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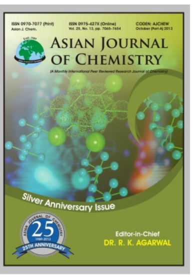

Thermodynamics and Aggregation Number of Surfactants in Water-Acetonitrile Mixtures

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Cationic surfactants of alkyl (dodecyl, tetradecyl and cetyl) trimethyl ammonium bromide (C_{12}TAB, C_{14}TAB and C_{16}TAB) respectively can be used to study micellization phenomenon in water-acetonitrile mixtures. Their critical micelle concentrations are measured by using different techniques such as conductivity, UV spectra and density at different mole fractions of acetonitrile and temperatures. Effects of adding NaBr to C_{12}TAB and C_{14}TAB solutions are discussed from conductance technique. Thermodynamics of micellization are studied by applying equilibrium model at different X_{AN} and temperatures. Gibbs energies of transfer per methylene group ($\delta\Delta G/\delta\, n_c$) are calculated at 298 K but at different X_{AN}. The differences in partial molar volume ($\Delta V_{sur.}$) for those solutions below and above (critical micelle concentration) formed are estimated *via* density measurements and the related aggregation numbers can be calculated from Huisman's treatment and compared with ΔV_{sur} values. Finally, the Krafft phenomena for given solutions are derived and discussed.

Key Words: Micellization, Solvophobic behaviour, Water-acetonitrile mixtures, Aggregation number, Krafft phenomena.

INTRODUCTION

Hydrophobic processes such as the aggregation of surfactants to form micelles, bilayer membranes and vesicles and the folding of globular proteins are important in understanding and controlling many industrial and biological processes. For examples, detergency, cleaning of surfaces, enhanced oil recovery, controlling drug delivery and the digestion of fats and cholesterol. All involve the aggregation of molecules containing hydrocarbon chains in aqueous solutions.

Two basic precise of this reexamination are (i) that water shares a number of solvophobic features with other solvents either polar hydrogen bonding such as ethylene glycol[1] and hydrazine[2] or dipolar aprotic solvents such as DMF[3], (ii) that water differs markedly in its structure by its unique three dimensional structure than all other solvents.

Comparing the data on hydrophobic process such as micelle in water and in their mixtures with acetonitrile will reveal part of the information's required to gain a deeper understanding of water. Several studies show that cosolvents with water can inhibit the formation of micelles due to the dielectric constant (ε) of the cosolvent and its hydrophobic character[4-9].

In this work, the micellization phenomenon for the above solutions in pure water or cooperative with AN makes this type research be more interesting.Accordingly some applications depending on the resulting critical micelle concentration (CMC) will carried out such as (a) Effect of adding common ion salt on micellization behaviour. (b) Thermodynamic of micelle. (c) The free energy associated with transfer of methylene group from the bulk of solution into the interior of micelle core. (d) Partial molar volume of the above solutions and the related aggregation number, finally the related (e) Krafft phenomena.

EXPERIMENTAL

Cationic surfactants of (C_{12}TAB) (C_{14}TAB) and (C_{16}TAB) (Eastman Kodak) with purity > 99.5 %, are recrystallized from acetone and dried in a vacuum at about 323.2 K. Surface tension measurements for these surfactants in water gave no indication of a minimum near the critical micelle concentration CMC values means that no impurities are present. NaBr (Merck) as added salt is used with purity > 98.5 %

Conductivity water was obtained by passing ordinary distilled water from a tin still over a 60 cm long Elgastat deionizer and kept CO_2 free using soda lime tube where the specific conductance γ is 2-5 × 10^{-7} S cm^{-1}.

Acetonitrile (AN) (Merck Analar) is dried over night in contact with 3°A molecular sieves; then distilled using fractionating column where middle fraction was only collected. Its γ is found to be 5 × 10^{-8} S cm^{-1}.

Each H_2O-AN mixture is prepared by weighing definite volume of AN in 250 mL measuring flask, then add the required amount of fresh conductivity water to give the desire X_{AN}.

Surfactant solutions are prepared by weighing definite amount of surfactant into 10 mL weighing bottles using Mettler

H 80 balance with accuracy of ± 10^{-4}. Add the required solvent either pure water or H_2O-CH_3CN mixtures to attain the required molar concentration.

Conductivity meter model (HI 8819) was used to measure specific conductance's γ of the above solutions at different temperatures with accuracy of ± 0.05 K.

Ultraviolet spectra are carried out on a Shimadzu (Japan) model 160-AUV visible spectrophotometer to define CMC at 298 K. In this field, UV absorbency at different surfactant solutions at given X_{AN} was carried out at maximum wave length λ_{max} = 210 nm.

Density measurements are carried out for surfactant solutions in small range of (H_2O-CH_3CN) mixtures (X_{AN} = 0.0, 0.2 and 0.4) as a function of molar concentration and temperature. The measurements are carried out using density meter model DMA 48 where the filling of liquid sample was drawn into the dry cell of this meter either manually using a syringe or semi automatically using a pump or an aspirator pump. The temperature is adjusted by a built in solid state thermostat.

RESULTS AND DISCUSSION

Critical micelle concentrations (CMCs) for C_{12}TAB, C_{14}TAB and C_{16}TAB are derived from conductance measurements at different X_{AN} and temperatures(298-318 K). In this field, measurement depends on the change in the behaviour of monomeric surfactant molecules during variation into micelle which CMC can be detected by plotting molar conductance Λ(S cm^2 mol^{-1}) against root mean squares of molar concentration $\sqrt{C_m}$ (mol L^{-1}) of surfactant to give CMC at broken down line. Table-1 shows CMCs for these surfactants derived from three different methods as conductance, density and UV spectra at different X_{AN} = 0.0, 0.2 and 0.4 and at 298, 308 and 318 K respectively where CMC is found to increase by increasing either AN or temperature.

