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Influence of organic solvents, head-groups and temperature on the micellization behavior of some cationic surfactants

A K Sood, Rupinderjit Kaur & T S Banipal*

*Department of Chemistry, Guru Nanak Dev University, Amritsar 143 005, Punjab, India
Email: tsbanipal@yahoo.com (TSB)/ aksoodchem@yahoo.co.in (AKS)/ rupinderrandhawa55@yahoo.com (RK)

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The effect of organic solvents, viz., dioxane, dimethylformamide and ethylene glycol on the micellization behavior of cationic surfactants, i.e., tetradecyltrimethyl ammonium bromide (TTAB), tetradecyldimethylbenzyl ammonium chloride (C14BCl) and their dimeric homologue, dimethylene-1,2-bis(tetradecyldimethyl ammonium bromide) (14-2-14) is studied in aqueous solutions using conductometric and viscometric techniques at different temperatures (288.15–318.15 K). It is observed that the critical micelle concentration and degree of counterion dissociation values increase with the increase in volume percentage and the temperature. Studies on the the temperature dependence of the CMC values show that the standard Gibbs free energy of micellization values increase with the concentration of organic solvents and temperature whereas the opposite trend is observed for enthalpy. The randomness of the system decreases in presence of solvents. The relative viscosity of the surfactants was found to be more in presence of ethylene glycol among the studied systems. The effect of temperature on relative viscosity for these systems has also been discussed.

Keywords: Solution chemistry, Micellization, Surfactants, Cationic surfactants, Organic solvents, Conductivity, Relative viscosity

The phenomenon of micellization is of immense importance as most of the applications of surfactants are dependent on the existence of micelles in solution[1]. The inclusion of different types of additives is well known to influence the micellar properties of surfactant solution by modifying the solvent structure[2-4]. The micellar properties of surfactants may also be affected by the nature of the hydrophilic and hydrophobic groups and temperature.

The micellization behavior of various conventional (anionic, cationic, nonionic and zwitterionic) and gemini surfactants in aqueous solutions has been studied in detail under variety of conditions[5-14]. In recent times, focus has been on how the change from aqueous solutions to organic solvents affects the micellization and related properties. Such studies are important because of increasing use of these materials for applications which require water-free or water-poor media, such as lubrication and cleaning operations[15-23]. In addition, the study of aggregation process in presence of different organic solvents can provide a better understanding of fields related to surface and interfacial science[24]. Besides, many surfactant applications, especially those related to pharmaceuticals, require the presence of mixed solvent systems[25]. In recent years, the dimeric surfactants known as gemini surfactants have generated attention in academic and industrial applications due to their improved physical properties in comparison to those of the monomeric surfactants[22–23, 25–26].

Although there are some studies on the micellar behavior of tetradecyltrimethyl ammonium bromide (TTAB) in presence of organic solvents[27–29], to the best of our knowledge, such reports on tetradecyldimethylbenzyl ammonium chloride (C14BCl) and their dimeric homologue, dimethylene-1,2-bis(tetradecyldimethyl ammonium bromide) (14-2-14) are missing. Moreover, a survey of the available literature reveals that micellar phenomenon of conventional as well as gemini surfactants possessing similar hydrophobic tail but different head groups has not been studied in polar non-aqueous solvents at different temperatures. Therefore, herein various micellar properties of cationic surfactants with the same hydrophobic chain length, i.e., TTAB, C14BCl and 14-2-14 are being reported in aqueous and in aqueous organic solvent media using conductometric and viscometric studies at 288.15, 298.15, 308.15 and 318.15 K. The organic solvents used are dioxane (DO), dimethylformamide (DMF) and ethylene glycol (EG). The objective of the work is (i) to investigate the effect of variation in the polarity of the bulk phase on CMC, and,

(ii) to analyze various thermodynamic parameters of micellization in the studied temperature range.

Materials and Methods

The cationic gemini surfactant, 14-2-14 was synthesized according to the method reported elsewhere[30]. Purity of 14-2-14 was established by elemental analysis using CHNSO analyzer (Thermo Flash 2000, UK) and was more than 98.5%. The other surfactants, TTAB and C14BCl (AR grade), were obtained from SD Fine, Mumbai and used as such without further purification; however, these were dried over anhydrous $CaCl_2$ in vacuum desiccator. The solvents, DO, DMF (SD Fine, Mumbai) and EG (SRL, Mumbai) were more than 99% pure. All solutions were prepared in degassed, doubly distilled and deionized water having conductivity range 2-6 µS cm^{-1}. The conductance measurements were carried out with a digital conductivity meter (Systronics-306) at a fixed frequency of 50 Hz using a dip-type cell having temperature stability ±0.01 K.

The viscosity of surfactant solutions was determined by using an Ubbelohde type suspended level capillary viscometer with a glass jacket through which water was circulated at a fixed temperature. 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 the case of dilute solutions. For each measurement, 3 to 5 readings were taken and average of three nearest values are reported.

Results and Discussion

Conductivity studies

The CMC values of TTAB, C14BCl and 14-2-14 (determined as shown in Fig. 1) were found to increase with temperature (Tables 1–3) and agreed well with the literature values[30–34]. The increase in CMC with the concentration of organic solvents indicates that the studied solvents provide a better medium than water for surfactant molecules and as a result the transfer of surfactant alkyl chain from the bulk phase into the micellar core becomes less favorable as the amount of the solvent increases[21]. The increase in CMC value is comparatively less in EG than in the other two solvents for TTAB at 298.15 K (Fig. 2). This may be due to resemblance of EG with water in terms of significant hydrogen bond donor ability, high dielectric constant and high cohesive energy[35]. Also, slightly higher CMC values in EG-water mixtures in comparison to that in pure water are due to the structure breaking characteristic of EG which causes lowering of hydrophobicity of surfactant molecules resulting in delayed micellization[36]. In the case of DMF-water mixture, although dielectric constant of DMF is almost similar to that of EG (37.3 for EG and 38 for DMF), the increase in CMC is maximum because DMF is a polar aprotic solvent with high dipole moment (µ = 3.82 D at 298.15 K)[37]. Therefore, with increasing volume percentage of DMF, the solvating ability of the bulk phase to solvate the surfactant ion through their negative dipole shall increase, resulting in the observed delay in micellization of all the studied surfactants in DMF-water systems. The increase in CMC of the studied surfactants is more in presence of DO as compared to EG-water mixture, because DO has the least value of dielectric constant among the studied solvents (2.20)[37]. The decrease in dielectric constant of the solvent results in greater repulsion in

