.37	12.9	18.3	6.97	2.20	0.057	22.5	6.33
0.7	56.8	0.37	12.7	19.1	6.95	3.17	0.057	22.1	7.55
0.9	56.6	0.38	12.5	20.3	6.92	4.68	0.057	21.4	9.94
C_{10}-val/C_{10}-leu									
0.1	56.1	0.37	12.0	22.0	6.88	6.88	0.057	20.3	15.1
0.3	56.1	0.37	11.9	22.0	6.87	6.87	0.057	20.3	15.6
0.5	56.0	0.37	11.9	21.9	6.86	6.86	0.057	20.2	16.2
0.7	55.9	0.37	11.8	21.9	6.85	6.85	0.057	20.1	16.9
0.9	55.8	0.37	11.8	21.8	6.84	6.84	0.057	20.0	17.6
$X_{C10\text{-val}}/X_{C10\text{-leu}}/X_{Mega\text{-}10}$	a_e (Å)^2	P	k^{-1}/ Å	$-\left(\frac{\Delta\mu_g^0}{kT}\right)_T$	$\left(\frac{\Delta\mu_g^0}{kT}\right)_I$	$\left(\frac{\Delta\mu_g^0}{kT}\right)_H$	$\left(\frac{\Delta\mu_g^0}{kT}\right)_P$	$-\Delta G_m^0$ kJ^{-1} mol^{-1}	cmc/(mM)
0.125/0.25/0.625	57.0	0.37	12.9	17.7	6.97	1.55	0.057	22.7	5.82
0.125/0.625/0.25	56.8	0.37	12.8	19.3	6.94	3.41	0.057	21.9	8.02
0.25/0.125/0.625	57.1	0.37	13.0	17.8	6.98	1.53	0.057	22.6	5.72
0.25/0.625/0.125	56.5	0.37	12.6	20.0	6.92	4.39	0.057	21.4	9.77
0.333/0.333/0.333	56.8	0.37	12.8	18.7	6.94	2.83	0.057	22.1	7.46
0.625/0.125/0.25	56.7	0.37	12.8	19.0	6.93	3.24	0.057	21.8	8.27
0.625/0.25/0.125	56.5	0.37	12.8	19.9	6.91	4.26	0.057	21.4	10.1

micelle forming amphiphilic species *i*, *j* and *k*, … can be presented in the form

$$\ln\ f_i = \sum_{\substack{j=1\\(j\neq i)}}^{n} \beta_{ij}{x_j}^2 + \sum_{\substack{j=1\\ i\neq j\neq k}}^{n} \sum_{k=1}^{j-1}(\beta_{ij}+\beta_{ij}+\beta_{ij})x_jx_k \tag{27}$$

where β_{ij} denotes the net interaction between the component *i* and *j*, and x_j is the mole fraction of the *j*th component in the micelle; β_{ik}, β_{jk} and x_k have similar significance.

Eqn (27) is valid at the cmc

$$x_i = X_iC_jf_jX_j/(C_iX_jf_i) \tag{28}$$

The cmcs of *i*th and *j*th components are represented by C_i and C_j, respectively. The mole fractions of *i*th and *j*th components are represented by X_i and X_j. The interaction parameter (β_R) obtained from Rubingh's theory for the binary compositions was used in eqn (27) to calculate the activity coefficients for a ternary system using the method of "successive substitution" with the help of a computer. The results are presented in Table 5. The mole fractions of the individual surfactants in the mixed micelles are different from the stoichiometric compositions: both $X^{\mathrm{RH}}_{\mathrm{C_{10}\text{-}val}}$ and $X^{\mathrm{RH}}_{\mathrm{C_{10}\text{-}leu}}$ are much lower than $X_{\mathrm{C10\text{-}val}}$ and $X_{\mathrm{C10\text{-}leu}}$, but $X^{\mathrm{RH}}_{\mathrm{Mega\text{-}10}}$ is fairly higher than $X_{\mathrm{Mega\text{-}10}}$. This indicates that nonionic component dominates in the mixed micelle. Similar types of results are observed for the CPC/Tween-40/Brij-56 (ref. 20) and CPC/CTAB/Brij-56 (ref. 42) systems. The activity coefficients are high and comparable among three surfactants. But in case of CPC/Tween-40/Brij-56,[20] $f_{\mathrm{Tween\text{-}40}}$ was moderately high and $f_{\mathrm{Brij\text{-}56}}$ was close to unity, while f_{CPC} was very low. In case of CPC/CTAB/Brij-56,[42] f_{CPC} and f_{CTAB} were very low whereas $f_{\mathrm{Brij\text{-}56}}$ was high and close to unity. Both the calculated (RH method) and experimental cmc values are lower than the $\mathrm{cmc_{Clint}}$ denoting the nonideal nature of the mixed ternary micellar system. The value of $\mathrm{cmc_{RH}}$ is higher than the experimental results; the maximum difference is observed for the fourth composition, the deviation of $\mathrm{cmc_{RH}}$ from $\mathrm{cmc_{obs}}$ can attribute to the discrepancy of the RH theory whereas the contributions of the molecular parameters of the component surfactants have been left out of consideration.

