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Self-assembly of tetradecyltrimethylammonium bromide in long chain alcohols

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The effect of organic additives, C_8-OH and C_9-OH (octan-1-ol and nonan-1-ol), on the micellar behavior of cationic surfactant, tetradecyltrimethylammonium bromide (TTAB) has been studied by fluorescence and NMR techniques. Fluorescence spectroscopy has been used to obtain critical micelle concentration values as well as the aggregation number of TTAB in the presence of the studied alcohols. The decrease in cmc of aqueous TTAB is observed in the presence of long chain alcohols. The alcohols form additive-TTAB mixed micelles and micellar growth takes place. The structural transformation is explained by hydrophobic interactions and electrostatic effects between the additive and TTAB micelle. The locus of solubilization of alcohols and consequent changes in structure of the micelles is inferred from NMR measurements. The unique role of long chain alcohols in changing properties of aqueous surfactant systems is demonstrated.

Keywords: Solution chemistry, Surfactants, Micelles, Self-assembly, Fluorescence spectroscopy, NMR spectroscopy, Tetradecyltrimethylammonium bromide, Alcohols

Surfactants are widely used in both, industry and everyday life and their properties in aqueous solutions have received considerable attention. In aqueous solutions, surfactant molecules self assemble to form small spherical micelles as well as large cylindrical micelles. At low concentrations, the micelles are generally spherical[1] but they grow when surfactant concentration is increased and micelle undergoes sphere to rod transitions[2]. The phenomenon of micellar solubilization has attracted significant attention in the area of surface science and solution chemistry[3-6]. The structural and chemical nature of both, the surfactant as well as the additive, play important roles to decide the extent of solubilization and the site occupied by the solubilizate[7-10]. In general, organic molecules (or ions) tend to reduce the cmc of surfactants, the reduction increasing with the size of the alkyl group. The alkyl chain length of the additive also has an appreciable effect on the total number of monomers which form a micelle. The effect of added low and medium chain alcohol molecules into aqueous micellar solution has been examined by several workers[7,8,11-15] using a wide range of techniques but very little attention has been directed towards the measurement of the effect of added hydrophobic molecules on the properties of surfactants, In the presence of medium to long chain alcohols the aggregation number of the surfactant are found to increase thus producing large alcohol surfactant mixed micelles[2,16]. The increase in micellar size is often explained in terms of the solubilization of alcohols to the micelles whereas, the cmc is visualized as the minimum surfactant concentration required for aggregation to occur.

In the present study, the surfactant undertaken is tetradecyltrimethylammonium bromide (TTAB), which is widely used in several fields including chemical, biochemical, pharmaceutical and various industries. Further, it has antibacterial properties and its aqueous solution with ethanol/isopropyl alcohol is useful in disinfection and sanitation. Many of its properties such as cmc and aggregation numbers have been widely studied in literature and a lot of work has been reported on the transition and self aggregation of the TTAB using various techniques[3,17,18]. The effect of water-organic mixed media, viz., ethylene glycol, glycerol, etc. on micellization behavior of alkyltrimethylammonium halides has been examined in literature using different methods[8,19-23]. Though solubilization of lower and medium chain alcohols in TTAB has been scrutinized by several workers[3,11,24], that with higher alcohols is very limited[21].

In continuation of previous work[11-15], the present article reports the effect of monohydric alcohol, C_8-OH and C_9-OH (octan-1-ol and nonan-1-ol) on the formation of micelles of TTAB in aqueous solution. The present work essentially involves the use of fluorescence and NMR spectroscopy. A comparative study has been made with the similar work on cetyltrimethylammonium bromide, CTAB, with alcohols, reported previously[7].

Experimental

TTAB of purity >97% was a Merck product and was dried under vacuum and stored over P_2O_5 in vacuum desiccators. The analytical grade C_8-OH of purity 99.5 % was obtained from Spectrochem Pvt. Ltd. Mumbai, India, whereas; C_9-OH was an Aldrich product with a purity of 98%. Alcohols were purified by fractional distillation before use. The purity of these liquids were ascertained by comparing ^{1}H NMR spectra with literature values. For NMR spectral studies, deuterium oxide (D_2O), supplied by Aldrich of 99.9 % isotopic purity was used. In fluorescence studies, the chemicals are used without any purification. Pyrene was received from Aldrich, cetylpyridinium chloride (CPC) from Loba Chemie, Mumbai, India and methanol (99.9% purity) was obtained from Ranbaxy Chemicals. For the experimental measurements, deionized, double distilled water of conductance 1×10^{-6} S·cm^{-1} at 298.15 K was used. For weighing an electronic balance, (Afcoset-R120A) with a precision of 0.0001 g was used.