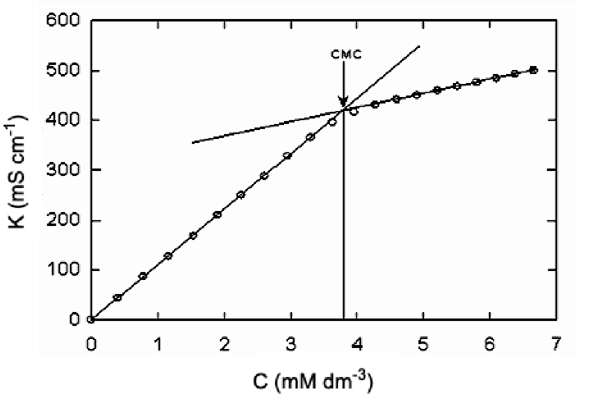

Fig. 1 – CMC value of TTAB at 298.15 K.

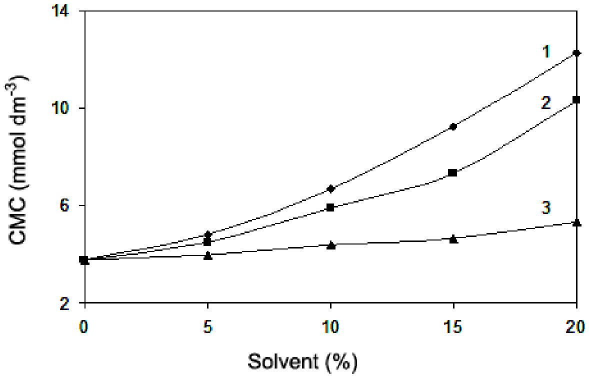

Fig. 2 – Effect of solvent concentration on the CMC of TTAB at 298.15 K. [1, DMF; 2, DO; 3, EG].

Table 1 – Micellization and thermodynamic parameters of TTAB in presence of organic solvents at different temperatures

Organic solvent (%)	T (K)	CMC (m*M*)	α	ΔG^{o}_{m} (kJ mol^{-1})	$\Delta G^{o}_{m,\ trans}$ (kJ mol^{-1})	ΔH^{o}_{m} (kJ mol^{-1})	ΔS^{o}_{m} (J mol^{-1}K^{-1})
—	288.15	3.69±0.04	0.236±0.008	-40.64±0.50	0.00	-05.44±0.11	122.15±0.34
	298.15	3.80±0.03 $(3.86)^{a}$ $(3.75)^{b}$	0.247±0.005	-41.66±0.61	0.00	-05.79±0.08	120.31±0.55
	308.15	3.89±0.05 $(4.08)^{a}$ $(3.92)^{b}$	0.258±0.004	-42.69±072	0.00	-06.15±0.07	118.57±0.88
	318.15	4.22±0.04 $(4.39)^{a}$	0.308 ±0.007	-42.44 ±0.50	0.00	-06.37 ±0.10	113.39±0.73
Dimethylformamide							
5	288.15	4.61±0.03	0.228±0.006	-39.88±0.47	0.76±0.10	-10.74±0.09	101.13±0.64
	298.15	4.84±0.04	0.284±0.003	-39.75±0.31	1.90±0.08	-11.14±0.04	095.99±0.61
	308.15	5.42±0.02	0.329±0.005	-39.53±0.63	3.16±0.08	-11.58±0.05	090.68±0.32
	318.15	6.00±0.05	0.374±0.007	-39.25±0.51	3.19±0.11	-12.01±0.06	085.62±0.43
10	288.15	6.40±0.04	0.278±0.005	-37.41±0.49	3.23±0.09	-10.15±0.07	094.57±0.51
	298.15	6.71±0.03	0.335±0.006	-37.23±0.68	4.43±0.12	-10.51±0.04	089.60±0.54
	308.15	7.72±0.06	0.375±0.008	-36.97±0.33	5.72±0.11	-10.96±0.06	084.40±0.30
	318.15	8.27±0.07	0.424±0.005	-36.73±0.82	5.71±0.08	-11.33±0.07	079.83±0.25
15	288.15	8.08±0.03	0.290±0.004	-36.19±0.74	4.45±0.07	-18.68±0.05	060.77±0.31
	298.15	9.25±0.04	0.331±0.005	-35.99±0.52	5.67±0.09	-19.52±0.06	055.24±0.49
	308.15	10.75±0.05	0.392±0.004	-35.99±0.43	7.47±0.11	-20.09±0.07	049.09±0.79
	318.15	12.99±0.03	0.421±0.002	-34.92±0.76	7.53±0.04	-21.02±0.09	043.64±0.83
20	288.15	10.17±0.07	0.322±0.008	-34.59±0.88	6.05±0.05	-20.42±0.03	049.16±0.77
	298.15	12.30±0.05	0.364±0.009	-34.12±0.97	7.54±0.08	-21.31±0.04	042.94±0.71
	308.15	16.20±0.08	0.468±0.003	-31.95±0.25	10.74±0.13	-21.32±0.05	034.46±0.68
	318.15	17.26±0.07	0.505±0.004	-31.93±0.67	10.51±0.11	-22.18±0.07	030.65±0.61
Dioxane							
5	288.15	4.30±0.03	0.245±0.006	-39.79±0.36	0.85±0.03	-09.04±0.06	106.70±0.76
	298.15	4.49±0.04	0.288±0.007	-39.98±0.49	1.68±0.08	-09.45±0.05	102.41±0.74
	308.15	4.89±0.04	0.324±0.006	-40.09±0.51	2.60±0.12	-09.88±0.07	098.03±0.87
	318.15	5.38±0.04	0.360±0.008	-40.08±0.55	2.35±0.07	-10.30±0.08	093.60±0.86
10	288.15	5.16±0.03	0.303±0.010	-37.74±0.62	2.90±0.05	-13.22±0.09	085.08±0.79
	298.15	5.89±0.04	0.345±0.009	-37.54±0.34	4.12±0.06	-13.80±0.05	079.60±0.55
	308.15	6.52±0.05	0.406±0.007	-36.96±0.45	5.73±0.07	-14.20±0.06	073.82±0.42
	318.15	7.24±0.04	0.442±0.008	-36.86±0.43	5.58±0.08	-14.80±0.07	069.33±0.74
15	288.15	6.50±0.04	0.303±0.005	-36.80±0.51	3.84±0.04	-19.64±0.06	059.54±0.76
	298.15	7.33±0.06	0.345±0.006	-36.64±0.47	5.02±0.08	-20.51±0.07	054.10±0.68
	308.15	8.75±0.03	0.397±0.004	-35.96±0.38	6.73±0.04	-21.22±0.08	047.81±0.35
	318.15	10.75±0.08	0.439±0.009	-35.30±0.41	7.14±0.06	-22.02±0.08	041.70±0.84
20	288.15	8.50±0.07	0.361±0.007	-34.49±0.42	6.15±0.06	-19.69±0.07	051.33±0.58
	298.15	10.30±0.04	0.408±0.008	-33.89±0.39	7.77±0.05	-20.48±0.12	044.97±0.66
	308.15	12.40±0.07	0.423±0.006	-33.96±0.66	8.72±0.04	-21.67±0.06	039.87±0.54
	318.15	14.33±0.07	0.484±0.005	-33.13±0.45	9.31±0.07	-22.21±0.09	034.31±0.28
Ethylene glycol							
5	288.15	3.80±0.04	0.236±0.008	-40.52±0.66	0.12±0.02	-08.02±0.03	112.80±0.95
	298.15	3.99±0.03	0.246±0.009	-41.48±0.71	0.19±0.05	-08.54±0.05	110.49±1.57
	308.15	4.30±0.04	0.279±0.010	-41.73±0.75	0.95±0.07	-08.95±0.07	106.40±1.19
	318.15	4.63±0.05	0.312±0.007	-41.93±0.87	1.06±0.04	-09.35±0.11	102.40±0.77
10	288.15	3.87±0.05	0.234±0.008	-40.49±0.46	0.15±0.03	-12.54±0.07	096.97±0.81
	298.15	4.38±0.04	0.269±0.005	-40.54±0.85	1.13±0.04	-13.16±0.15	091.79±0.63
	308.15	4.87±0.05	0.279±0.008	-40.87±0.54	1.81±0.07	-13.87±0.12	087.60±0.61
	318.15	5.27±0.06	0.312±0.007	-41.40±0.63	1.04±0.08	-14.63±0.16	084.12±0.89