In Nagarajan's model,[47,48] the standard free energy change $\left(\frac{\Delta\mu_g^0}{kT}\right)$ associated with the formation of micelle of a surfactant from its infinitely dilute state in water to an aggregate of size g (aggregation number) has four contributions: (a) $\left(\frac{\Delta\mu_g^0}{kT}\right)_T$, which is a negative free energy contribution arising from transfer of surfactant tail from solution to the more favorable aggregate core, (b) the aggregate core–water interfacial free energy contribution $\left(\frac{\Delta\mu_g^0}{kT}\right)_I$ is a positive quantity, which accounts for the allowance of the penetration of water molecules to the aggregate core, (c) $\left(\frac{\Delta\mu_g^0}{kT}\right)_H$ is a positive contribution arising out of the repulsive interaction between the head groups at the aggregate surface and (d) $\left(\frac{\Delta\mu_g^0}{kT}\right)_P$ is the contribution of the packing of a monomer within the core of the aggregate. Thus, the total contribution to $\left(\frac{\Delta\mu_g^0}{kT}\right)$ can be given by

$$\left(\frac{\Delta\mu_g^0}{kT}\right) = \left(\frac{\Delta\mu_g^0}{kT}\right)_T + \left(\frac{\Delta\mu_g^0}{kT}\right)_I + \left(\frac{\Delta\mu_g^0}{kT}\right)_H + \left(\frac{\Delta\mu_g^0}{kT}\right)_P \tag{29}$$

Thus, Gibbs free energy of micellization can be determined from the following equation:

$$\Delta G_m^0 = \exp\left[\left(\frac{\Delta\mu_g^0}{kT}\right)_\mathrm{T} + \left(\frac{\Delta\mu_g^0}{kT}\right)_\mathrm{I} + \left(\frac{\Delta\mu_g^0}{kT}\right)_\mathrm{H} + \left(\frac{\Delta\mu_g^0}{kT}\right)_\mathrm{P}\right] \times 55.55 \tag{30}$$

The detailed calculation for the four free energy contributions to the standard free energy is given in ESI.† Four contributions to the standard free energy and other parameters obtained from Nagarajan's model are presented in Table 6. The micellar mole fractions obtained from Rubingh's theory for binary systems (X_R) and Rubingh–Holland theory for ternary mixtures were considered to calculate the contributions of four free energies [$\left(\frac{\Delta\mu_g^0}{kT}\right)_T$, $\left(\frac{\Delta\mu_g^0}{kT}\right)_I$, $\left(\frac{\Delta\mu_g^0}{kT}\right)_H$ and $\left(\frac{\Delta\mu_g^0}{kT}\right)_P$] to the total free energy. The total free energy change, critical micellization concentration and packing parameters for the pure surfactants and their binary and ternary mixtures are also shown in Table 6. The values of the packing parameters show a slight tendency for non-spherical micelles. There is a good correlation between the experimental data and those obtained from Nagarajan's model.

