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SHORT COMMUNICATION

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Hydration of dodecyltrimethylammonium hydroxide micelles

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Abstract The hydration of dodecyltrimethylammonium hydroxide (DTAOH) micelles was determined by viscosity measurements, giving 39.2 ± 7.0 water molecules per micellized dodecyltrimethylammonium ion. This result is lower than the hydration of DTAB micelles, which is about 65. This difference may be due to the effect of the electrorestrictive structure-making hydroxide ion on the hydration of the alkyltrimethylammonium head group, in comparison with the less hydrated structure-breaking bromide ion.

Key words Micelles – hydration – hydroxide surfactants – cationic surfactants

Introduction

Alkyltrimethylammonium hydroxides (RTAOH) are rarely studied surfactants with some striking properties [1–3]. Much of the literature data is contradictory. The properties of DTAOH are of theoretical and practical interest, in the interpretation of micellar catalysis [4].

Some physicochemical properties of the dodecyltrimethylammonium hydroxide (DTAOH) aqueous solutions were studied in this laboratory. The micelle hydration provides valuable information about micelle structure and the interaction between surfactant ion, counterion and solvent.

Experimental

The preparation of dodecyltrimethylammonium hydroxide (DTAOH) was reported in a previous paper [5]. A concentrated solution of DTAOH was employed to make two series of dilutions: one of which was with water, and the other with 10^{-4} M NaOH aqueous solution as the solvent. Two independent runs were made on each series. Double distilled CO_2 – free water was employed. Measurements were performed in a CO_2 – free atmosphere to avoid contamination. Viscosity measurements were performed in an Ostwald viscosimeter at 20.0 ± 0.1 °C, using double-distilled water as a standard. Density measurements were performed using a Chainomatic density balance at the same temperature. Two independent runs were performed on each system.

Confidence intervals were computed with Student's t-distribution with a confidence level of 0.90. Straight lines were fitted with the least squares method and the averages were computed with the least variance unbiased linear estimation [6].

Theory

The reduced specific viscosity of micelles is defined by [7]:

$$\eta_{sp}/c_M = (\eta/\eta_0 - 1)/c_M \,, \tag{1}$$

where η and η_0 are the viscosity of the micellar solution and of the solvent, which is commonly taken as the viscosity at the critical micellar concentration (CMC). The concentration of the micellized surfactant c_M, in g/cm^2, is

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taken as:

$$c_{\mathrm{M}} = \frac{(c_{\mathrm{T}} - [\mathrm{DTA}^+]_{\mathrm{free}})\mathrm{M}}{1000}, \tag{2}$$

where c_{T} is the total (molar) concentration and $[\mathrm{DTA}^+]_{\mathrm{free}}$ is the concentration of free DTA^+ ions, which is determined with a DTA^+ ion – selective electrode, and M is the molecular weight of the surfactant.

By extrapolation to $c_{\mathrm{M}} = 0$ the intrinsic viscosity may be obtained [8]:

$$[\eta] = vE(v_2 + w \cdot v_1), \tag{3}$$

where v is the shape factor, v_1 and v_2 are the specific volumes of the solvent (water) and the dry surfactant, and w is the grams of water per gram of surfactant ratio in micelles. E is the electroviscous effect correction, which may be computed with Booth's theory [9]:

$$E = 1 + \frac{\pi(\sum c_{\mathrm{i}} z_{\mathrm{i}}^2 u_{\mathrm{i}}^{-1})(\sum c_{\mathrm{i}} z_{\mathrm{i}}^2 u_{\mathrm{i}})(\varepsilon\zeta/2\pi)^2(\chi a)^2(1-\chi a)^2 Z}{(\sum c_{\mathrm{i}} z_{\mathrm{i}}^2)^2 \kappa_{\mathrm{sp}} \eta_0}, \tag{4}$$

where c_{i} and z_{i} are the concentration and charge (in e units) of the ion i, whose electrophoretic mobility is u_{i}, ε, κ_{sp} and η_0 are the dielectric constant, specific conductivity and viscosity of the solvent (taken at the CMC), ζ is the zeta potential of the micelles, whose radius is a, and χ^{-1} is the Debye distance. Z is a function of χa.

The micelle radius a may be computed by:

$$a = \sqrt[3]{3V_{\mathrm{M}}/4\pi} \tag{5}$$

where V_{M} is the micelle volume, computed by $V_{\mathrm{M}} = \bar{n} \cdot V_{\mathrm{M}}/N_{\mathrm{A}}$, n being the aggregation number, N_{A} Avogadro's number, and V_{M} the partial molar volume of micellized surfactant, obtained from density measurements. The Debye distance is computed from the Debye–Hückel equation (10).

Results and computations

Figure 1 shows the viscosity–concentration curve for the DTAOH–water system. Table 1 shows the data of the straight lines which best fit the data. Figure 2 shows the reduced specific viscosity for the DTAPH–water system. The DTAOH–10^{-4} M NaOH aqueous system showed similar results.