UV absorbance at 298 K is taken at λ_{max} = 210 nm for C_{12}TAB and C_{14}TAB solutions separately at X_{AN} equals 0.2 and 0.4 where CMC can be detected at the broken slope from plotting maximum absorbance against the related molar concentration.

The equilibrium between monomers and micelle can be given by:

$$NS^+ + (N\text{-}p)\ Br^- \rightarrow M^{P+} \tag{1}$$

where S^+, represents cationic surfactant, M^{p+} is the formed micelle and N is the aggregated number of the micelle. The equilibrium constant:

$$K = C_M^{P+}/[(C_{s+})^N\ (C_{Br^-})^{N-p}] \tag{2}$$

can be related to standard free energy of micellization per monomer by:

$$\Delta G_m/(NRT) = -1/N\ \ln C_M^{P+}\ \ln C_S + (1\text{-}p/N)\ \ln C_{Br^-} \tag{3}$$

Since N is highly in water within (50-100), the C_M^{p+} term is small and insensitive to be estimated.

In absence of added salt, both C_{S+} and C_{Br}- can be replaced by the CMC in eqn. (3) hence:

$$\Delta G_m/(NRT) = (2\text{-}\beta)\ \ln CMC \tag{4}$$

where β = p/N is the degree of dissociation of the micelle. For completely ionized micelle β = 1 while for neutral one either zwitter ionic or nonionic surfactants, β = 0.

To introduce β value in eqn. (4), another treatment is adopted by Mukerjee *et al.*[10] related CMC in presence of added NaBr as common ion at different media with the above equilibria as following:

$$\ln CMC = 1/N\ [\ln C_M^{P+} - \ln K]\text{-}(1\text{-}\beta)\ \ln C_i \tag{5}$$

where C_i is the sum of surfactant and molar concentration of NaBr added which represents the concentration of the free counter ions.

TABLE-1
CMC'S FOR C_nTAB IN (H_2O-CH_3CN) MIXTURES AT DIFFERENT TEMPERATURES

X_{AN}	Method	CMC (mol^{-1})		
		C_{12}TAB	C_{14}TAB	C_{16}TAB
		298 K		
0.0	a	0.0156	0.0029	0.0020
	b	0.0155	0.0029	0.0021
	c	0.0157	0.0029	0.0020
0.2	a	0.0161	0.0090	0.0050
	b	0.0162	0.0091	0.0049
	c	0.0160	0.0090	0.0050
0.4	a	0.0167	0.0103	0.0070
	b	0.0169	0.0100	0.0068
	c	0.0168	0.0102	0.0069
		308 K		
0.0	a	0.0163	0.0033	0.0030
	b	0.0160	0.0031	0.0029
	c	0.0162	0.0029	0.0031
0.2	a	0.0169	0.0100	0.0040
	b	0.0170	0.0110	0.0039
	c	0.0168	0.0100	0.0041
0.4	a	0.0178	0.0108	0.0080
	b	0.0178	0.0109	0.0079
	c	0.0179	0.0110	0.0075
		318 K		
0.0	a	0.0173	0.0036	0.0040
	b	0.0174	0.0035	0.0039
	c	0.0172	0.0036	0.0041
0.2	a	0.0178	0.01040	0.0060
	b	0.0179	0.01039	0.0059
	c	0.0179	0.01040	0.0058
0.4	a	0.0187	0.0112	0.0080
	b	0.0186	0.0111	0.0079
	c	0.0188	0.0113	0.0080

a = from conductance measurements, b = from absorbance measurements, c = from density measurements

Qualitative treatment to test the effect of adding NaBr is carried out for C_{12}TAB and C_{14}TAB surfactants. For most surfactants, the presence of electrolytes in aqueous solutions causes a decrease in CMC with the greatest effect being found for ionic surfactants[11,12].

In this field, CMC is determined in presence of 0.01, 0.018 and 0.025 mol L^{-1} NaBr by conductance measurements for C_{12}TAB and C_{14} TAB solutions at only X_{AN} = 0.2 at 298-318 K. The accurate CMC in presence of NaBr is fitted from mean least squares method as shown in Table-2. At any given temperature, the new CMC, is obtained at lower molar concentration than before adding NaBr solution while increases by increasing temperature as shown from Figs. 1 and 2 respectively when plotting Λ_m against $\sqrt{C}$. The lowering in CMC value is primarily due to a reduction in the electrostatic repulsions between polar head groups in presence of the excess counter ions of the electrolyte. The repulsion between head groups of the surfactant is one of the main factors causes destabilization of micelle structures[13].