(Contd)

Table 1 – Micellization and thermodynamic parameters of TTAB in presence of organic solvents at different temperatures—(*Contd*)

Organic solvent (%)	T (K)	CMC (m*M*)	α	ΔG^{o}_{m} (kJ mol^{-1})	$\Delta G^{o}_{m,\ trans}$ (kJ mol^{-1})	ΔH^{o}_{m} (kJ mol^{-1})	ΔS^{o}_{m} (J mol^{-1}K^{-1})
Ethylene glycol—(*Contd*)							
15	288.15	4.10±0.05	0.239±0.004	-40.13±0.98	0.51±0.05	-16.16±0.11	083.18±0.74
	298.15	4.65±0.04	0.266±0.006	-40.35±0.76	1.32±0.06	-17.04±0.09	078.17±0.32
	308.15	5.56±0.05	0.301±0.009	-40.08±0.87	2.60±0.07	-17.83±0.12	072.19±0.94
	318.15	6.11±0.04	0.335±0.012	-41.40±0.99	2.30±0.04	-18.63±0.08	067.60±0.73
20	288.15	4.50±0.06	0.246±0.011	-39.58±0.45	1.06±0.06	-19.08±0.11	071.15±0.74
	298.15	5.33±0.03	0.263±0.007	-39.82±0.77	1.85±0.05	-20.23±0.12	065.68±0.81
	308.15	6.11±0.07	0.289±0.008	-39.95±0.84	2.74±0.09	-21.28±0.11	060.57±0.88
	318.15	7.22±0.08	0.321±0.006	-39.74±0.87	2.71±0.08	-22.26±0.14	054.90±0.80

[a]Ref. 31; [b]Ref. 32

Table 2 – Micellization and thermodynamic parameters of C14BCl in presence of organic solvents at different temperatures

