An Ultrasonic Study of Sphere to Rod Transitions in Aqueous Solutions of Hexadecyltrimethylammonium Bromide

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Surfactants are amphiphilic molecules that dynamically associate in aqueous solution above a certain critical concentration, c.m.c., to large molecular aggregates of colloidal dimensions, *i.e.* micelles.[1,2] At surfactant concentrations close to the c.m.c. micelles are spherical, but at increasing concentrations rodlike micelles form.[3]

It has been documented that ultrasound measurements are sensitive to structural changes in solutions. For instance, micelle formation and stacking can be detected by this method.[4–6] In this work we have used the method of ultrasonic measurements to examine aqueous solutions of hexadecyltrimethylammonium bromide (HTAB) in order to gain information about reported changes in the shape of the HTAB micelles with increasing concentration.

In the absence of added electrolyte, HTAB micelles apparently undergo changes from a spherical to a rodlike shape as the concentration exceeds a certain limit. This has been documented by conductivity measurements,[7,8] small angle X-ray scattering,[9] viscosity and light scattering measurements [10] and nuclear magnetic relaxation data.[11,12]

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It has been suggested that these rod-like micelles have considerable flexibility.[12] The results so far have been summarized in Table 1. It appears that the transition does not occur at a specific molality but takes place over a relatively wide range. The agreement between the various sets of data is not particularly good, but such discrepancies are likely to occur if the transition region is wide.

In Fig. 1, the relative speed of sound (relative to the speed of sound of the solvent) of HTAB solutions has been plotted *versus* molality, m_{HTAB}. In the temperature range 300 – 305 K a transition point, $m^{\mathrm{t}}_{\mathrm{HTAB}}$, can be observed. It appears to be a rather distinct point at 0.27 molal at 300.7 K, increasing to 0.32 at 305.1 K. At 308 K and higher temperatures no transition point could be detected in the concentration range investigated.

The result is in good agreement with the data presented in Table 1. The ultrasonic data, however, do not show a wide transitional region, at least not as wide as indicated by viscosity or ^{81}Br NMR measurements. On the other hand, there is agreement that the transition molality increases with temperature. Note that the aggregation number of spherical ionic micelles decreases with temperature as shown by membrane osmometry.[13,14]

The enthalpy change of transition from spheres to rods has been estimated from the temperature dependence of the transition molality, $m^{\mathrm{t}}_{\mathrm{HTAB}}$. The value thus obtained is -30 ± 1 kJ mol^{-1}.

It is well-known that addition of a third component, electrolyte or nonelectrolyte, can cause structural changes in micelles. Furthermore, this change is highly specific depending on the nature of the additive. Larsen *et al.*[15] thus found from viscosity measurements that while both ethanol and hexane had little or no effect, hexanol caused a pronounced change of structure in a 0.1 M HTAB – 0.1 M NaBr solution. In the absence of NaBr the effect of hexanol on the viscosity of HTAB solutions was small. On the other hand, Tominaga *et al.*[16]

Table 1. Sphere to rod transition of HTAB micelles in aqueous solution.

T / K	$m^{\mathrm{t}}_{\mathrm{HTAB}}$ / mol kg^{-1}	Method	Ref.
298.2	~0.45	Conductivity	8
308.2	~0.56		
300.2	0.304	Small angle X-ray	9
323.2	0.562		
343.2	0.915		
298.2	0.271 – 0.339	Viscosity, light scattering	10
300 ± 2	0.207 – 0.447	^{81}Br NMR	11
301.2 ± 0.5	0.28	^{14}N NMR	12

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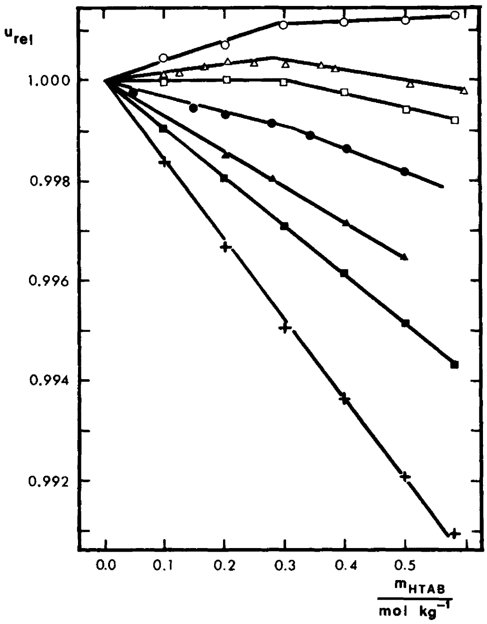

Fig. 1. Relative speed of sound, u_{rel}, in pure HTAB solutions as a function of the HTAB molality at 300.7 (○); 303.1 (△); 303.4 (□); 305.1 (●); 308.2 (▲); 310.7 (■); 315.6 K (+).