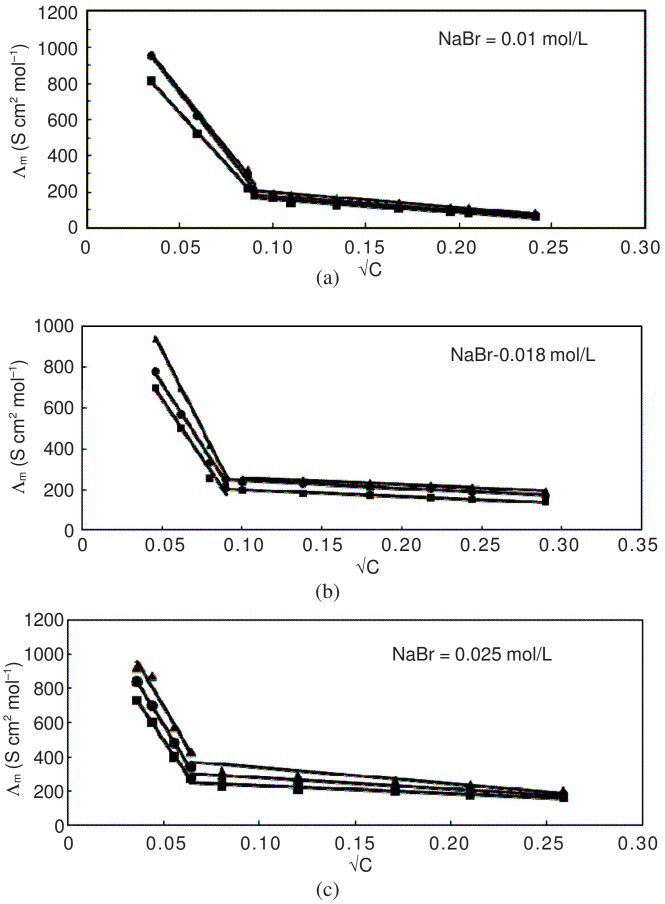


Fig. 1. Variation of Λ_m with √C of $C_{12}TAB$ in X_{AN} = 0.2, in presence of NaBr at ■ 298 K, ● 308 K and ▲ 318 K

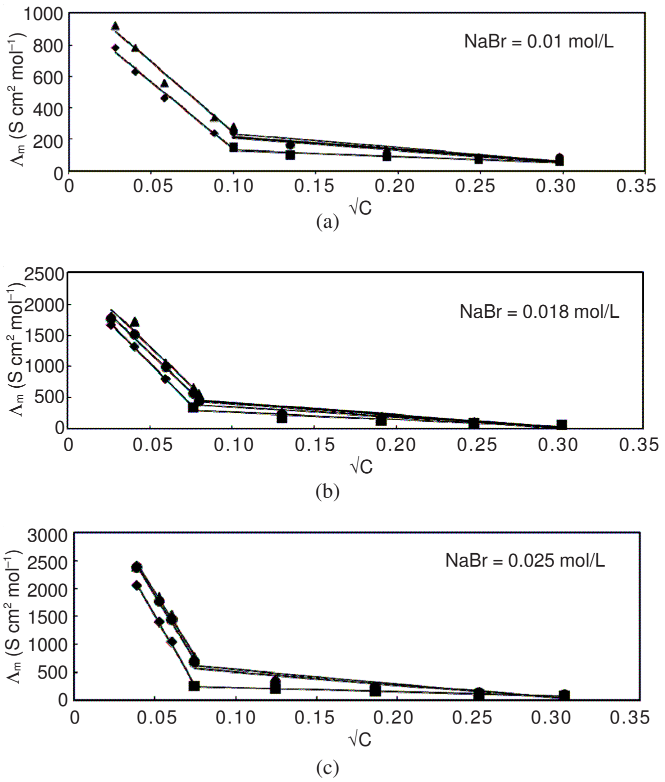


Fig. 2. Variation of Λ_m with √C of $C_{14}TAB$ in X_{AN} = 0.2, in presence of NaBr at ■ 298 K, ● 308 K and ▲ 318 K

The observed inflection in the two intersected lines below and above CMC may attributed to the excess addition of Br^-, as well as to relative binding affinities of the counter ions to the micelle as a result of relative hydration or solvation of these ions. It is possible to explain the effect of counter ion size on the basis of water structure properties which enforced ion pairing or structural salting in or out solution system.

According to eqn. (5), β can be derived from the slope of any system ($C_{12}TAB$ or $C_{14}TAB$) when plotting ln CMC against ln C_i at 0.01, 0.018 and 0.025 mol L^{-1} NaBr at different temperature β value is taken as an average of 0.2 in pure and in mixed solvents. Table-2 related to the decrease in charge density of the Stern layer of the formed micelles[14], thereby decreasing the number of bromide ions bound to micelles[15]. Ramadan *et al.*[16] tested the validity of eqn. (5) from fluorescence techniques when NaCl is added as a common ion (Na^+) solution with sodium dodecyl sulphate (SDS) in pure hydrazine as most similar in properties to water. They obtained an average β value equals 0.2, agreed well with those obtained from light scattering, combination of surfactant and bromide electrode[17], conductance, emf and finally from change of CMC with added salt[18]. Kresheck[19] had found that (1-β) estimated from eqn. (5) is higher by 10 % than obtained from other methods.

Last column of Table-2 concludes the differentiated β values with respect to temperature (δβ/δT) for both $C_{12}TAB$ and $C_{14}TAB$ at X_{AN} = 0.2 which found to be 0.003 at all allowed temperatures agreed with those recorded by Evans *et al.*[20]. They estimated (δβ/δT) for $C_{14}TAB$ in water and found to be 0.003 which attributed to different binding affinities of the counter ions to the micellar surface.

Thermodynamics of the micellization process are obtained from applying equilibrium model. Gibbs free energy of transferring the surfactant hydrocarbon chain into micelle core could be derived from eqn. (4) while enthalpy of micellization ΔH_m is given by:

$$\Delta H_m = RT^2\ [(2-\beta)[\delta \ln CMC/\delta T]_p\ -\ln(CMC)(\delta\beta/\delta T)_p] \quad (6)$$

Finally, the standard entropy of micellization ΔS_m can be obtained from the well known relationship.

$$\Delta S_m = (\Delta H_m - \Delta G_m)/T \quad (7)$$

In all the above equations, the activity has been replaced by molar concentration where the effect of neglecting activity coefficients is estimated from the limiting Debye -Huckel expression.