Organic solvent (%)	*T* (K)	CMC (m*M*)	α	ΔG^{o}_{m} (kJ mol^{-1})	$\Delta G^{o}_{m,\ trans}$ (kJ mol^{-1})	ΔH^{o}_{m} (kJ mol^{-1})	ΔS^{o}_{m} (J mol^{-1}K^{-1})
—	288.15	2.04±0.03 (2.05)[a]	0.414±0.006	-38.79±0.65	0.00	-05.31±0.33	116.19±1.03
	298.15	2.00±0.04 (1.99)[a]	0.456±0.008	-39.15±0.74	0.00	-05.54±0.45	112.74±1.25
	308.15	2.09±0.03 (2.09)[a]	0.494±0.009	-39.30±0.84	0.00	-05.77±0.47	108.81±0.96
	318.15	2.36±0.03	0.530±0.011	-39.13±0.43	0.00	-06.00±0.68	104.13±1.02
Dimethylformamide							
5	288.15	2.93±0.05	0.430±0.004	-37.04±0.55	1.75±0.12	-10.97±0.25	090.47±0.88
	298.15	3.40±0.03	0.463±0.007	-36.95±0.64	2.19±0.14	-11.50±0.47	085.38±0.85
	308.15	3.61±0.07	0.515±0.006	-36.67±0.47	2.62±0.09	-11.87±0.36	080.50±0.74
	318.15	3.97±0.04	0.554±0.008	-36.50±0.98	2.62±0.13	-12.32±0.51	076.02±0.62
10	288.15	4.30±0.06	0.427±0.007	-35.66±0.38	3.12±0.08	-13.53±0.23	076.81±1.53
	298.15	4.83±0.05	0.483±0.005	-35.15±0.42	4.00±0.17	-13.97±0.27	071.03±1.24
	308.15	5.39±0.07	0.505±0.009	-35.38±0.61	3.91±0.25	-14.71±0.18	067.09±0.96
	318.15	6.25±0.04	0.520±0.007	-35.59±0.28	3.54±0.34	-15.52±0.62	063.06±1.08
	308.15	7.72±0.06	0.375±0.008	-36.97±0.35	5.72±0.24	-10.96±0.44	084.40±1.16
	318.15	8.27±0.03	0.424±0.009	-36.73±0.52	5.71±0.41	-11.33±0.36	079.83±0.84
15	288.15	5.89±0.04	0.460±0.006	-33.76±0.81	5.03±0.23	-18.25±0.27	053.80±1.32
	298.15	7.11±0.05	0.488±0.004	-33.59±0.96	5.56±0.15	-19.19±0.43	048.29±1.06
	308.15	8.12±0.04	0.534±0.005	-33.16±0.74	6.14±0.18	-19.87±0.35	043.11±1.19
	318.15	9.86±0.05	0.574±0.007	-32.57±0.78	6.56±0.31	-20.60±0.28	037.60±0.86
20	288.15	8.26±0.06	0.495±0.008	-31.77±0.65	7.02±0.25	-21.23±0.19	036.58±0.72
	298.15	9.31±0.02	0.534±0.006	-31.59±0.44	7.56±0.18	-22.14±0.27	031.68±0.64
	308.15	9.92±0.03	0.634±0.004	-30.20±0.53	9.10±0.31	-22.04±0.34	026.47±0.42
	318.15	15.25±0.04	0.655±0.005	-29.17±0.88	9.96±0.22	-23.13±0.42	018.97±0.33
Dioxane							
5	288.15	2.67±0.05	0.436±0.008	-37.25±0.68	1.54±0.41	-09.53±0.24	096.18±0.69
	298.15	3.17±0.04	0.474±0.007	-36.95±0.57	2.19±0.35	-09.96±0.36	090.55±0.76
	308.15	3.23±0.06	0.525±0.005	-36.85±0.48	2.45±0.26	-10.28±0.21	086.21±0.99
	318.15	3.48±0.05	0.569±0.006	-36.62±0.95	2.51±0.38	-10.63±0.15	081.70±0.82
10	288.15	3.70±0.03	0.461±0.009	-35.45±0.77	3.34±0.44	-11.98±0.32	081.44±1.03
	298.15	4.33±0.04	0.507±0.010	-35.00±0.96	4.15±0.63	-12.44±0.17	075.66±1.25
	308.15	4.69±0.03	0.564±0.009	-34.50±0.84	4.80±0.78	-12.78±0.42	070.47±0.63
	318.15	5.19±0.04	0.588±0.008	-34.65±0.76	4.48±0.25	-13.40±0.33	066.78±0.97
15	288.15	4.87±0.05	0.507±0.009	-36.80±0.48	3.84±0.46	-19.64±0.26	059.54±0.85
	298.15	5.47±0.05	0.578±0.005	-36.64±0.73	5.02±0.66	-20.51±0.21	054.10±0.75
	308.15	6.03±0.05	0.618±0.006	-35.95±0.65	6.73±0.84	-21.22±0.13	047.81±0.63
	318.15	7.78±0.06	0.648±0.007	-35.29±0.94	7.14±0.62	-22.02±0.34	041.70±0.92

(*Contd*)

Table 2 – Micellization and thermodynamic parameters of C14BCl in presence of organic solvents at different temperatures—(*Contd*)

Organic solvent (%)	T (K)	CMC (mM)	α	ΔG^{o}_{m} (kJ mol^{-1})	$\Delta G^{o}_{m,\ trans}$ (kJ mol^{-1})	ΔH^{o}_{m} (kJ mol^{-1})	ΔS^{o}_{m} (J mol^{-1}K^{-1})
Dioxane—(*Contd*)							
20	288.15	7.17±0.08	0.526±0.011	-31.61±0.74	7.17±0.71	-18.38±0.19	045.91±0.44
	298.15	8.06±0.09	0.569±0.009	-31.34±0.86	7.80±0.63	-19.11±0.24	041.03±0.35
	308.15	9.33±0.08	0.633±0.012	-30.43±0.66	8.86±0.78	-19.50±0.33	035.48±0.26
	318.15	12.33±0.07	0.629±0.009	-30.50±0.38	8.63±0.44	-20.84±0.36	030.35±0.41
Ethylene glycol							
5	288.15	2.22±0.04	0.372±0.009	-39.49±0.64	-0.69±0.02	-06.91±0.39	113.07±0.98
	298.15	2.33±0.03	0.436±0.010	-39.07±0.75	0.08±0.01	-07.11±0.41	107.19±1.04
	308.15	2.43±0.03	0.470±0.007	-39.34±0.82	-0.03±0.00	-07.43±0.25	103.55±1.62
	318.15	2.67±0.04	0.505±0.005	-39.31±0.46	-0.17±0.01	-07.73±0.34	099.24±1.57
10	288.15	2.33±0.03	0.396±0.003	-38.72±0.95	0.07±0.01	-13.17±0.64	088.66±0.72
	298.15	2.67±0.04	0.429±0.008	-38.71±0.87	0.44±0.07	-13.82±0.27	083.50±1.22
	308.15	2.93±0.05	0.463±0.006	-38.78±0.63	0.52±0.08	-14.44±0.62	078.98±1.05
	318.15	3.33±0.03	0.498±0.015	-38.62±0.54	0.51±0.12	-15.04±0.44	074.10±0.88
15	288.15	2.40±0.04	0.411±0.012	-38.25±0.82	0.54±0.09	-18.40±0.38	068.88±0.96
	298.15	2.90±0.04	0.437±0.011	-38.19±0.74	0.95±0.21	-19.38±0.42	063.12±1.12
	308.15	3.23±0.03	0.467±0.007	-38.29±0.66	1.00±0.13	-20.30±0.15	058.39±0.96
	318.15	2.97±0.04	0.486±0.006	-38.22±0.59	0.91±0.15	-21.37±0.28	052.96±1.06
20	288.15	2.90±0.08	0.414±0.003	-37.46±0.84	1.33±0.18	-17.62±0.31	068.85±1.12
	298.15	3.37±0.07	0.480±0.008	-36.58±0.93	2.57±0.14	-18.08±0.47	062.05±0.94
	308.15	3.73±0.06	0.488±0.009	-37.21±0.78	2.08±0.16	-19.21±0.55	058.42±0.87
	318.15	4.73±0.07	0.526±0.008	-36.55±0.68	2.57±0.22	-19.96±0.47	052.15±0.74