The fluorescence emission measurements were made using a RF-5301PC spectrofluorometer (Shimadzu) by exciting the pyrene (Py) (10^{-5} mol dm^{-3}) at 334 nm. For the study of aggregated systems like micelles, fluorescence probe analysis technique provides a versatile method[7,22-25]. Pyrene is one of the few condensed aromatic hydrocarbons that shows significant fine structure of vibrational bands in their monomer fluorescence spectra in solution. The five major peaks are labeled I_I-I_V and some show a strong sensitivity towards polarity of the solvent. This is due to its excited state having a different, non-polar structure than the ground state. Certain emission bands are unaffected but others show variations in intensity due to the interaction with the solvent[25].

Figure 1 shows the variations of the pyrene polarity ratio (I_1/I_3) with the surfactant concentration at 298.15 K. It can be seen that as the surfactant concentration increases, the plot of the pyrene polarity ratio (I_1/I_3) versus the surfactant concentration has the sigmoidal shape with a rapid decrease of (I_1/I_3) at low surfactant concentrations and a leveling off at high surfactant concentrations. This abrupt decrease in (I_1/I_3) forms the basis of cmc determination for micelle forming surfactant solutions. The non-polar pyrene partitions into the hydrophobic micellar phase resulting in an abrupt decrease in (I_1/I_3). The cmc values are listed in Table 1. The emission spectrum of pyrene was recorded in the wavelength range 350-600 with excitation and emission slit widths of 5.0 nm and 3.0 nm respectively. To determine the aggregation number, N_{agg}, surfactant and CPC solutions were freshly prepared. Details of the solution preparations and fluorescence measurements have been reported elsewhere[7].

^{1}H NMR spectra were recorded on a Bruker Avance NMR (300 MHz) spectrophotometer. Deuterated water (D_2O) was used for the preparation of the solutions to weaken the water signal for all solutions. The ability of the alcohols to affect the chemical shift of different proton signals of the surfactant molecules was utilized. ^{1}H spectra of 0.1 mol kg^{-1} surfactant solution were recorded. Tetramethylsilane (TMS) was used as the internal reference in NMR measurements. The chemical shift

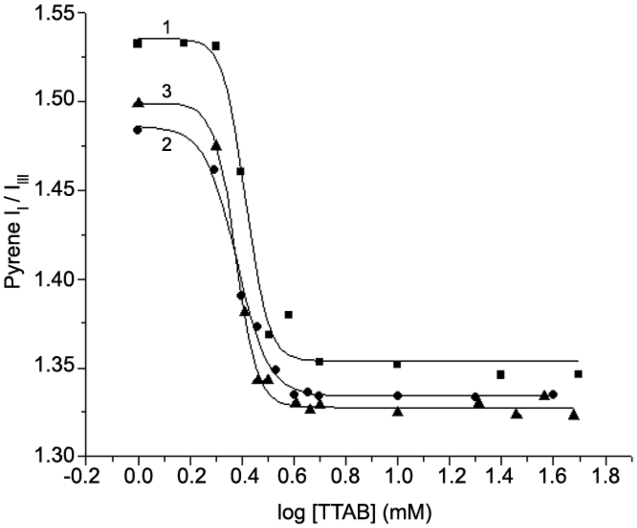
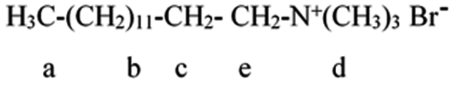


Fig. 1 — I_I/I_{III} versus log [TTAB] at ambient conditions. [λ_{ex} = 334 nm; slit widths: 5 and 3 nm in the absence (1, ■) and presence of aqueous 0.003 mol dm^{-3}solutions of C_8-OH (2, ●) and C_9-OH (3, ▲). The curve represents fit to a simple sigmoidal expression].

Table 1 — CMC and aggregation number (N_{agg}) of 50 m*M* aqueous TTAB in presence of varying concentrations of alcohols at ambient conditions[a]

M (mol dm^{-3})	CMC (m*M*)	(N_{agg})
C_8-OH		
0	3.40	59±3 (55)$^{\text{Ref. 18}}$
0.0027	3.20	62±4
0.0125	3.13	65±3
0.0189	3.09	69±7
0.0244	3.05	79±7
C_9-OH		
0.0030	3.12	65±8
0.0135	3.00	67±3
0.0181	3.07	73±7
0.0232	3.04	75±6

[a] Room temp. & atmospheric pressure



$H_3C\text{-}(CH_2)_{11}\text{-}CH_2\text{-}\ CH_2\text{-}N^+(CH_3)_3\ Br^-$

Scheme 1

measurements of various resonance peaks of studied surfactants are given on the δ scale in parts per million (ppm) of the applied frequency. Further information about the experimental techniques has been provided in literature[15]. Chemical structures and proton numberings of TTAB is shown in Scheme 1.