The CMC value is 0.01108 ± 0.00010 mol/dm^3 in the DTAOH–water system [5] and 0.0107 ± 0.0027 mol/dm^3 in the DTAOH–NaOH solution system [11]. The extrapolation to $c_{\mathrm{M}} = 0$ gave $[\eta] = 10.80 \pm 0.04$ cm^3/g for the DTAOH–water system and $[\eta] = 10.25 \pm 0.03$ cm^3/g for the DTAOH–NaOH solution system.

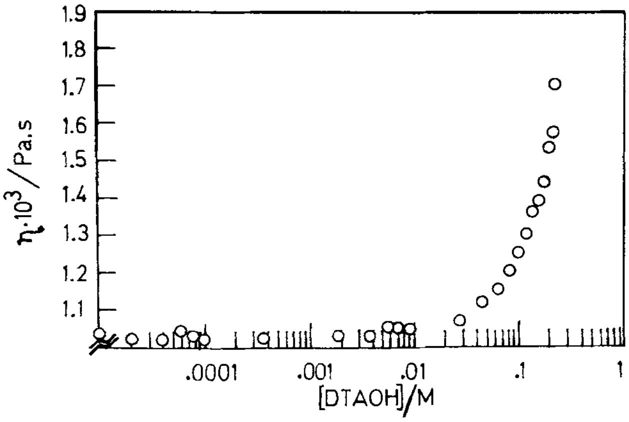

Fig. 1 Viscosity vs. concentration of DTAOH in water

Since literature data indicate that RTAOH micelles have small aggregation numbers and are spherical [1, 12], the shape factor is that of Einstein: $v = 2.5$ [13].

In a previous paper [5], we have shown that DTA^+ ions form small aggregates at very low concentrations, which grew with concentration, giving true micelles at a larger concentration. At this CMC, the concentration of free DTA^+ ions is very small and micelles are strongly ionized. From references [5, 11], we took $[\mathrm{DTA}^+]_{\mathrm{free}} = 2.45 \times 10^{-6}$ mol/dm^3 and $[\mathrm{OH}^-]_{\mathrm{free}} = 0.0111$ mol/dm^3 at the CMC in the DTAOH–water system and $[\mathrm{DTA}^+]_{\mathrm{free}} = 3.85 \times 10^{-6}$ mol/dm^3, $[\mathrm{OH}^-]_{\mathrm{free}} = 0.0108$ mol/dm^3 and $[\mathrm{Na}^+] = 0.0001$ mol/dm^3 in the DTAOH–aqueous NaOH system. The resulting ionic strengths were $I = 0.00554$ mol/dm^3 and 0.0054 mol/dm^3, respectively. The values of χ were 0.244 and 0.242 nm^{-1} for both systems. The aggregation number of DTAOH micelles was measured by Lianos and Zana [1] and is 20.5 on average. The partial molar volume of the micellized DTAOH is 333.5 ± 1.4 cm^3/mol in water and 339.2 ± 1.7 cm^3/mol in aqueous 10^{-4} M NaOH [14]. By using Eq. (5), the average micelle radius was 1.6314 ± 0.0045 nm, and the average value of $\chi a = 0.3964 \pm 0.0016$. The value of ζ was determined by electrophoresis measurements giving 16.2 mV [15].

The ionic mobilities were computed from the literature conductivity data [16]. We obtained $u_{\mathrm{Na}^+} = 5.275 \times 10^{-4}$ cm^2 s^{-1} V^{-1}, $u_{\mathrm{OH}^-} = 1.842 \times 10^{-3}$ cm^2 s^{-1} V^{-1}, $u_{\mathrm{Br}^-} = 8.093 \times 10^{-4}$ cm^2 s^{-1} V^{-1}. With this value and the equivalent conductivity of DTAB from literature [17], we computed the mobility of DTA^+, 2.518×10^{-4} cm^2 s^{-1} V^{-1}.

The specific conductivity at the CMC was $\kappa_{\mathrm{sp}} = 1.50 \times 10^{-3}$ S·cm^{-1} in the DTAOH–water system [5] and 1.77×10^{-3} S·cm^{-1} in the DTAOH–aqueous NaOH system [11]. The viscosities at the CMC were $\eta_0 = 9.97 \times 10^{-4}$ Pa·s and 9.9×10^{-4} Pa·s, respectively.

Table 1 Viscosity vs. concentration lines pre and post CMC Viscosity in Pa · s, concentration in mol · dm^{-3}

[NaOH] mol · dm^{-3}	pre CMC		post CMC	
	intercept	slope	intercept	slope
0	1.0285×10^{-3} $\pm 0.0040 \times 10^{-3}$	5.60×10^{-4} $\pm 0.27 \times 10^{-4}$	9.66×10^{-4} $\pm 0.18 \times 10^{-4}$	2.83×10^{-4} $\pm 0.12 \times 10^{-4}$
10^{-4}	1.0147×10^{-3} $\pm 0.0043 \times 10^{-3}$	1.64×10^{-3} $\pm 0.94 \times 10^{-3}$	9.63×10^{-4} $\pm 0.30 \times 10^{-4}$	2.63×10^{-3} $\pm 0.32 \times 10^{-3}$