[a]Ref. 33

the ionic head groups of the surfactant molecules, which leads to increase in CMC values. Further, the high value of the CMC in presence of DO is also due to the fact that DO is a non-polar aprotic cyclic ether which can exist in two isomeric (either boat or chair) forms. It provides a larger surface area resulting in decrease in solvophobicity of the surfactant molecules which causes solvation of greater amount of surfactant monomer than that in pure water[38–39].

Degree of counterion dissociation (α)

The degree of counterion dissociation (α) has been determined by taking the ratio of postmicellar slope and premicellar slope of the plot of κ versus C (Tables 1–3) for various surfactants. These values increase with the percentage (*v/v*) of organic solvent and for a particular surfactant and are higher in DO/DMF than in EG mixtures (except for TTAB in 5% EG at 288.15 K). The decrease in polarity of a particular medium on addition of an organic solvent leads to an increased repulsion between the charged groups[40]. In order to balance this, a larger fraction of the counterions may be moved to the micellar surface from their dissociated state and decrease in the α values may be expected for at least low percentages of organic solvent as observed for 5% DMF in the case of TTAB and 5% EG for 14-2-14 at 288.15 K (Tables 1 & 3). The increase in percentage of organic solvents decreases the micellar surface charge density leading to the increase in α values[41]. Moreover, the increase in CMC of the surfactants caused by the presence of organic solvents results in an increase in ionic strength because of increase in monomer concentration. Hence, the electrostatic repulsions between the charged head groups in the micelles decrease due to screening affect which results in increase in α values[42].

Among the studied surfactants, the α values are higher in the case of C14BCl as compared to TTAB and 14-2-14, due to decrease in surface charge density because of steric hindrance and repulsive interactions of the bulky head groups in C14BCl which would keep the head groups further apart[43]. Also, the increase in α values for conventional monomeric surfactants following addition of organic solvent is larger than for 14-2-14 due to non-uniformity of the charge distribution for the latter causing the nearest charges on the neighboring molecules to be further apart[21]. Therefore, the electrostatic repulsive energy is reduced and the additional reduction provoked by the increase in ionic strength due to organic solvent will be less important, causing only a slight increase in α values.

Table 3 – Micellization and thermodynamic parameters of 14-2-14 in presence of organic solvents at different temperatures

