Effect of Monohydroxy Alcohols and Urea on the CMC of Surfactants

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The effect of monohydroxy alcohols on the critical micelle concentration (CMC) of anionic and cationic surfactants have been studied by a conductometric method. The CMC was found to decrease by adding small quantities of alcohol and raised again at higher alcohol concentrations. The CMC decreasing effect has been discussed on the basis of more ordered water cavity formed around the added alcohol molecules and their increasing effect by the partition of alcohol between the micellar and the bulk phase leading to the break-down of the micelles. The effect of urea on CMC in alcohol–water mixtures has been studied and its CMC increasing effect explained.

The properties of aqueous solutions of aliphatic monohydric alcohols are of interest in the field of surface chemistry; especially their effect on the phenomenon of micellization of surfactants. Since water–alcohol-surfactant systems are so frequently used as media in the studies of chemical equilibria and reaction rates,[1] it is very essential to investigate the nature of the alkyl groups in the alcohol on the CMC of surfactants.

The driving force for the formation of nonionic micelles in water being the hydrophobic interactions between the hydrocarbon portion of the surfactant has been treated quantitatively,[2] but this treatment in case of ionic micelles was less satisfactory.[3] The most satisfactory way of investigating the effect of hydrophobic interaction on ionic micelle formation would be to study the micellar properties of ionic surfactants in altered water structure by adding small quantities of alcohols of varying chain length. But one could not rule out the possibility of incorporation of alcohol molecules into the micelles.

The CMC decreasing effect due to incorporation of alcohol molecules between the soap micelles has been advocated by many workers.[4–6] Branched chain alcohols at low concentrations were found ineffective while the higher homologous alcohols caused depression of the CMC. Addition of various amphiphiles to micellar soap solutions caused the electrical conductivity to increase.[8] The effect of C_2—C_{10} alcohols on the CMC of soap solutions was investigated by electrical conductivity and distribution methods.[9–10] The CMC raising effect of ethanol and methanol at higher concentration is well studied.[12–19]

Virtually all substances containing hydrophobic moities decrease the concentration of an amphiphile in equilibrium with its micelles.[20] This decrease can be explained only by the incorporation of the added substances into the micelle, since simple addition of the alcohol and similar substances to the solvent must diminish the hydrophobic effect, that is, it would decrease the standard chemical potential of monomer for the micelle forming amphiphile without any effect on the standard chemical potential of micelle and would therefore increase the CMC. In related work, the effect of urea on micelle formation has been found to increase the CMC, though, it could not be incorporated into the micelle.[21–23]

From the detailed literature survey on the effect of additives, particularly alcohols and other related substances, which markedly influence the hydrophobic effect and the micelle formation,[24] it seems that there exist two different views regarding the effect of additives on micelle formation. The first deals with the solubilization of alcohols in micelle[11,21,25] and the second view is that additives have direct effect on the water structure.[26–28]

Recent investigations[29,30] further indicate that the role of alcohols in micelle formation could be explained on the basis of several factors. It may be possible that the alcohol molecules may modify water structure if present in very small concentration. At higher concentrations some other effects like the alteration in the dielectric constant of the solvent or the partition of alcohol molecules between bulk and the micellar phase[31–33] or the diminishing of the hydrophobic effect[20] may be more important. At very high alcohol concentration a shift in equilibrium between surfactant monomers and micelles towards monomer may be possible due to high solvent power of alcohol for the hydrophobic part of the surfactant ion.

The main objects of the present investigation were (a) to extend information on the influence of the solvent on the micelle formation due to alteration in water structure by gradual addition of alcohols in very small amounts and (b) to study the effect of urea on micelle formation in the altered water structure.