Values of ΔG_m, ΔH_m and ΔS_m for $C_{12}TAB$ and $C_{14}TAB$ at different X_{AN} are calculated according to the above related equations at 298 to 318 K. The data are collected in Table-3.

In comparing ΔG_m for the two surfactants $C_{12}TAB$ and $C_{14}TAB$ in aqueous solutions, it is found that $C_{14}TAB$ has more negative values than $C_{12}TAB$ at all given temperatures where the negativity for $C_{12}TAB$ is slightly decreases by increasing AN content. ΔG_m for $C_{12}TAB$ at 298 K ranged in between -18.45 and -18.15 kJ mol^{-1}, that at 308 K in between -18,87 and -18.47 kJ mol^{-1} while at 318 K are ranged in between -19.20 and -18.83 kJ mol^{-1}, all at the same range of X_{AN}. The related ΔG_m's for $C_{14}TAB$ at the same trend are obviously within [(-25.91) - (-20.29)], [(-26.19), (-20.76)] and [(-26.63)-(-21.26)] kJ mol^{-1} at 298, 308 and 318 K respectively. This trend can be attributed to the difference lengths of the alkyl

TABLE-2
CMC, β AND (δβ/δT) VALUES IN PRESENCE OF NaBr AT X = 0.2 AND AT DIFFERENT TEMPERATURES

Temp. (K)	NaBr (mol L^{-1})	CMC	-log CMC	log C_i	β ≈ 0.2	(δβ/δT)
			$C_{12}TAB$			
298	0.0100	0.00848	2.0716	1.7333	0.164	0.003
	0.0180	0.00687	2.1629	1.6043		
	0.0250	0.00557	2.2541	1.5147		
308	0.0100	0.00930	2.0315	1.7144	0.194	0.003
	0.0180	0.00760	2.1191	1.5917		
	0.0250	0.00630	2.2007	1.5044		
318	0.0100	0.00980	2.0088	1.7033	0.220	
	0.0180	0.00810	2.0915	1.5833		
	0.0250	0.00680	2.1675	1.4975		
			$C_{14}TAB$			
298	0.0100	0.00800	2.0969	1.7447	0.170	0.003
	0.0180	0.00640	2.1938	1.6126		
	0.0250	0.00520	2.2839	1.5199		
308	0.0100	0.00940	2.0269	1.7122	0.200	0.003
	0.0180	0.00760	2.1192	1.5417		
	0.0250	0.00630	2.2007	1.5045		
318	0.0100	0.00950	2.0223.	1.7099	0.230	
	0.0180	0.00790	2.1023	1.5867		
	0.0250	0.00650	2.1804	1.5003		

TABLE-3
THERMODYNAMICES OF CATIONIC SURFACTANTS AT DIFFERENT TEMPERATURES

X_{AN}	298 K			308 K			318 K		
	ΔG_m (KJ/mol)	ΔH_m (KJ/mol)	ΔS_m (J/mol K)	ΔG_m (KJ/mol)	ΔH_m (KJ/mol)	ΔS_m (J/mol K)	ΔG_m (KJ/mol)	ΔH_m (KJ/mol)	ΔS_m (J/mol K)
				(a) $C_{12}TAB$ in (H_2O- CH_3CN) mixture					
0.00	-18.4510	-15.0160	0.0115	-18.8690	-15.9370	0.0095	-19.2000	-18.0160	0.0037
0.20	-18.3110	-15.5540	0.0092	-18.7030	-16.5010	0.0071	-19.0650	-17.7140	0.0042
0.40	-18.1490	-17.4950	0.0022	-18.4660	-18.5380	0.0002	-18.8320	-18.5480	0.0009
				(b) $C_{14}TAB$ in (H_2O-CH_3CN) mixture					
0.00	-25.9130	-30.0200	-0.0138	-26.1900	-31.7610	-0.0181	-26.6280	-30.4620	-0.0120
0.20	-20.8900	-24.3600	-0.0116	-21.1080	-25.7710	-0.0151	-21.6080	-22.3960	-0.0025
0.40	-20.2920	-16.4000	0.0131	-20.7550	-17.4060	0.0109	-21.2570	-17.6330	0.0114

chain where $C_{14}TAB$ needs more work to study the effect of solvent and enter the micellar core and finally associate solvent molecules around the formed micelle.

Aguiar *et al.*[21] calculated ΔG_m for $C_{14}TAB$ in formamide-water system, found that its value in water is negative where its negativity be decreases by increasing formamide content. They also stated that ΔG_m was roughly dependent on temperature where no valuable variation was observed by increasing it. Moya *et al.*[22] attributed the decrease in the interfacial Gibbs energy term upon increasing the organic solvent content at least partially responsible for the observed decrease in aggregated number.

ΔH_m is strongly affected by medium nature in which hydrogen bonding may strengthened or weakened, formed or broken between H_2O and H_2O-CH_3CN molecules. Also there must be an interaction between the charge on the counter ions in the formed micelle and the totality of charges in the solvent. Accordingly, ΔH_m for $C_{12}TAB$ at 298 K is found to vary from -15.02 kJ mol^{-1} in pure water into -17.50 kJ mol^{-1} at $X_{AN} = 0.4$ where the negativity is increased also by increasing temperatures. In case of $C_{14}TAB$, ΔH_m is showed to start in pure water with more negative value than in their co solvent at all allowed temperatures due to difference in hydrophobic tendency in water and mixtures. In comparing ΔH_m for $C_{12}TAB$ and $C_{14}TAB$ it is found that the second surfactant in water at all temperatures has twice value than the former gives evidence that $C_{14}TAB$ hydrocarbon chain is more exothermic for micellization process.