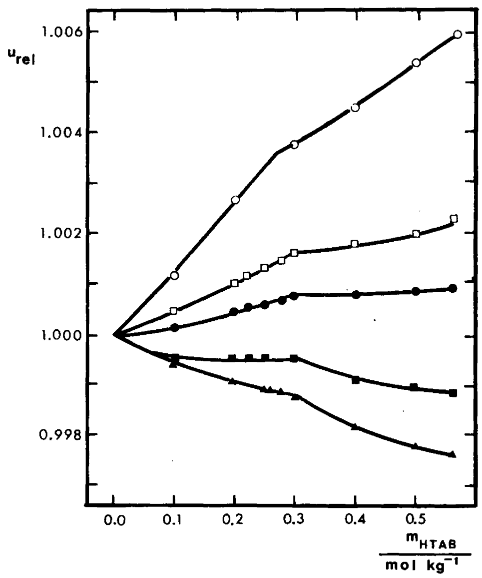

Fig. 2. Relative speed of sound, u_{rel}, in HTAB – 0.01 mol kg^{-1} pentanol solutions as a function of the HTAB molality at 293.2 (○); 298.2 (□); 300.2 (●); 303,.2 (■); 305.2 K (▲).

point out that the viscosity increases rapidly upon addition of hexanol to HTAB solutions suggesting sphere to rod transitions. Lindblom *et al.*[11] also find that small amounts of hexanol appear to promote a sphere to rod transition.

In Fig. 2 the relative speed of sound of HTAB in 0.01 mol kg^{-1} pentanol has been plotted at various temperatures. With pentanol added it was possible to carry out the measurements at lower temperatures, and in this case the temperature ranges from 293.2 – 305.2 K. Otherwise the curves are of a similar character as those in Fig. 1. They show a transition point around 0.30 mol kg^{-1} slightly lower at 293 K. The effect of a little added pentanol is thus small as far as the sphere to rod transition is concerned.

However, the Fig. 3 the same curves have been plotted, the only difference being a pentanol content of 0.05 mol kg^{-1}. At this pentanol content there appears to be a totally different situation. In the HTAB concentration range that has been investigated, there is no longer any sign of changes in micellar structure, at least not any that are signified by abrupt changes in the curvature. Since alcohols apparently promote rods, this result suggests that most of the HTAB molecules are present as rod-like micelles in 0.05 mol kg^{-1} pentanol solutions.

In conclusion, it appears that ultrasound measurements provide a well-suited way to measure changes in micellar structure. As far as HTAB micelles are concerned, a transition takes place

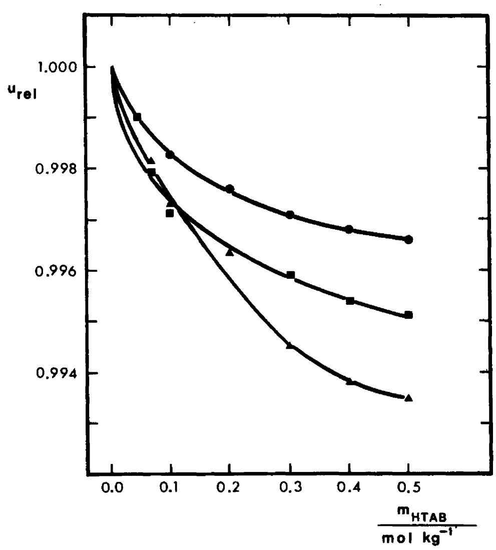

Fig. 3. Relative speed of sound u_{rel}, in HTAB – 0.05 mol kg^{-1} pentanol solutions as a function of the HTAB molality at 303.2 (●); 305.2 (▲); 308.2 K (■).

around 0.3 mol kg^{-1} both in water and in aqueous (0.01 mol kg^{-1}) pentanol. The transition depends on temperature. In pure water no transition can be observed at 308 K and higher temperatures. In aqueous (0.05 mol kg^{-1}) pentanol no transition appears at any of the measured temperatures.

Experimental. Hexadecyltrimethylammonium bromide (HTAB) (purity *ca.* 99 %) was from Sigma. It was dried in an evacuated desiccator and used without further purification n-pentanol (*puriss* quality) was used as supplied by Fluka. The ultrasound measurements were made by the "sing-around" method as previously described.[17] The relative speed of sound, u_{rel}, was calculated as $u_{rel}=f(1-f^*\tau)/f^*(1-f\tau)$. Here τ is the delay time and f and f^* the measured frequencies in solution and solvent, respectively. The temperature in water thermostats were controlled to within ± 0.01 K. The error in the speed of sound is estimated to ± 0.02 m s^{-1}.

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