Conclusions

A study of binary and ternary combinations of two ionic surfactants ($\mathrm{C_{10}}$-val and $\mathrm{C_{10}}$-leu) with nonionic surfactant Mega-10 has not been conducted before. The tails of the three surfactants are same but the head groups are different. The binary ($\mathrm{C_{10}}$-val/Mega-10, $\mathrm{C_{10}}$-leu/Mega-10 and $\mathrm{C_{10}}$-val/$\mathrm{C_{10}}$-leu) and ternary ($\mathrm{C_{10}}$-val/$\mathrm{C_{10}}$-leu/Mega-10) combinations have lower cmc values than that obtained from Clint's model. That combinations show nonideal behavior. This nonideality arises from the interaction between the head groups of the surfactants. The interaction parameters (β) obtained from Rubingh, Rosen and Maeda are negative, indicating an attractive interaction between the system $\mathrm{C_{10}}$-val/Mega-10 and $\mathrm{C_{10}}$-leu/Mega-10. The mole fractions obtained theoretically are not the same with the stoichiometric composition. Both ΔG_m^0 and ΔG_{ads}^0 are negative, indicating the spontaneity of micelle formation and ΔG_m^0 becomes less negative with increasing concentration of ionic surfactant in the binary mixture. ΔG^0_m values for binary systems obtained from Maeda's model are lower than those obtained from the regular solution theory. The magnitude of ΔG^0_{ads} is more negative than ΔG^0_m, signifying that adsorption at the air–water interface is more spontaneous than micellization. From the study of the polarity index of all binary compositions, we can say that the surface area per head group decreases with decreasing concentration of Mega-10 and more compact micelles are formed with increasing concentration of ionic surfactant, which resists the penetration of the solvent.

Acknowledgements

S.D. thanks CSIR, Govt. of India, for senior research fellowship, Prof. S. C. Bhattacharya, Department of Chemistry for using DLS facility and Jadavpur University for laboratory facilities.