The arrangement affinity for water or acetonitrile as co solvent molecules around the aggregated surfactants differ markedly from one system to another due to different interactions between the two solvents. This phenomena is reflected on the calculated ΔS_m as tabulated in Table-3 for $C_{12}TAB$ and $C_{14}TAB$ surfactants at different X_{AN} and temperatures.

In comparing ΔS_m of $C_{12}TAB$ and $C_{14}TAB$ at different X_{AN}, they accept either positive or negative values depending on the ability of water in pure or in co solvent to be more ordering or more distorted around micelles.

It is found that $C_{12}TAB$ have always positive values while $C_{14}TAB$ have negative one.This is because the large hydrocarbon tail seeks for a suitable vacancy where water molecules are highly ordered around it *i.e.* it is hydrophobic structure making.

The Gibbs energy associated with transfer of methylene (-CH_2-) group from given medium into the oil-like interior of the micelle, can be obtained from the change in CMC chain length for a homologous series of surfactants[23] using the following equation.

$$\log X_{CMC} = a_o - a_1 n_c \quad (8)$$

where n_c is the number of carbon atoms in the non-polar side chain ($8 < n_c < 18$). while a_o and a_1 are constants can be obtained from the intercept and slope respectively when plotting log X_{CMC} against n_c where CMC is taken in mole fraction scale.

Table-4 includes the computerized a_1 according to eqn. (8) for each hydrocarbon series at X_{AN} equal to 0.0, 0.2 and 0.4 and temperatures (298 -318 K).

TABLE-4
CALCULATION OF a_1, a_o AND ($\delta\Delta G/\delta n$) FOR C_nTAB IN WATER-AN MIXTURES AT DIFFERENT TEMPERATURES

T (K)	ln X_{CMC}	n_c	ln $X_{CMC}/n_c = a_1$	($\delta G/\delta n_c$) kJ mol^{-1}
		$X_{AN} = 0.0$		
298	-4.1759	12	-0.70035	-3.1254
	-5.8459	14		
	-6.7266	16		
308	-4.1327	12	-0.6558	-3.0247
	-5.7171	14		
	-6.4393	16		
318	-4.0914	12	-0.7804	-3.7161
	-5.6332	14		
	-7.2651	16		
		$X_{AN} = 0.2$		
298	-4.1449	12	-0.5276	-2.3546
	-4.7190	14		
308	-4.0970	12	-0.5057	-2.3324
	-4.6151	14		
318	-4.0462	12	-0.4991	-2.3767
	-4.5763	14		
		$X_{AN} = 0.4$		
298	-4.1089	12	-0.4969	-1.7247
	-4.5858	14		
308	-4.0462	12	-0.4883	-2.2524
	-4.5389	14		
318	-2.5753	12	-0.4819	-2.2947
	-3.9977	14		

Inspection of this table, a_1 has been found to give more negative value in pure water ranged between (-0.7004) to (-0.7804) related to 298 and 318 K respectively. The negativity in a_1 is obviously decreases by increasing both acetonitrile content and temperature.

Verral *et al.*[24] and Zana[25] applied eqn. (8) only in pure water for [$C_{12}H_{25}$ C_mH_{2m+1}) $N^+(CH_3)_2Br$] where m varies from 1 to 10 as a function of chain length.

In comparing eqns (4) and (8) and after minor modifications, the free energy for (-CH_2-) group can be obtained from

$$(\delta\Delta G/\delta\, n_c) = (2-\beta)\, RT\, a_1 \quad (9)$$

The calculated ($\delta\Delta G/\delta\, n_c$) for cationic surfactant series at different H_2O-AN mixtures are recorded in the previous Table-4. The ($\delta\Delta G/\delta n_c$) in pure water is found equals -3.125 kJ mol^{-1} at 298 K for $C_{12}H_{25}$ $N^+(CH_3)_3Br$ be consisted with the same value obtained by Ramadan *et al.*[16,26]. They applied eqn. (9) to calculate the Gibbs free energy of transfer per -CH_2 -from water into micelle interior for series of sodium alkyl sulphates in both water and hydrazine at constant temperature. They obtained ($\delta\Delta G/\delta n_c$) values -3.177 and -2.97 kJ mol^{-1} in water and hydrazine respectively attributed the smallest differences between them to the greatest similarity in most their physical properties indicating that transfer of -CH_2- depends mainly on the nature of the medium.

It can be seen from Table-4 that ($\delta\Delta G/\delta\, n_c$) in water have more negative values than in water-acetonitrile mixtures indicating that water gave different behaviour in the process of micellization due to its own unique tetrahedral structure[27].

Absolute density (d = g mL^{-1}) measurements for only ($C_{14}TAB$) in H_2O-acetonitrile mixtures at 298. K are carried out as a function of concentration. CMCs are obtained from plotting (d) against molar concentration where abrupt changes are obviously obtained at roughly (CMC) values. Accurate CMC value is calculated by using the least mean squares method where CMC is found to increase by increasing X_{AN} as well as temperature Table-1.

It must be mentioned here that not all of the above surfactants are used simultaneous in cutting all applications but be selected among them.