Results and discussion

In the present study pyrene was used as a fluorescence probe to obtain the cmc of the aqueous TTAB and that in the presence of each of the additive. Figure 1 presents I_I/I_{III} versus log [TTAB] in the absence and presence of monohydric alcohols and the curves represent simple sigmoid expression. The cmc values of aqueous TTAB and in the presence of studied alcohols at different concentrations, obtained from the fluorescence studies, are reported in Table 1. The cmc of aqueous TTAB is 3.40 mmol dm^{-3}, indicating good agreement with the values obtained from conductance measurements[19]. However, in the presence of additives the, C_8-OH and C_9-OH, cmc of TTAB decreases (at C_8-OH and C_9-OH concentration ≈ 0.003 mol dm^{-3}, the cmc of TTAB is 3.17 mmol dm^{-3} and 3.12 mmol dm^{-3} respectively). Similar experiments have been performed with CTAB in the presence of C_8-OH and C_9-OH[5]. The decrease in cmc of aqueous CTAB was observed in the presence of long chain alcohols possessing cosurfactant-type behavior[7]. A comparison between the behaviors of the two cationic surfactants i.e. CTAB and TTAB revealed that the extent of decrease in cmc in the case of TTAB with increased percentage composition of the additive alcohol was more prominent than in the case of CTAB.

The aggregation number (N_{agg}) of aqueous TTAB and that in the presence of alcohols, C_8-OH and C_9-OH was obtained from fluorescence quenching of pyrene using cetylpyridinium chloride (CPC) according to the following equation:

$$\mathrm{In}\left(\frac{I_0}{I_Q}\right)=\frac{Q_{\text{micelle}}}{[\text{micelle}]}=\frac{[CPC]_{\text{micelle}}}{[\text{micelle}]}=[\text{CPC}]_{\text{micelle}}\left[\frac{N_{\text{agg}}}{[\text{TTAB}]-\text{cmc}}\right] \quad \ldots(1)$$

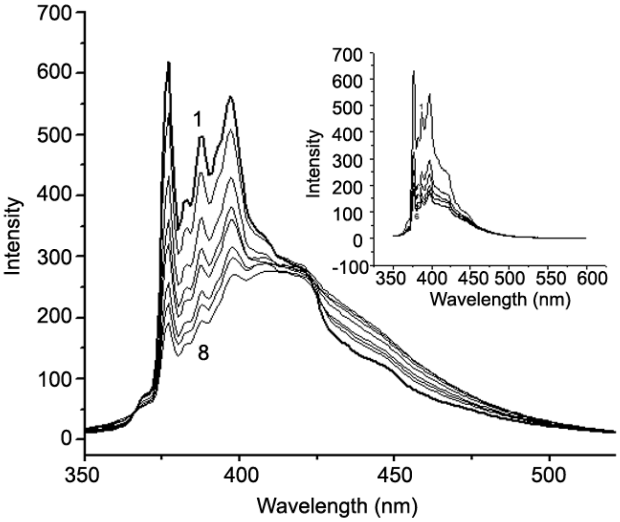


Fig. 2 — Emission fluorescence spectra of 10^{-5} *M* solution of pyrene in aqueous solution of TTAB (50 m*M*) in the presence of 0.0189 *M* C_8-OH at ambient conditions in the absence of CPC (curve 1) and in the presence of CPC (curves 2-8) with concentration ranging from 6.7×10^{-5} to 1.1×10^{-3} *M*. Inset: emission fluorescence spectra of a 10^{-5} *M* pyrene in aqueous solution of TTAB (50 m*M*)].

where I_0 and I_Q represent the fluorescence intensities of pyrene in the absence and presence of quencher CPC, respectively. Q_{micelle} or $[\text{CPC}]_{\text{micelle}}$, [micelle] and [TTAB] are concentrations of quencher CPC within the micellar phase, micelles, and TTAB, surfactant respectively. Figure 2 shows the emission fluorescence spectra of a 10^{-5} *M* solution of pyrene in an aqueous solution of TTAB (50 m*M*) in the presence of 0.0189 *M* C_8-OH at ambient conditions (curve 1) and in the absence of CPC (curves 2-8) with concentration ranging from 6.7×10^{-5} to 1.1×10^{-3} *M*. The inset of Fig. 2 shows the fluorescence emission spectra of pyrene (10^{-5} *M*), solubilized inside the aqueous TTAB micelles (50 m*M*) in the absence and presence of increasing quencher concentrations (ranging from 2.3×10^{-6} to 1.5×10^{-5} *M*). A perusal of Fig. 2 indicates that the intensity of the emission of pyrene decreases as long as the [CPC] increases (from curves 1-6).