References

1 T. Furutani, H. Ooshima and J. Kato, *Enzyme Microb. Technol.*, 1997, **20**, 214.
2 S. E. Godtfredsen and F. Bjoerkling, World Patent No. 90/14429, 1990.
3 B. Gallot and H. H. Hassan, *Mol. Cryst. Liq. Cryst.*, 1989, **170**, 195.
4 M. Takehara, H. Moriyuki, I. Yoshimura and R. Yoshida, *J. Am. Oil Chem. Soc.*, 1972, **49**, 143.
5 M. Takehara, *Colloids Surf.*, 1989, **38**, 149.
6 M. R. Infante, A. Pinazo and J. Seguer, *Colloids Surf., A*, 1997, **123–124**, 49.
7 M. R. Infante, J. Molinero, P. Erra, R. Julia, J. J. Garcia Dominguez and M. Robert, *Fette, Seifen, Anstrichmittel*, 1986, **88**, 108.
8 C. Das, T. Chakraborty, S. Ghosh and B. Das, *Colloid J.*, 2010, **72**, 788.
9 G. Basu Ray, S. Ghosh and S. P. Moulik, *J. Chem. Sci.*, 2010, **122**, 109.
10 D. Tikariha, B. Kumar, S. Ghosh, A. K. Tiwari, N. Barbero, P. Quagliotto and K. K. Ghosh, *J. Nanofluids*, 2013, **2**, 316.
11 T. Chakraborty and S. Ghosh, *J. Surfactants Deterg.*, 2008, **11**, 323.
12 K. H. Kang, H. U. Kim, K. H. Lim and N. H. Jeong, *Bull. Korean Chem. Soc.*, 2001, **22**, 1009.
13 T. Lu, F. Han, Z. Li, J. Huang and H. Fu, *Langmuir*, 2006, **22**, 2045.
14 Y. Wang and E. F. Marques, *J. Mol. Liq.*, 2008, **142**, 136.
15 E. Rodenas, M. Valiente and M. del Sol Villafruela, *J. Phys. Chem. B*, 1999, **103**, 4549.
16 P. K. Khatua, S. Ghosh, S. K. Ghosh and S. C. Bhattacharya, *J. Dispersion Sci. Technol.*, 2004, **25**, 741.
17 P. del Burgo, E. Junquera and E. Aicart, *Langmuir*, 2004, **20**, 1587.
18 G. Basu Ray, I. Chakraborty, S. Ghosh and S. P. Moulik, *J. Colloid Interface Sci.*, 2007, **307**, 543.
19 A. A. Dar, G. M. Rather, S. Ghosh and A. R. Das, *J. Colloid Interface Sci.*, 2008, **322**, 572.
20 S. Ghosh, *J. Colloid Interface Sci.*, 2001, **244**, 128.
21 G. Basu Ray, I. Chakraborty, S. Ghosh and S. P. Moulik, *Colloid Polym. Sci.*, 2007, **285**, 457.
22 J. F. Scamechorn, in *Mixed Surfactant Systems*, ed. P. M. Holland and D. N. Rubingh, Washington, DC, 1992, ch. 27, p. 329, ACS Symposium Series 501, *J. Am. Chem. Soc.*.
23 S. Ghosh, A. Das Burman, G. C. De and A. R. Das, *J. Phys. Chem. B*, 2011, **115**, 11098.
24 S. Ghosh and T. Chakraborty, *J. Phys. Chem. B*, 2007, **111**, 8080.
25 J. J. Lopata, K. M. Werts, J. F. Scamehorn, J. H. Harwell and B. P. Grady, *J. Colloid Interface Sci.*, 2010, **342**, 415.
26 S. B. Sulthana, P. V. C. Rao, S. G. T. Bhat, T. Y. Nakano, G. Sugihara and A. K. Rakshit, *Langmuir*, 2000, **16**, 980.
27 K. Szymczyk and B. Jańczuk, *Langmuir*, 2007, **23**, 4972.
28 J. H. Clint, *J. Chem. Soc., Faraday Trans. 1*, 1975, **71**, 1327.
29 D. N. Rubingh, in *Solution Chemistry of Surfactants*, ed. K. L. Mittal, Plenum, New York, 1979, vol. 1, p. 337.
30 M. J. Rosen and M. Dahanayake, *Industrial Utilization of Surfactants, Principles and Practice*, AOCS Press, Champaign, IL, 2000, pp. 28–29.
31 K. Motomura, M. Yamanaka and M. Aratono, *Colloid Polym. Sci.*, 1984, **262**, 948.
32 H. Maeda, *J. Colloid Interface Sci.*, 1995, **172**, 98.
33 S. Ghosh and S. P. Moulik, *J. Colloid Interface Sci.*, 1998, **208**, 357.
34 A. Ohta, K. Toda, Y. Morimoto, T. Asakawa and S. Miyagishi, *Colloids Surf., A*, 2008, **317**, 316.
35 J. Sánchez-Quesada, M. P. Isler and M. R. Ghadiri, *J. Am. Chem. Soc.*, 2002, **124**, 10004.
36 G. Von Maltzahn, S. Vauthey, S. Santoso and S. Zhang, *Langmuir*, 2003, **19**, 4332.
37 J. M. Hierrezuelo, J. Aguiar and C. C. Ruiz, *Langmuir*, 2004, **20**, 10419.
38 J. M. Hierrezuelo, J. Aguiar and C. C. Ruiz, *J. Colloid Interface Sci.*, 2006, **294**, 449.
39 S. Miyagishi and M. Nishida, *J. Colloid Interface Sci.*, 1978, **65**, 380.
40 S. Miyagishi, Y. Ishibai, T. Asakawa and M. Nishida, *J. Colloid Interface Sci.*, 1985, **103**, 164.
41 F. M. Winnik and S. T. A. Regismond, *Colloids Surf., A*, 1996, **118**, 1.
42 T. Chakraborty, S. Ghosh and S. P. Moulik, *J. Phys. Chem. B*, 2005, **109**, 14813.
43 M. J. Rosen, *Surfactants and Interfacial Phenomena*, John Wiley, New York, 3rd edn, 2004.
44 H. Maeda, *J. Phys. Chem. B*, 2005, **109**, 15933.
45 D. G. Hall, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 3529.
46 P. M. Holland and D. N. Rubingh, *J. Phys. Chem.*, 1983, **87**, 1984.
47 R. Nagarajan and E. Ruckenstein, *Langmuir*, 1991, **7**, 2934.
48 R. Nagarajan, *Langmuir*, 2002, **18**, 31.