Journal of Molecular Liquids 208 (2015) 137–144

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Tensiometric studies on the mixtures of nonionic Cremophor RH and cationic gemini surfactants

Andleeb Z. Naqvi *, Sahar Noori, Kabir-ud-Din [1]

Department of Chemistry, Aligarh Muslim University, Aligarh 202 002, India

ARTICLE INFO

Available online xxxx

Keywords:
Cationic gemini surfactants
Nonionic surfactant
Surface tension
Mixed systems

ABSTRACT

Surfactant solutions used in practical applications are generally mixtures of ionic and nonionic surfactants. These surfactants mostly show synergism on mixing. In this work, mixing behavior of cationic gemini surfactants, alkanediyl — α, ω — bis(dimethylalkylammonium bromide (alkyl: 14 or 16 and alkane: butane, pentane or hexane)), (m-s-m) and Cremophor RH over the entire mole fraction range was investigated tensiometrically. Results indicate that these mixtures show a negative deviation in the cmc^{id} (cmc value at ideal mixing conditions). Micellar mole fraction of RH (X_1^m) values indicate that RH has slightly higher contribution in mixed micelles than of geminis. X_1^m values are greater than of X_1^σ (mole fraction of RH at mixed interface). Adjustment of cationic head group of gemini is easier at the planar interface than in curved micellar head group area. Surface excess increases with the increase in α_1. Different thermodynamic parameters (i.e., ΔG°_{mic}, ΔG°_{ads}, ΔG^m_{ex}, ΔG^σ_{ex}, G_{min}) also support mixed micelle formation. R_p value and radius of micelles suggest that the mixed micelles at high α_1 are almost cylindrical in shape.

1. Introduction

Surfactants are widely employed in many technological applications, such as detergency, food and cosmetic industries, pharmaceuticals, floatation, enhanced oil recovery and many more [1,2]. Conventional surfactants, however, have critical micelle concentration (cmc) values in a millimolar range [2] and a large amount of surfactant would be required in practical applications. Also, it is well known that conventional surfactants, especially cationics, show good stability towards chemicals and microbes and, hence, are toxic. In the last few decades, gemini surfactants (surfactants having two hydrophobic tails and two hydrophilic head groups joined by a spacer) have attracted considerable attention due to their low cmc values and other improved properties [3–6]. As their cmc values are low (around 10–100 times lower than those of their conventional counterparts), they can be used as fabric softeners and detergents. Their properties can be tuned by changing the length of hydrophobic tails as well as by changing the type and length of spacer. However, their high cost of production hampers their use. Hence, in parallel with the search and synthesis of geminis with better properties, studies on mixed systems of conventional and gemini surfactants are gaining special attention. This reduces the cost and at the same time enhances the product properties. This also reduces the required amount of surfactants [7].

Surfactant mixtures are known to have better surface activity and colloidal behavior such as micellization and adsorption than of single surfactant systems. In practical fields, surfactant mixtures prove better than single systems since the composition of the mixture (and, as a result, their properties) can be optimized for each particular application. This improved behavior can be explained by synergism between the components. These mixed systems are also important from a theoretical point of view as it is important to have thermodynamic models with both predictive and interactive properties.

It is well known that mixtures of nonionic surfactants [8,9] and mixtures of surfactant homologues with the same hydrophilic head groups [10,11] usually exhibit ideal mixing while mixtures of ionic–nonionic, anionic–cationic and hydrocarbon–fluorocarbon surfactants deviate from ideal behavior [12–14].

Mixed micellization of oxyethylene based nonionic surfactants with cationic [15], anionic [16], dimeric anionic [17] and dimeric cationic surfactants [18] has been studied extensively. This work presents a physico-chemical study on mixtures of a nonionic surfactant Cremophor RH 40 (RH) and cationic geminis of alkanediyl — α, ω — bis(dimethylalkylammonium bromide (alkyl: 14 or 16 and alkane: butane, pentane or hexane)), (m-s-m) type. RH is used as a solubilizer for fat-soluble vitamins, essential oils and other hydrophobic pharmaceuticals. It has very little odor and in aqueous solutions is almost tasteless. Cationic geminis show antibacterial properties [19]. Properties of mixed surfactant systems have been studied by various techniques [20–22]. Pure as well as mixed surfactant systems of RH and m-s-m at different stoichiometric ratios (0.2, 0.4, 0.5, 0.6, 0.8) were studied tensiometrically to evaluate

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* Corresponding author.
E-mail address: naqviaz@gmail.com (A.Z. Naqvi).

[1] Present address: Department of Chemistry, Faculty of Natural Sciences, Arba Minch University, Arba Minch, Ethiopia.

http://dx.doi.org/10.1016/j.molliq.2015.04.009

Table 1
Various physico-chemical parameters for RH-gemini mixed systems in solution.