The N_{agg} values calculated from Eq. (1) using the cmc obtained by fluorescence spectroscopy are reported in Table 1. The N_{agg} of aqueous TTAB is compared with that reported in the literature[23]. A series of similar spectra of pyrene quenching by CPC within 50 m*M* TTAB were performed in the presence of different concentrations of C_8-OH and C_9-OH respectively. The calculated values of N_{agg} are reported in Table 1. From Table 1, it is clear that the values of N_{agg} increases on increasing the concentration of the studied alcohols. As proposed in the literature[26], an additive which is surface active to a hydrocarbon-water interface will be mainly solubilized at the micellar surface and will promote the micellar growth. Therefore, in the present studies, the alcohols under consideration are expected to get embedded between TTAB monomers of the micelle and hence may increase the volume of the micelle. Thus, as expected, TTAB–higher chain length additives have a tendency to form large micelles and an increase in N_{agg} takes place. The results obtained from the present studies show the role of organic additives like alcohols on the aggregation behavior of ionic surfactants. The extent of increase of N_{agg} of aqueous TTAB in the presence of studied alcohols is almost similar at the studied concentration range.

The NMR spectral studies help to interpret the solubilization of alcohols in the micelles and the changes in structure of the micelles due to the presence of alcohol. The ^{1}H NMR techniques have been found useful in the evaluation of the micellar morphology in single and in mixed micelles[6,27-29]. The site of solubilization of an aromatic molecule can range anywhere from the micelle core to the hydrated surface area near the head group and solubilization at different locus of the micelles may affect the micelle size in different ways. The size of the ionic micelle, at a given composition, is mainly affected by the surface charge density. If the micelle shape is altered, a change in charge density is expected. Thus, it is obvious that geometric factors have to be considered in determining the change in micelle size and shape as well as the location of solubilizate in the micelle.

In the present study, ^{1}H signals of aqueous surfactant and that with C_9-OH at various concentrations were recorded. ^{1}H NMR chemical shift studies of TTAB solutions in the presence of C_8-OH have already been reported in a previous communication[11]. The variation range of ^{1}H NMR chemical shift of TTAB solutions (0.10 mol kg^{-1}) with varying concentrations of C_9-OH are reported in Table 2. A close perusal of the various ^{1}H signals of pure surfactant solution and the change in the position of these signals in the presence of different concentrations of alcohol helps to interpret the most preferred solubilization sites of alcohol in aqueous TTAB solution. In the case of TTAB solutions, the chemical shift data at different C_9-OH concentrations show slight changes in frequencies when compared with that in aqueous TTAB solution. A careful inspection of various ^{1}H signals in the case of pure surfactant solution and that in the presence of added alcohol shows that as the alcohol is added, the frequencies of proton peaks show some changes near the hydrophilic head group of the surfactant. In TTAB solution at the studied concentrations, peaks e and d (d_1 and d_2) show a small upfield shift with increase in alcohol concentration which go downfield on increasing the concentration of alcohols further up to 0.0202 mol kg^{-1}. On increasing the concentrations of alcohols further, an upfield shift of protons can be seen. The changes in the chemical shift may be due to the –OH groups which cause destabilization of cations or electron poor structure.

Table 2 — Chemical shift (δ) of protons of TTAB solutions (0.10 mol·kg^{-1}) in absence and presence of C_9-OH at 295 K

Alcohol (mol·kg^{-1})	-CH_2-N (e)	Protons peaks of head group (ppm)	
		(d_1)	(d_2)
0.0000	3.151	3.436	3.412
0.0039	3.116	3.391	3.335
0.0089	3.109	3.385	3.329
0.0135	3.123	3.398	3.342
0.0202	3.164	3.405	3.525
0.0253	3.09	3.350	3.503

The chemical shift of methyl protons of hydrophilic head and the terminal protons of the surfactant remains unchanged. The peaks for the aliphatic protons of surfactants overlap with the peaks due to methylene protons, which makes it difficult to comment about the chemical shift in their positions. Moreover, the presence of a large number of aliphatic protons of hydrophobic part, appearing over a narrow range of chemical shift makes their exact assignment unrealistic to a certain extent.

In the present investigations, the strong alcohol-aqueous surfactant interactions have been indicated. The magnitude of cmc decreases on addition of an alcohol**.** TTAB–higher chain length additives show a tendency to form large micelles and a rise in N_{agg}. From ^{1}H NMR studies, it is clear that the site for preferential solubilization of alcohol is at the hydrophilic head group as well as at the palisade layer of the surfactant.

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