Organic solvent (%)	T (K)	CMC (mM)	α	ΔG^{o}_{m} (kJ mol^{-1})	$\Delta G^{o}_{m,\,tail}$ (kJ mol^{-1})	$\Delta G^{o}_{m,\,trans}$ (kJ mol^{-1})	ΔH^{o}_{m} (kJ mol^{-1})	ΔS^{o}_{m} (J mol^{-1}K^{-1})
—	288.15	0.138±0.005	0.191±0.005	-80.94±0.56	-40.46	0.00	-22.05±0.63	204.35±1.82
	298.15	0.151±0.004 (0.15)[a] (0.14)[b]	0.248±0.006	-79.53±0.89	-39.76	0.00	-22.58±0.74	191.04±1.42
	308.15	0.168±0.003 (0.17)[a]	0.285±0.004	-79.11±0.47	-39.55	0.00	-23.40±0.55	180.77±1.68
	318.15	0.199±0.006 (0.20)[a]	0.312±0.003	-78.80±0.74	-39.40	0.00	-24.39±0.42	171.00±1.14
Dimethylformamide								
5	288.15	0.204±0.007	0.192±0.002	-78.42±0.46	-39.21	2.51±0.24	-31.45±0.74	163.01±2.54
	298.15	0.230±0.005	0.256±0.001	-76.43±0.58	-38.21	3.10±0.26	-32.02±0.68	148.95±1.74
	308.15	0.287±0.004	0.308±0.004	-74.34±0.69	-37.17	4.76±0.35	-32.78±0.85	134.88±1.68
	318.15	0.344±0.006	0.354±0.008	-72.69±0.78	-36.34	6.10±0.42	-33.59±0.62	122.90±1.35
10	288.15	0.293±0.005	0.246±0.007	-73.01±0.85	-36.50	7.92±0.18	-41.65±0.52	108.83±1.08
	298.15	0.359±0.002	0.309±0.008	-70.55±0.27	-35.27	8.98±0.22	-42.35±0.74	094.57±0.86
	308.15	0.452±0.004	0.295±0.006	-72.33±0.35	-36.16	6.77±0.15	-45.77±0.76	086.20±0.77
	318.15	0.603±0.003	0.330±0.006	-70.74±0.47	-35.37	8.05±0.34	-47.37±0.80	073.45±0.94
15	288.15	0.406±0.004	0.269±0.005	-69.74±0.98	-34.87	11.19±0.25	-48.75±0.95	072.86±0.63
	298.15	0.537±0.006	0.296±0.004	-68.91±0.87	-34.45	10.62±0.18	-51.05±0.34	059.92±0.73
	308.15	0.713±0.004	0.350±0.008	-66.36±0.63	-33.18	12.75±0.33	-52.08±0.72	046.32±0.85
	318.15	0.960±0.008	0.337±0.007	-67.46±0.42	-33.73	11.34±0.31	-56.15±0.83	035.55±0.75
20	288.15	-	-	-	-	-	-	-
	298.15	0.767±0.007	0.425±0.007	-59.63±0.58	-29.81	19.90±0.28	-42.52±0.74	057.36±0.76
	308.15	1.060±0.007	0.474±0.008	-57.12±0.63	-28.56	21.99±0.27	-43.35±0.62	044.66±0.67
	318.15	1.310±0.008	0.547±0.008	-53.71±0.74	-26.85	25.08±0.33	-42.93±0.75	033.89±0.74
Dioxane								
5	288.15	0.183±0.002	0.257±0.005	-75.17±0.87	-37.58	5.76±0.18	-29.78±0.55	157.53±2.13
	298.15	0.225±0.004	0.298±0.005	-73.98±0.64	-36.99	5.55±0.14	-30.83±0.63	144.73±1.76
	308.15	0.285±0.003	0.326±0.006	-73.26±0.74	-36.63	5.85±0.28	-32.16±0.47	133.36±1.65
	318.15	0.308±0.001	0.385±0.008	-71.38±0.28	-35.69	7.42±0.42	-32.56±0.72	122.00±1.02
10	288.15	0.250±0.002	0.208±0.009	-76.20±0.85	-38.10	4.73±0.34	-40.85±0.84	122.68±1.08
	298.15	0.317±0.002	0.253±0.010	-74.63±0.64	-37.31	4.90±0.27	-42.21±0.63	108.73±0.95
	308.15	0.390±0.003	0.278±0.008	-74.29±0.36	-37.14	4.81±0.19	-44.19±0.88	097.69±0.46
	318.15	0.497±0.007	0.306±0.004	-73.41±0.42	-36.70	5.38±0.22	-46.02±0.72	086.09±0.57
15	288.15	0.361±0.005	0.234±0.006	-72.44±0.57	-36.22	8.49±0.34	-40.22±0.79	111.82±0.36
	298.15	0.458±0.006	0.285±0.003	-70.50±0.77	-35.25	9.03±0.17	-41.32±0.63	097.86±0.42
	308.15	0.577±0.009	0.337±0.007	-68.37±0.36	-34.18	10.73±0.25	-42.25±0.74	084.75±0.74
	318.15	0.720±0.004	0.376±0.005	-66.91±0.54	-33.45	11.89±0.25	-43.53±0.68	073.47±0.52
20	288.15	0.519±0.008	0.255±0.008	-69.07±0.74	-34.53	11.86±0.34	-39.82±0.85	101.51±0.89
	298.15	0.593±0.010	0.257±0.004	-70.53±0.64	-35.20	09.00±0.31	-42.56±0.92	093.81±0.76
	308.15	0.812±0.010	0.303±0.006	-68.27±0.63	-34.13	10.84±0.45	-43.78±0.73	079.44±0.72
	318.15	1.040±0.009	0.353±0.005	-66.04±0.84	-33.02	12.75±0.33	-44.72±0.72	067.01±0.42
Ethylene glycol								
5	288.15	0.131±0.002	0.188±0.004	-81.45±0.56	-40.72	-0.51±0.05	-35.80±0.99	158.43±2.66
	298.15	0.136±0.004	0.254±0.005	-79.80±0.47	-39.90	-0.26±0.07	-36.39±0.86	145.50±2.54
	308.15	0.190±0.002	0.268±0.006	-79.44±0.84	-39.72	-0.33±0.03	-38.44±0.84	133.05±2.12
	318.15	0.237±0.003	0.290±0.002	-79.14±0.67	-39.57	-0.34±0.04	-40.24±0.92	122.26±1.47
10	288.15	0.130±0.004	0.207±0.004	-80.32±0.74	-40.16	0.62±0.08	-45.66±0.75	120.29±1.62
	298.15	0.173±0.004	0.246±0.006	-78.82±0.78	-39.41	0.72±0.05	-47.40±0.62	105.37±1.74
	308.15	0.206±0.002	0.273±0.004	-78.61±0.63	-39.30	0.50±0.06	-49.55±0.48	094.32±1.02
	318.15	0.280±0.006	0.296±0.005	-77.69±0.58	-38.84	1.11±0.04	-51.82±0.66	081.29±0.96
15	288.15	0.145±0.005	0.201±0.005	-80.01±0.94	-40.00	0.93±0.07	-46.76±0.58	115.4±0.84
	298.15	0.191±0.003	0.242±0.004	-78.45±0.76	-39.23	1.08±0.03	-48.48±0.74	100.54±0.99
	308.15	0.250±0.004	0.258±0.003	-78.34±0.28	-39.17	0.77±0.02	-51.13±0.63	088.31±0.75
	318.15	0.317±0.002	0.276±0.003	-78.17±0.53	-39.09	0.63±0.01	-53.71±0.47	076.90±0.63
20	288.15	0.169±0.004	0.191±0.005	-79.67±0.67	-39.83	1.27±0.04	-53.97±0.84	089.16±0.84
	298.15	0.235±0.003	0.224±0.005	-78.26±0.48	-39.13	1.27±0.03	-56.32±0.67	073.57±. 0.77
	308.15	0.308±0.003	0.238±0.008	-78.25±0.86	-39.12	0.85±0.03	-59.51±0.38	060.82±0.88
	318.15	0.414±0.004	0.254±0.006	-77.82±0.69	-38.91	0.98±0.04	-62.63±0.61	047.73±0.63

[a]Ref. 34; [b]Ref. 30.

Effect of temperature on CMC and α

The CMC and α values for all the studied surfactants in various organic solvents are found to increase with the increase in temperature (Tables 1–3). In aqueous solutions, an increase in temperature can influence the CMC of the surfactants by two ways. Firstly, it causes disruption of the water structure surrounding the hydrophobic groups, which does not favor micellization. Secondly, it decreases the degree of hydration of the hydrophilic group, which favors micellization. In the present case, it first effect appears to predominate over the second in the studied temperature range. This is due to considerable change in the three dimensional water structures in comparison to the dehydration of the hydrophilic head groups during micellization[44, 45]. Similar observations have been reported in the past for conventional as well as gemini surfactants[32, 46–48]. In pure water, the increase in CMC with temperature is less than that in the presence of organic solvents. The increase in CMC with respect to temperature becomes more pronounced as the organic solvent content increases in the medium. It has also been seen that the variation in CMC values with temperature is less in the case of EG than in the other two solvents (Fig. 3) because EG has similar physical properties as that of water as discussed earlier. As the temperature increases, a large fraction of the surfactant and counterions remain in dissociated form leading to increase in α at a particular composition of the solvent[49].