Experimental

Sodium dodecylsulfate (SDS) was purchased from BDH (England). It was first recrystallized from ethanol–acetone mixture. Traces of unreacted alcohol were removed by extracting it with petroleum ether (60 h) and chloroform (100 h). The surfactant was dried after filtration in a hot air oven to a constant weight. The absence of any unreacted alcohol was ascertained from the absence of OH peak in the IR spectrum. The microanalysis of the compound showed: C=49.73, H=9.02, S=11.00%; calculated values C=49.8, H=8.9, S=11.06%. The purity was also confirmed from the absence of minimum in the surface tension *vs.* log concentration plots. Cetyltrimethylammonium bromide (CTMAB) was BDH reagent grade quality. It was recrystallized from acetone, repeated thrice. Demineralized double distilled water was used throughout this work. The specific conductivity of water was 20.0×10^{-6} to 21.7×10^{-6} ohm^{-1} cm^{-1}. CMC values of SDS and CTMAB, determined by conductivity method in water at 30 °C were 8.6 and 0.97 mmol/dm^3 respectively, are in good agreement with literature values[12] at 25 °C. 1-Propanol, 1-butanol, 1-hexanol, and cyclohexanol were all BDH laboratory reagents while 1-pentanol and cyclopentanol were E. Merk products. These alcohols were distilled under reduced pressure and the middle fractions of the distillate were used.

Water-alcohol mixtures of several compositions were prepared by mixing requisite quantity of alcohol in water. Stock solutions of surfactants were prepared by weighing. The conductometric measurements of surfactant solutions were made by a Philips conductivity meter model PR 9500 at a frequency of 1000 Hz using platinized electrodes of known cell constant. After measuring the conductivity of the solvent, small volumes of the stock solution (50 mmol/dm^3 surfactant solution) were added and the conductivity noted after each addition and thorough mixing to a constant reading. The specific conductivity was calculated after applying the solvent correction. The CMC values were determined at the break points of nearly two straight line portion of the specific conductivity *versus* concentration plots.

Results

The specific conductivity, K, *vs.* concentration, C, plots for SDS and CTMAB in different compositions of 1-propanol-water mixtures are shown in Fig. 1. The plots for other alcohol-water mixtures were similar. The variation of CMC with the mole fraction of alcohol, χ, are shown in Fig. 2 and the effect of urea on the CMC in alcohol-water mixtures resulting in minima in CMC, where the water is supposed to be in most ordered form, are given in Table 1. The slopes of K *vs.* C plots for SDS below and above CMC in different alcohols are given in Table 2.

Discussion

The highly structured tetrahedral arrangement of water molecules in the liquid state would have to be disrupted by the addition of any solute.[20] When alcohols are added into water, some hydrogen bonds must be broken, and new hydrogen bonds between water and alcohol would be formed. But the hydrogen bond formation between alcohol and water does not seem very tangible because in liquid alcohol the tendency for O–H···O bond formation is likely to be as strong as in water, though such hydrogen bonds cannot comprise an isotropic net work filling the entire solvent space due to the presence of alkyl side chains. However, the addition of alcohols to water, if results in the rapture of hydrogen bonds of the latter, the major contribution to the free energy of transfer of alcohol to water would be a positive enthalpy term. Instead, as reported[34] earlier, the transfer to water is actually slightly favored energetically. The positive value of change in standard chemical potential for the transfer of aliphatic alcohols from pure liquid to water resulting from a negative entropy change has been explained by the fact that the water molecules at the surface of the cavity created by a nonpolar part must be capable of rearranging themselves in order to regenerate the broken hydrogen bonds, create a higher degree of local ordering than exists in pure liquid water.[20] Hence it is reasonable to expect that the addition of higher alcohols to water may result in the ordering of water structure at concentrations lower than their lower counterparts.