Partial molar volume (PMV) is one of the most important properties which must be applied to surfactant solutions derived from density measurements of these solutions either in pure or in mixed water-acetonitrile. In this field, the change in density of the surfactant solutions is very sensitive to varying (i) medium accompanied the breaking down hydrogen bonds for the clusters network when adding organic solvent (ii) transfer the monomers into micelles is accompanied by solvated molecules around micelle units differ markedly in their bulk structure.

In order to investigate the formation of surfactant aggregation, Vikholm *et al.*[28] measured (partial molar volume) of the surfactant V_{sur} either for monomer $V_{(mon)}$ or for micelle $V_{(mic.)}$ by using eqn. 10.

$$V_{sur} = M_2/d-[(W_1 + W_2)/d^2]\, [\delta d/\delta\, n_2]_{n1} \quad (10)$$

where M_2 is the molar mass of given surfactant, W_1 and W_2 are weights of solvent (either in pure or in mixed water-acetonitrile) and that of surfactant respectively. n_1 and n_2, are the molar concentrations of solvent and surfactant solution respectively.

Vikholm measured ΔV as the difference between partial molar volume below $V_{(mon.)}$ and above $V_{(mic.)}$ CMC of $C_{16}TAB$ in hexanol-H_2O system from density measurements at 298. K as followed eqn. 11.

$$\Delta V = V_{(mic).} - V_{(mon.)} \quad (11)$$

Fig. 3 gives the relation between V_{C14TAB} and C mol L^{-1} at 298 K, in water-acetonitrile mixtures where the lower scattered points represent $V_{(mon.)}$ while the above line is related to $V_{(mic)}$.

Important features can be observed from the above Fig. 3 that $V_{(mon.)}$ values are scattered dramatically through small concentration range while the above $V_{(mic)}$ points have fitted straight lines parallel to abscissa. This observation generally indicated that (i) the formed micelles have higher stabilities than monomers and (ii) the formed micelles in water have higher globular structure and be more stable than those formed in mixtures with smaller spherical or globular structures. The stability of aggregated micelle formed depends mainly on the constancy between attractive and repulsive components as polar and counter ions responsible to the free energy of micellization.

TABLE-5
PARTIAL MOLAR VOLUME ΔV_{sur} AND THE AGGREGATION NUMBER N_g FOR C_nTAB AT DIFFERENT X_{AN} AND TEMPERATURES

X_{AN}	$C_{12}TAB$		$C_{14}TAB$		$C_{16}TAB$	
	ΔV_{sur} (dm mol^{-1})	N_g	ΔV_{sur} (dm mol^{-1})	N_g	ΔV_{sur} (dm mol^{-1})	N_g
298 K						
0.0	8.5	57	8.9	58	9.1	60
0.2	8.4	56	8.8	57	9.0	58
0.4	6.8	52	7.8	53	8.8	54
308 K						
0.0	7.3	54	7.8	57	8.1	58
0.2	7.0	53	7.5	54	7.8	56
0.4	6.4	51	7.1	52	7.3	53
318 K						
0.0	5.0	52	5.1	54	5.4	56
0.2	4.8	51	4.9	52	5.2	53
0.4	3.7	50	3.9	51	4.2	52

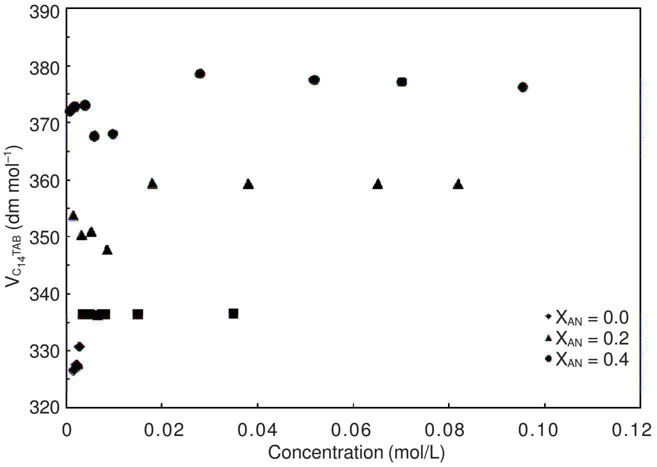


Fig. 3. Variation of $V_{C_{14}TAB}$ with molar concentration in (H_2O-CH_3CN) mixtures at 298 K

In order to study the effect of temperature on partial molar volume for the above surfactant solutions, an additional two surfactants $C_{12}TAB$ and $C_{16}TAB$ at different X_{AN} are selected to calculate $V_{sur.}$ at temperature range from 298 to 318 K, ΔV for all solutions are found to decrease by increasing temperature and X_{AN} but increases by increasing the length of the hydrocarbon chain as shown in Table-5.

The effect of varying alkyl chain on ΔV is studied in pure water by comparing ΔV for homologous series of $C_{12}TAB$, $C_{14}TAB$ and $C_{16}TAB$ at 298 K, where ΔV are found to be 9.1, 8.9 and 8.6 dm mol^{-1} respectively. Backlund *et al*[29] tried to estimate ΔV for $C_{14}TAB$ at 303.2 K in ethylene glycol as mixed solvent with water. They found that ΔV be decreases while CMC increases by increasing (ethylene glycol) contents.

Aggregation number: N_g: Micellar aggregation number is one of the important characteristic of surfactant solutions at above CMC and classically be determined by several methods[30-32].

In general,the average aggregation number[27] is strongly depends on (i) the nature of the solvent (ii) the number of alkyl chain per amphiphilar, (iii) the length of the amphiphilar, (iv) the steric requirements of the tail close to the polar head group and finally on (v) the temperature.