Thermodynamics of micellization

The thermodynamic parameters of micellization of the studied surfactants were obtained from the temperature dependence of CMC and α. The Gibbs energy of micelle formation, ΔG^{o}_{m}, of TTAB/C14BCl and 14-2-14 have been given by the following equations respectively.

$$\Delta G^{o}_{m} = (2-\alpha)RT\ln(X_{CMC})$$

$$\Delta G^{o}_{m} = (3-2\alpha)RT\ln(X_{CMC})$$

where R, T and X_{CMC} are the gas constant, temperature and the CMC in mole fraction units respectively. To study the effect of solvent on micellization process, the Gibbs free energy micellization per alkyl chain ($\Delta G^{o}_{m,tail}$) of 14-2-14 and Gibbs free energy of transfer ($\Delta G^{o}_{m,trans}$) have been calculated using the following equations.

$$\Delta G^{o}_{m,tail} = {\Delta G^{o}_{m}}/{2}$$

$$\Delta G^{o}_{m,trans} = \Delta G^{o}_{m(\text{organic solvent + water})} - \Delta G^{o}_{m(\text{pure water})}$$

The values of ΔG^{o}_{m}, $\Delta G^{o}_{m,tail}$ and $\Delta G^{o}_{m,trans}$ obtained for various surfactants are given in Tables 1–3. ΔG^{o}_{m} values were found to be negative in all the cases and become less negative with increasing percentage of organic solvent at a given temperature. The bulk phase of the solvent system acts as a better solvent for the hydrophobic tail of the surfactant molecule as compared to pure water with increasing percentage of organic solvent causing a less spontaneous process of micellization. The values of ΔG^{o}_{m} in case of 14-2-14 seem to be much higher as compared to TTAB/C14BCl, but the values of ΔG^{o}_{m} per alkyl tail i.e. $\Delta G^{o}_{m,tail}$ are comparable with the values of ΔG^{o}_{m} obtained for monomeric surfactants TTAB/C14BCl as shown in Table 3. In comparison with the solvent DO and DMF, the micellization process of the studied surfactants is little bit more spontaneous in EG and this may be due to similarity in properties of EG to water.

To further support the effect of organic solvents on the spontaneity of the micellization process, $\Delta G^{o}_{m,trans}$ values have also been calculated (Tables 1–3). The positive values of $\Delta G^{o}_{m,trans}$ become more positive on increasing the percentage of organic solvent due to the reduction in solvophobicity[44]. Furthermore, the values of $\Delta G^{o}_{m,trans}$ at a particular composition of organic solvent are more positive in presence of DO/DMF than that for EG mixtures. In fact, at low concentrations of EG (5%), the $\Delta G^{o}_{m,trans}$ values were found to be slightly negative in the case of C14BCl and 14-2-14 (Tables 2 & 3) which further strengthens

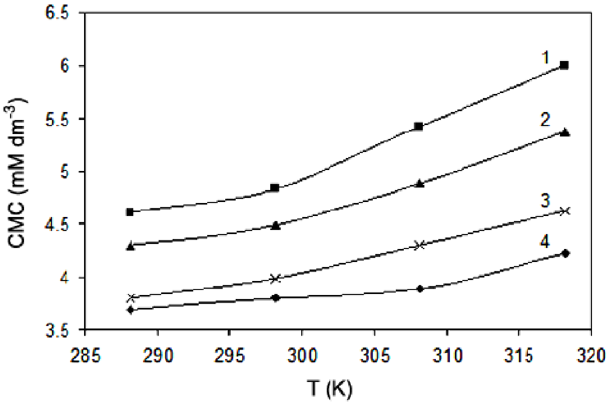

Fig. 3 – Variation of CMC of TTAB with temperature in 5% aqueous solvent solutions. [1, water; 2, DMF; 3, DO; 4, EG].

the resemblance of EG with water. At a fixed concentration of the water-organic solvent mixture, the ΔG^{o}_{m} values for all the studied surfactants were found to vary slightly with rise in temperature, suggesting that the micellization is weakly dependent on temperature in the studied range.

The enthalpy change ΔH^{o}_{m} upon micellization has been calculated as

$$\Delta H^{o}_{m} = -(2-\alpha)RT^{2}\frac{d\ \ln(X_{CMC})}{dT}$$

$$\Delta H^{o}_{m} = -(3-2\alpha)RT^{2}\frac{d\ \ln(X_{CMC})}{dT}$$

The ΔH^{o}_{m} values thus calculated for the surfactants at various temperatures are given in Tables 1–3. These values were found to be negative indicating that the London dispersion forces are the main attractive forces in the micelle formation[22]. The ΔH^{o}_{m} values were found to decrease with increase in temperature due to change in hydration of ionic head groups[50]. These values were also found to decrease with increase in percentage of the organic solvent at a fixed temperature in the studied concentration range. At all the temperatures, the magnitude of ΔH^{o}_{m} was found to be higher in the presence of organic solvent.

The entropy of micellization ΔS^{o}_{m} has been estimated from the calculated values of free energy and enthalpy as

$$\Delta S^{o}_{m} = \frac{\Delta H^{o}_{m} - \Delta G^{o}_{m}}{T}$$

The positive values of ΔS^{o}_{m} thus calculated (Tables 1–3) decrease with increase in temperature for a fixed concentration and showed a rough decrease with increase in volume percentage of the organic solvent at a particular temperature. This indicates that the ordering of the randomly oriented cationic surfactant from the solvated form into the micellar structure is more pronounced than the destruction of the water structure, either due to the presence of organic solvent or increase in temperature, resulting in an effective decrease in the degree of randomness of the system. Since the enthalpy of micellization is negative and becomes more negative with the rise in temperature, the positive entropy change becomes less positive. Thus, the two terms tend to compensate each other during the micellization of the studied surfactants in the presence of the organic solvents.