In fact, the CMC lowering of surfactants by the small addition of alcohols may be due to their direct action on water structure and the subsequent addition

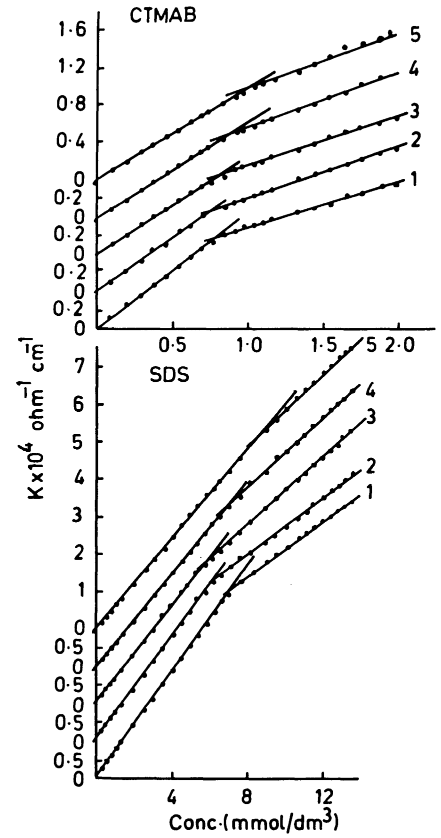

Fig. 1. Specific conductivity *vs.* concentration plots for surfactants in 1-propanol-water mixture at 30 °C.
1: $\chi=23\times10^{-4}$, 2: $\chi=72\times10^{-4}$, 3: $\chi=124\times10^{-4}$, 4: $\chi=177\times10^{-4}$, 5: $\chi=251\times10^{-4}$.

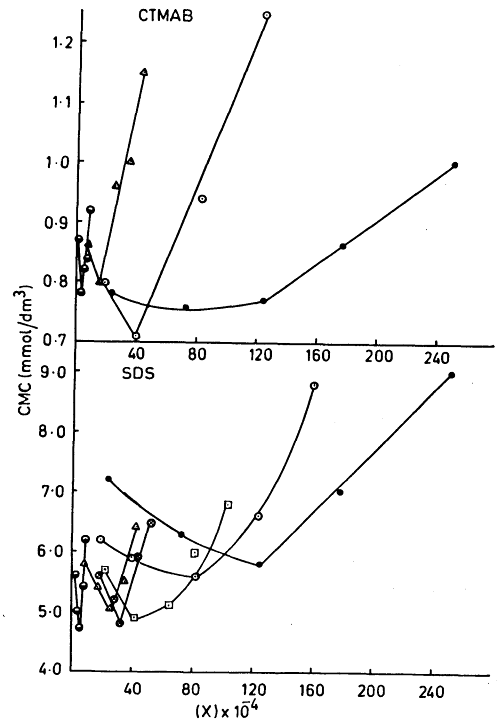

Fig. 2. The variation of CMC with χ.
—●—: 1-Propanol, —⊙—: 1-butanol, —△—: 1-pentanol, —◒—: 1-hexanol, —⊡—: cyclopentanol, —○—: cyclohexanol.

TABLE 1. CMC (mmol/dm^3) VALUES OF SDS AND CTMAB IN PRESENCE OF VARIOUS CONCENTRATIONS OF UREA AT 30 °C

The mole fraction (χ) of alcohol in water is taken at minimum in CMC.

SDS

Urea	1-Propanol ($\chi=124\times10^{-4}$)		1-Butanol ($\chi=82\times10^{-4}$)		1-Pentanol ($\chi=25\times10^{-4}$)		1-Hexanol ($\chi=5.7\times10^{-4}$)		Cyclopentanol ($\chi=40\times10^{-4}$)		Cyclohexanol ($\chi=32\times10^{-4}$)	
	CMC	%CMC increase	CMC	%CMC increase	CMC	%CMC increase	CMC	%CMC increase	CMC	%CMC increase	CMC	%CMC increase
0M[a]	5.8	—	5.6	—	5.0	—	4.7	—	4.9	—	4.8	—
1M	6.5	12	6.2	11	5.8	16	5.6	19	6.0	22	5.7	18
3M	8.0	38	7.5	34	7.2	44	6.9	47	7.4	51	7.0	25
6M	No micelles		No micelles		No micelles		10.0	112.76	No micelles		No micelles	