It can be readily seen that empirical relation between CMC and alkyle chain C_n is obeyed eqn. 8 in modified formula:

$$\log CMC = A - B\,C_n \qquad (12)$$

On the other hand, the aggregation number (N_g) of surfactant is found related to number of carbon atoms in side chain n_c by the following equation[33].

$$\log N_g = A' - B'\,n_c \qquad (13)$$

where A′ and B′ are new constants. Combining eqn. (12) with (13) yields Huisman's equation[34] in terms of the molecular weight (MW) of the surfactant monomer as follows:

$$\log N_g = a - b\,\log(CMC) - \log(MW) \qquad (14)$$

where a and b are constants. Fitting data for a homologous series of (C_nTAB) in water and in mixed solvents at different temperatures yield those constants at various X_{AN} and temperatures found to give a = 3.7 ± 0.4 and b = 0.262 ± 0.01 where N_g be calculated for $C_{12}TAB$, $C_{14}TAB$ and $C_{16}TAB$ as shown in Table-5. In our solutions, the aggregated number of surfactant is found to increase by increasing the length of the hydrocarbon chain at given X_{AN} and temperature. Also it's found that N_g values decrease by increasing temperature at given X_{AN} and found to be consisted with Evans[35] view.

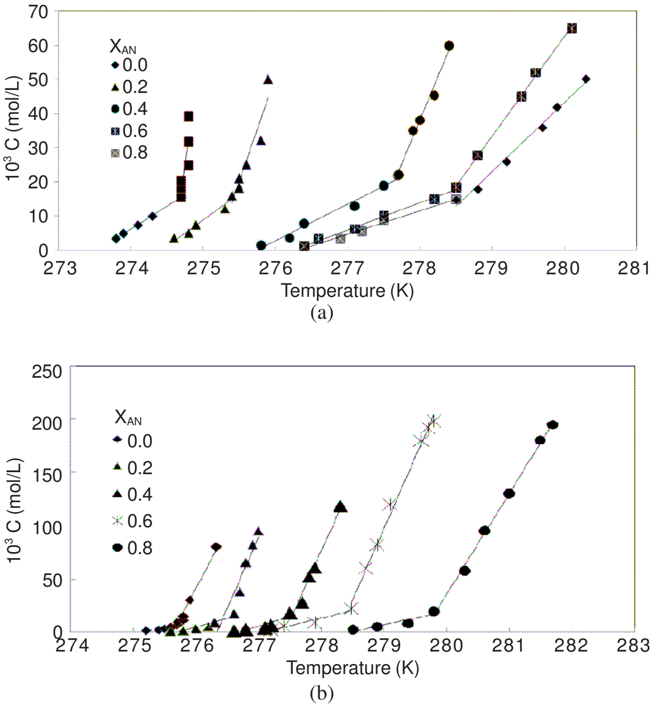
Since the ability of aggregation is decreased by decreasing the dielectric constant (ε) of the medium, hence, in rich acetonitrile region, relative small aggregated numbers for micelles are found parallel to small ΔV. In contrast, the resulting size distribution in pure water is such that under all conditions larger amounts of surfactant molecules are collected within larger size of each micelle unit.

Krafft phenomena: Krafft temperature (K.T.) and the related critical micelle temperature (CMT) are obtained as a result of the abrupt change when plotting surfactant concentration below solidification against the solubility temperature (S.T.) for given solvent composition. The above relations for $C_{12}TAB$ and $C_{14}TAB$ at different X_{AN} are represented graphically by Fig. 4a and 4b, respectively while Table-6 shows the collection of their data.

It can be readily seen from Table-6 that Krafft temperature and CMT values are increases by increasing either X_{AN} or cationic size and mainly found to responsible to the degree of micelle stability. As clearly mentioned before that the basicity of acetonitrile be more stronger when added to another protic solvent like water where the attractive forces between acetonitrile and water co-operate to give more stable micellar form needed more temperature to decompose it. The cohesion between hydrocarbon chains is favoured when increasing their lengths.

TABLE-6
KRAFFT TEMPERATURES (K.T) AND CRITICAL MICELLE TEMPERATURES (CMT) FOR $C_{12}TAB$ AND $C_{14}TAB$ IN (H_2O-CH_3CN) MIXTURES

X_{AN}	$C_{12}TAB$		$C_{14}TAB$	
	K.T (K)	CMT (K)	K.T (K)	CMT (K)
0.0	274.3	274.6	275.6	275.5
0.2	275.3	275.3	276.2	276.4
0.4	277.1	277.2	277.25	277.5
0.6	278.2	277.9	277.9	278.3
0.8	278.5	278.0	279.6	279.6



(a)

(b)

Fig. 4. Krafft temperatures for (a) $C_{12}TAB$ and (b) $C_{14}TAB$ at different X_{AN}

Mehrotra *et al*.[36] observed larger Krafft temperature values in alcohols than in pure water while Bales *et al.*[37] determined Krafft temperature of cesium dodecyl sulphate CsDoS in water in absence and in presence of common salt. They suggested that Krafft temperature measurements may form the basis to determine the degree of counter ion dissociation in ionic micelles. Alternatively when two different configurated surfactants with the same hydrocarbon chain like $C_{10}N(CH_3)_3Br$ and $C_{10}OSO_3Na$ each in hydrazine[26] are examined, it found that Krafft temperature to be close to each other 17.4 and 17.8 ºC respectively. This result supported that Krafft temperature depends mainly on the chain length of the hydrocarbon tail not to polar head group.