Viscosity studies

In order to evaluate the effect of these organic solvents on the micellar size, shape and organization of micelles, the relative viscosity (η_r) of the studied surfactants in aqueous and aqueous solvent solutions have also been calculated at different temperatures. Figure 4 shows the variation of η_r with temperature for the studied surfactants in aqueous solutions. Since the viscosity of a solution is an indicator of the size of the micelle formed, the size of the micelle formed follows the trend: TTAB > C14BCl > 14-2-14. The η_r values were found to decrease with the temperature in the case of TTAB and C14BCl, whereas for 14-2-14, η_r increased slightly with temperature from 288.15 to 298.15 K and decreased with further increase in temperature. The initial increase in η_r may be related to increased hydrophobic interactions between the twin tails of 14-2-14, which gets reduced due to dominance of repulsions between the similarly charged head groups at higher temperatures.

The environment of solubilization of different additives in or around surfactant micelles can be correlated with their structural organization and mutual interactions[51–52]. Mukerjee[53] had proposed that an additive which is surface active to a hydrocarbon-water interface will be mainly solubilized at the micellar surface and will promote micellar growth. At low concentrations of the solvent (5%), η_r of both TTAB and C14BCl increases as the temperature rises from 288.15 to 298.15 K and then decreases with further rise in temperature as shown in Fig. 5a. The initial increase in this case may be due to increase in solubility of these additives causing reduction in hydrophobic interactions.

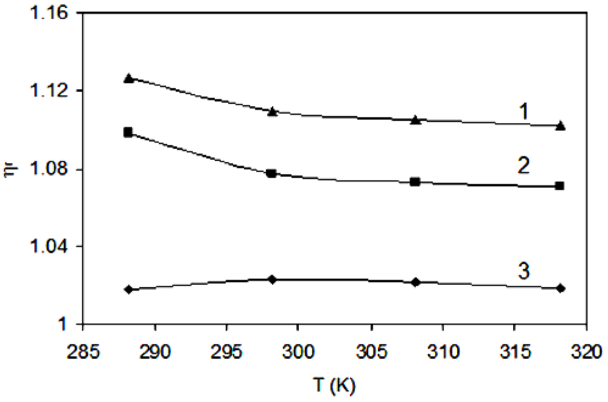

Fig. 4 – Variation of η_r with temperature for 14-2-14, C14BCl and TTAB in aqueous solutions. [1, 14-2-14; 2, C14BC1; 3, TTAB].

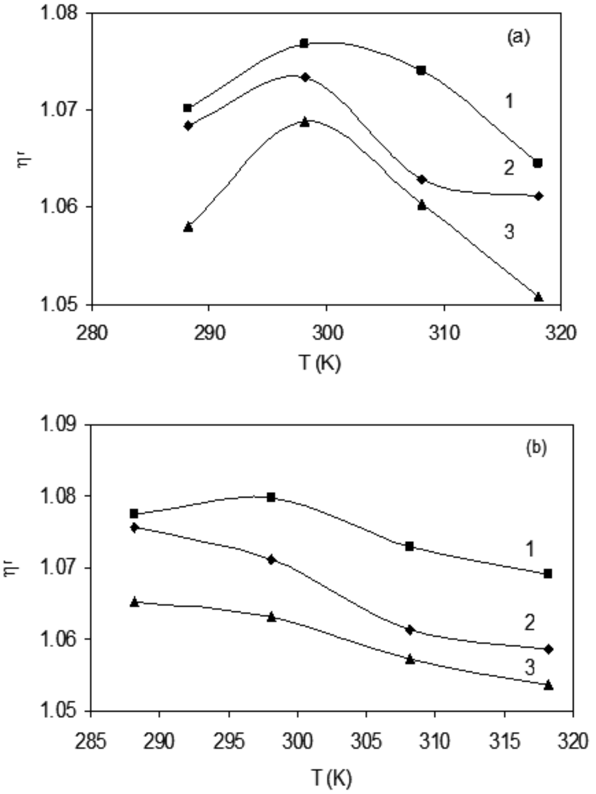

Fig. 5 – Effect of temperature on η_r of C14BCl in (a) 5 and (b) 10% aqueous solvent solutions. [1, DMF; 2, EG; 3, DO].

Further rise in temperature causes disruption of water structure surrounding the hydrophobic groups resulting in the formation of shorter micelles. The η_r values were found to be higher in presence of ethylene glycol among the studied solvents, due to high cohesive energy of ethylene glycol leading to high viscosity of these solutions. With the rise in concentration of the organic solvent (10%), the η_r values increase and follow almost a similar trend as in 5% solvents in the case of TTAB. However, for C14BCl these values decrease with increase in temperature (Fig. 5b). In the case of 14-2-14 in presence of 5% solvents, the η_r values increase with rise in temperature from 288.15 to 298.15 K and remain almost the same with further rise in temperature which might be due to the fact that the increase in temperature is counter balanced by enhanced hydrophobic interactions between the two tails of 14-2-14. However, at higher concentrations of these solvents, the η_r values of 14-2-14 increase with temperature.

Conclusions

The CMC of the studied surfactants increases in presence of ethylene glycol, dioxane and dimethyl formamide as these are better solvents than pure water. The increment in the CMCs in presence of ethylene glycol is the least among the studied solvents. Both CMC and α values increase with temperature and concentration of the solvents. The ΔG^{o}_{m} values show that the micellization process become less favorable as the concentration of the organic solvent increases. Similarly, the decrease in positive ΔS^{o}_{m} with increase in organic solvent concentration indicates the ordering of the randomly oriented cationic surfactants. The viscosity studies indicate that the size of the micelles formed follow the trend: TTAB > C14BCl > 14-2-14. Further, the higher η_r values of these surfactants in the presence of ethylene glycol may be attributed to its higher cohesive energy.

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