CTMAB

Urea	1-Propanol ($\chi=72\times10^{-4}$)		1-Butanol ($\chi=40\times10^{-4}$)		1-Hexanol ($\chi=28\times10^{-4}$)	
	CMC	%CMC increase	CMC	%CMC increase	CMC	%CMC increase
0M	0.76	—	0.72	—	0.78	—
1M	0.82	7.9	0.79	9.7	0.80	2.6
3M	1.33	75	1.08	50	0.92	18
6M	1.55	10	1.21	68	—	—

[a] 1M=mol/dm^3.

TABLE 2. SLOPES (ohm^{-1} cm^{-1}/mol dm^{-3}) ABOVE AND BELOW THE CMC OF ALCOHOL-WATER MIXTURES AT 30 °C

1-Propanol (χ)		0	23×10^{-4}	72×10^{-4}	124×10^{-4}	177×10^{-4}	251×10^{-4}
Slope	above CMC	0.030	0.030	0.035	0.040	0.045	0.047
	below CMC	0.065	0.070	0.069	0.070	0.068	0.069
1-Butanol (χ)		0	19×10^{-4}	40×10^{-4}	82×10^{-4}	123×10^{-4}	159×10^{-4}
Slope	above CMC	0.030	0.040	0.050	0.052	0.055	0.057
	below CMC	0.065	0.069	0.070	0.071	0.070	0.070
1-Pentanol (χ)		0	8×10^{-4}	17×10^{-4}	25×10^{-5}	34×10^{-4}	42×10^{-4}
Slope	above CMC	0.030	0.040	0.043	0.050	0.052	0.055
	below CMC	0.065	0.070	0.069	0.069	0.070	0.070
1-Hexanol (χ)		0	2.8×10^{-4}	4.3×10^{-4}	5.7×10^{-4}	7.6×10^{-4}	8.4×10^{-4}
Slope	above CMC	0.030	0.040	0.042	0.044	0.046	0.049
	below CMC	0.065	0.072	0.070	0.070	0.070	0.069
Cyclopentanol (χ)		0	21×10^{-4}	40×10^{-4}	63×10^{-4}	81×10^{-4}	102×10^{-4}
Slope	above CMC	0.030	0.040	0.045	0.050	0.055	0.057
	below CMC	0.065	0.070	0.069	0.070	0.070	0.069
Cyclohexanol (χ)		0	17×10^{-4}	28×10^{-4}	32×10^{-3}	43×10^{-4}	52×10^{-4}
Slope	above CMC	0.030	0.042	0.050	0.055	0.058	0.055
	below CMC	0.065	0.070	0.070	0.071	0.070	0.069

may cause secondary effects such as their solubilization in micelle and decrease of hydrophobic effect. A perusal of Fig. 2 shows that the CMC values of SDS decrease by the gradual increase in the mole fraction of alcohol in water and increase further after attaining a minimum value. The mole fraction of alcohols where the CMC minima occur also depend upon the length of the hydrocarbon chain. It may, therefore, be concluded from these observations and the above mentioned facts that the initial addition of alcohol to water causes the ordering of water which in turn reduces the CMC to a minimum value. From Fig. 2 it is also noted that the CMC values at the minimum decrease gradually with increase of the length of the hydrocarbon chain in the alcohol. This further supports the view[20] that the formation of the cavity of more ordered water molecules is favored by the long hydrocarbon chain of the alcohols. In presence of such a cavity a decrease in CMC is not unexpected.

In case of cyclic alcohols, *viz.*, cyclopentanol and cyclohexanol, the CMC minimum occurs at higher mole fraction of alcohols as compared with their linear-chain counterparts. This indicates that these alcohols possess less proton accepting capacity in solvent water to result in the well organized alcohol-water hydrogen bond formation or to create a cavity of more ordered water molecules. Apart from these mixtures having a more organised solvent structure, the higher CMC values at the minimum further suggest that the degree of association of the surfactant is slightly restricted due to steric reasons.