Mole fraction of RH (α_1)	cmc (mM)	cmc^{id} (mM)	$\Delta cmc/cmc^{id}$	X_1^m	X_1^M	X_1^{id}	β^m	f_1^m	f_2^m
14-4-14									
0	0.0990								
0.2	0.0152	0.0684	0.778	0.487		0.458	−6.05	0.204	0.238
0.4	0.0186	0.0523	0.645	0.562		0.519	−4.34	0.433	0.255
0.5	0.0261	0.0468	0.442	0.624		0.569	−2.69	0.683	0.351
0.6	0.0249	0.0423	0.411	0.664		0.562	−2.72	0.735	0.301
0.8	0.0261	0.0355	0.265	0.773		0.594	−2.42	0.883	0.235
1	0.0306								
14-5-14									
0	0.1650								
0.2	0.0200	0.088	0.768	0.519	0.127	0.466	−5.88	0.257	0.205
0.4	0.0227	0.060	0.621	0.600	0.292	0.694	−4.40	0.495	0.205
0.5	0.0229	0.052	0.556	0.638	0.402	0.552	−4.07	0.586	0.191
0.6	0.0247	0.045	0.456	0.686	–	0.565	−3.53	0.706	0.189
0.8	0.0249	0.037	0.319	0.774	0.832	0.636	−3.39	0.841	0.131
14-6-14									
0	0.1730								
0.2	0.0188	0.0896	0.790	0.521	0.131	0.465	−6.30	0.236	0.181
0.4	0.0214	0.0605	0.646	0.599	0.300	0.547	−4.74	0.467	0.183
0.5	0.0136	0.0520	0.738	0.604	–	0.665	−6.38	0.368	0.098
0.6	0.0187	0.0456	0.590	0.655	0.580	0.918	−4.87	0.560	0.124
0.8	0.0222	0.0366	0.394	0.749	–	0.822	−4.05	0.775	0.103
16-4-16									
0	0.0156								
0.2	0.0103	0.0173	0.404	0.302		0.113	−3.08	0.223	0.755
0.4	0.0115	0.0194	0.407	0.378		0.254	−2.38	0.398	0.711
0.5	0.0161	0.0207	0.221	0.392		0.338	−1.08	0.671	0.847
0.6	0.0203	0.0221	0.081	0.443		0.433	−0.34	0.899	0.935
0.8	0.0226	0.0257	0.119	0.637		0.671	−0.56	0.928	0.796
16-5-16									
0	0.0313								
0.2	0.0184	0.0312	0.409	0.353		0.204	−2.57	0.341	0.726
0.4	0.0187	0.0310	0.397	0.453	0.236	0.405	−2.06	0.540	0.655
0.5	0.0189	0.0309	0.389	0.503		0.506	−1.97	0.614	0.607
0.6	0.0211	0.0309	0.317	0.560	0.421	0.605	−1.56	0.739	0.612
0.8	0.0250	0.0307	0.186	0.716	0.676	0.804	−1.12	0.914	0.564
16-6-16									
0	0.0380								
0.2	0.0115	0.0361	0.681	0.418		0.361	−5.07	0.180	0.413
0.4	0.0156	0.0346	0.548	0.482		0.389	−3.21	0.423	0.474
0.5	0.0167	0.0338	0.506	0.523		0.425	−2.86	0.522	0.457
0.6	0.0161	0.0331	0.515	0.562		0.442	−3.02	0.560	0.385
0.8	0.0191	0.0318	0.400	0.669		0.503	−2.67	0.969	0.880

(i) mixture cmc (Table 1), (ii) composition of mixed micelles (Table 1) and mixed monolayers (Table 2), (iii) interaction between the two components in mixed micelles (Table 1) and mixed monolayers (Table 2), (iv) related thermodynamic parameters (Table 3) and (v) micellar size parameters (Table 4). For this, theories of Clint [11], Rubingh [23], Motomura [24] and Rosen [2] were applied.

2. Experimental section

Gemini surfactants were prepared by refluxing α,ω-dibromoalkanes and excess N, N-dimethylalkylamine (1:2.1) in dry ethanol solution at 80 °C for 48 h. The progress of the reaction was monitored by using the thin-layer chromatography (TLC) technique. After completion of the reaction, the solvent was removed under vacuum, followed by more than three recrystallizations from a mixture of ethanol and ethyl acetate [4,25]. All the products have satisfactory ^{1}H NMR spectra, which were characterized on a Brucker Avance system. Cremophor RH 40 was received from Sigma (CAS: 61788-85-0) and was used without further purification. (See Scheme 1.)

Aqueous solutions of pure surfactants were prepared in double-distilled water whose surface tension was in the range of 71 and 72 mN m^{-1}. The equimolar stock solutions were mixed in different ratios to obtain different mole fractions. The surface tension (γ) of the surfactant solutions at the air/water interface was measured with a Hardson tensiometer based on the du Noüy ring detachment method. Concentrated solution of surfactant (or surfactant mixtures) was progressively added in steps in water (30 ml) with the help of a Hamilton microsyringe. The surface tensions were measured allowing more than 10 min time for equilibration after each addition. The experiments were duplicated to check their reproducibility. The γ values were accurate within ±0.5 mN m^{-1}.

3. Results and discussion

When surfactant molecules are dissolved in water they form micelles above a concentration range known as cmc. The value of cmc is specific for each surfactant and it depends upon the type of surfactant. For example, in conventional surfactants, cmc of nonionic surfactants is lower than that of ionic surfactants. In ionic surfactants, a micelle is formed when hydrophobic interactions between chains dominate the Coulombic repulsions among head groups. In nonionic surfactants, as these repulsions are absent, cmc values are lower than in ionic surfactants. In ionic geminis, although there is Coulombic repulsions among head groups, hydrophobic interactions are also strong due to