Conclusion

The hydrophobic behaviour of surfactant solutions in pure water encourage us to study its properties in mixed solvent with water to know solvophobic properties related to micelle process. It is known that water is characterized by its unique three dimensional tetrahydral structure. Accordingly the studying properties in H_2O-CH_3CN mixtures such as addition of NaBr to cationic surfactants like C_{12}, C_{14} and $C_{16}TAB$, ΔV between micelle and monomers, the related aggregation number and Krafft temperature phenomena reveals more informations about water.

In addition, the thermodynamics and -CH_2- transfere into micelle core help in understanding the nature of this solvent relative to mixtures.

REFERENCES

1. C. Seguin, J. Eastoe, R.K. Heenan and I. Grillo, *J. Colloid Interf. Sci.*, **7**, 14, 315 (2007).
2. M.N. Khan and Z. Arifin, *Colloid Surf. A*, **125**, 149 (1997).
3. M. delMar Graciani, M. Munoz, A. Rodriguoz and M.L. Moya, *Langmuir*, **21**, 3303 (2005).
4. M.S. Bakashi, *Bull. Chem. Soc. Japan*, **69**, 2723 (1996).
5. R. Palepu, H. Gharibi, D.M. Bloor and E. Wyn-Jones, *Langmuir,* **110**, 9 (1993).
6. N. Alizadeh, H. Gharibi and M. Shamsipur, *Bull. Chem. Soc. Japan*, **68**, 730 (1995).
7. K. Garcie, D. Turner and R. Palepu, *Can. J. Chem.*, **74**, 1616 (1996).
8. H. Gharibi, B.M. Razavi Zadeh and A.A. Rafati, *Colloid Surf. A*, **136**, 123 (1998).
9. D.O. Shah, Micelles, Microemulsions and Monolayers, CRC Press, Boca Raton (1988).
10. P. Mukerjee, K. Mysels and P. Kapauan, *J. Phys. Chem.*, **71**, 4166 (1967).
11. D. Myers, Surfactant Science and Technology, VCH Publishers, Weinheim (1988).
12. M. Shampsipur, N. Alizadeh and H. Gharibi, *Indian J. Chem.*, **36A**, 1031 (1997).
13. C. Tanford, *J. Phys. Chem.*, **78**, 2469 (1974).
14. Y. Moroi, Micelles; Theoretical and Applied Aspects, Plenum Press, New York (1992).
15. M.S. Chanhan, K. Sharm and G. Kumar, *Colloid Surf. A*, **221**, 135 (2003).
16. M. Sh. Ramadan, D.F. Evans and R. Lumry, *J. Phys. Chem.*, **87**, 4538 (1983).
17. K.M. Kale, E.L. Cussler and D.F. Evans, *J. Phys. Chem.*, **84**, 593 (1980).
18. A.S. Kerts and H. Gutrmann, in ed.: E. Matijevic, Surface and Colloid Science, Wiley, NewYork, 8 (1976).
19. G.C. Kresheck, in ed.: F. Franks, Water, A Comprehensive Treatise, Plenum Press: N.Y. vol. 4, Chap. 2 (1975).
20. D.F. Evans and P.J. Wieghtman, *J. Colloid Interf. Sci.*, **86**, 515 (1982).
21. J. Aguiar, J.A. Molina Bolivar, J.M. Peula-Garcia and C. Carnero Ruiz, *J. Colloid Interf. Sci.*, **2**, 155 (2002).
22. M.L. Moya, A. Rodriguez, M.D.M. Graciani and G. Fernandez, *J. Colloid Interf. Sci.*, **316**, 787 (2007).
23. V. Mosquera, J.M. del Rio, D. Attwood, M. Garcia, M.N. Jones, G. Prieto, M.J. Suarez and F. Sarmiento, *J. Colloid Interf. Sci.*, **66**, 206 (1998).
24. R.E. Verral, S. Milito and R. Zana, *J. Phys. Chem.*, **92**, 3939 (1988).
25. R. Zana, *J. Colloid Interf. Sci.*, **78**, 330 (1980).
26. M. Sh. Ramadan, D.F. Evans, R. Lumry and S. Philson, *J. Phys. Chem.*, **89**, 3405 (1985).
27. T.M. Herrington and S.S. Sahi, *Colloid Surf.*, **17**, 103, 103 (1986).
28. I. Vikholm, G. Douhert, S. Backlund and J.H. Hoiland, *J. Colloid Interf. Sci.*, **116**, 2, 582 (1987).
29. S. Backlund and B. Bergenstahl, O. Molander and T. Warnheim, *J. Colloid Interf. Sci.*, **131**, 395 (1989).
30. B. Lindman, *J. Phys.Chem.*, **87**, 1377 (1983).
31. M. Corti, V. Degiorgio, J. Hayter and M. Zulauf, *Chem. Phys. Lett.*, **109**, 579 (1984).
32. E. Ruckenstein and R. Nagarajan, *J. Phys. Chem.*, **84**, 1349 (1980).
33. H.B. Kleven, *J. Am. Oil Chem. Soc.*, **30**, 74 (1953).
34. H.F. Huisman, *Proc. Kon. Ned. Akad. Wetensch.*, **B67**, 367 (1964).
35. D.F. Evans, The Colloidal Domain' Where Physics, Chemistry, Biology and Technology Meet, 2nd Ed. Wiely VCH, Chap. 4 (1999).
36. K.N. Mehrotra, V.P. Mehta and T.N. Nagar, *J. Prakt. Chem.*, **313**, 607 (1971).
37. B.L. Bales, M. Benrraou and R. Zana, *J. Phys. Chem. B*, **106**, 9033 (2002).