Studies have also been made with a cationic surfactant, CTMAB. The CMC values of CTMAB in different compositions of alcohols are given in Fig. 2.

In all the alcohol–water mixtures, the CMC values initially decrease, pass through a minimum and increase further, with the increase in the mole fraction of alcohols. Unlike anionic surfactant (SDS) no systemetic trend in the CMC values at the minimum is observed with the increase in the length of the hydrocarbon chain in alcohols. At this stage it is difficult to comment on the behavior of a cationic surfactant in alcohol–water mixtures.

The role of the water cavity in micelle formation has been further verified by studying the effect of urea on CMC. Urea is a strong water structure breaker, in presence of alcohols it may destroy the cavity of ordered water structure. It is, therefore, expected that the CMC should increase with the increase in the concentration of urea. Table 1 shows the effect of urea on the CMC of SDS and CTMAB in presence of constant concentration of alcohols. The percent increase in the CMC values are also included in Table 1. These results indicate that the addition of urea results in the breaking of water structure even at the concentration of alcohols where it is expected to be more ordered. This effect is so pronounced in lower alcohols that no micelle formation takes place when the concentration of urea exceeds 3 mol/dm^3. It is intresting to note that the CMC increasing effect of 1 mol/dm^3 urea is much smaller for cyclopentanol and cyclohexanol which further supports the conclusion that the water cavity formed in presence of cyclic alcohols is less ordered. However, an irregular change in the CMC values of CTMAB (Fig. 2) with the hydrophobicity of the alcohol indicates that the water molecules do not have a unique way of arranging themselves, but that different arrangements are possible depending upon the precise spatial requirements.[20] A comparison of percent increase in CMC in 3 mol/dm^3 urea (Table 1) may lead to the conclusion that the higher alcohols may be readily partitioned in cationic micelle than in an anionic micelle.

In case of anionic surfactants a further increase in CMC in higher concentration of alcohols suggests that some other factor, influencing the micelle formation, must be taken into account. A micelle formed in presence of an alcohol is likely to contain alcohol molecules in its oriented structure.[4,5] These alcohol molecules, introduced between the soap ions and the micelle, will produce a further charge separation. Owing to the lowered charge density the conditions are thus more favorable to abnormally small atmosphere and inclusion effects. This partition of additive between the solution and the micelles may be sensitive to the structure of the polar third component and the temperature. It is probably due to the above fact that no micelle formation is observed in all the alcohol–water mixtures in presence of 6 mol/dm^3 urea except in 1-hexanol which is less polar.

The inclusion and the micelle breakdown effect of alcohols[11,25,30] may further be reflected from the slopes of *K vs. C* plots below and above the CMC in different compositions of alcohols. The slopes for SDS in alcohol–water mixtures are given in Table 2.

A perusal of Table 2 shows that the slopes below the CMC remain nearly constant irrespective of the composition and the chain length of the added alcohol which indicate that alcohol molecule is not incorporated at all with the surfactant monomers. Approximately 8% higher values of slopes than in pure water may be due to modification of water structure by the added alcohols. The inclusion of alcohol molecules into the surfactant micelle is clearly reflected from the decrease in slopes above the CMC. It is also clear that the inclusion effect is stronger for alcohols with larger alkyl chains which brings about the reduction of the surface-charge density on the micelle. Similar conclusions have been given by Shirahama and Kashiwabara.[24] Larger values of slopes in higher alcohols (C_4—C_6) and their gradual increase with alcohol content indicates that the partition of alcohol into the micelle results in a slight increase in the conductivity due to release of few surfactant anions from the micellar to the bulk phase. The high solvent power of alkyl chains of the alcohol for surfactant tails may shift the equilibrium from aqueous micellar to the alcoholic environment (hydrocarbon like) in higher alcohols which could create a separate phase of reversed micelles.[35,36]

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