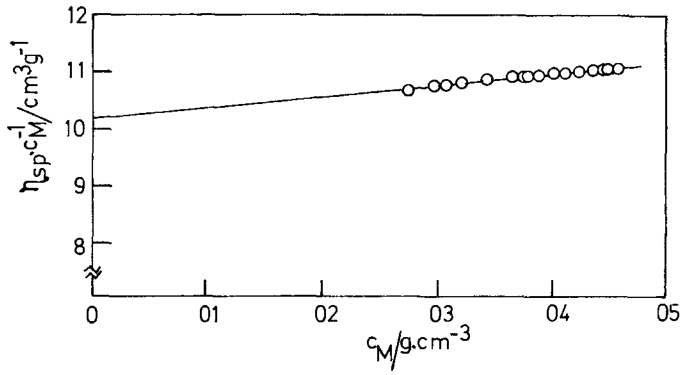

Fig. 2 Specific reduced viscosity vs. micelle concentration of DTAOH in aqueous 10^{-4} mol · dm^{-3} NaOH

The Z value was obtained from ref. [18], giving $Z = 0.004487 \pm 0.000011$. With the above data, we computed the value of $E = 1.210$ for the DTAOH–water system and $E = 1.013$ for the LTAOH–aqueous NaOH system.

The specific volume of water was $w_1 = 0.81659\,cm^3/g$, computed from literature data [19]. The specific volume of the dry micellar surfactant was computed from that of anhydrous DTABr micelles, $2.36 \times 10^{-19}\,cm^3$ [20], being its aggregation number $n = 53$ [20] and its dissociation degree $\alpha = 0.19$–0.30 [21, 22], and the Br^- and OH^- volumes, $0.03154\,nm^3$ and $0.009634\,nm^3$, obtained from their crystallographic radius in literature [23]. The volume of a dry micellized unit of DTAOH is:

$$V_{dry\,DTAOH,\,m} = V_{dry\,DTAB,m} - \beta_{DTAB} V_{Br^-} + \beta_{DTAOH} V_{OH^-} \tag{6}$$

where $\beta = 1 - \alpha = m/n$ is the fraction of counterions bound to the micelle per surfactant ion. $\beta = 0.20$ for DTAOH [1, 5, 12]. Equation (6) gave $V_{dry\,DTAOH,m} = 266.775\,cm^3$. The weight of the micellized unit is $M_{DTAOH,m} = M_{LTA^+} + \beta M_{OH^-} = 233.797$ g/mol and $w_2 = V_{dry\,DTAOH,m}/M_{DTAOH,m} = 1.1407\,cm^3/g$.

With Eq. (3), we obtained $w = 2.975 \pm 0.010$ grams of water per gram of surfactant for DTAOH–water and $w = 3.560 \pm 0.009$ for DTAOH–aqueous NaOH. These ratios correspond to 32.2 ± 0.1 and 46.2 ± 0.1 molecules of water per micellized surfactant molecule. The difference may not be of real significance, because of the various assumptions made in the computation. The average value is 39.2 ± 7.0.

Discussion

The obtained hydration value (39.2) is lower than that of RTAB: 60–70 [24]. Having the same polar head, the reduction in micelle hydration must reflect counterion characteristics. Bromide ion is structure-breaking [25], has a hydration number of 2 ± 1 [26] and is present in a larger proportion in the micelle Stern layer ($\beta \approx 0.76$) than hydroxide ion ($\beta = 0.20$), which has a hydration number much larger than bromide, ranging from 3 to 4 in the first hydration shell [27, 28] and 6 to 8 in the second hydration shell [27]. The bromide has only $0.76 \times 2 = 1.52$ water molecules per micellized surfactant molecule. The other 58 to 68 water molecules in RTAB micelles must be associated with the hydration of the polar head group and the hydrocarbon–water interface in the micelle. The micellized hydroxide ions only explain the presence of $0.20 \times (9$ to $12) = 1.8 - 2.4$ water molecules per surfactant molecule, the other ~ 37 water molecules pertain to the surfactant ion hydration of DTAOH micelles. The trimethylammonium ion hydrates as an apolar molecule [29, 30]. There is evidence of a cage-like average hydration structure, with 20–25 [29, 31] water molecules with no evidence of any enhanced structural ordering of the water close to the exposed methyl groups [29, 32]. Thus, the other 38–48 water molecules associated to a micellized DTAB molecule are probably associated with "hydrophobic hydration" of the hydrocarbon–water interface. Water penetrated into the micelle hydrocarbon core to a depth of two or three methylene groups, while a structure less ordered than that of pure water was proposed by several authors [33], and may be the explanation for the extra water molecules in micelles. It was found that the value of water molecules per polar head was independent of aggregation number [34]. The apolar hydration structure is incompatible with the hydration of structure-making ions. Then, the low hydration of DTAOH micelles is probably due to the interaction between the strongly hydrophilic, strongly electrorestrictive structure-making hydroxile ion and the apolar hydration shell of the alkyltrimethylammonium group, which may be partially destroyed in the process.

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