# Effect of Solubilized Amines on the Structural Transition of Cetyltrimethylammonium Bromide Micelles in Aqueous Potassium Bromide

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**Rod-shaped micelles were produced by mixing 0.1 M cetyltrimethylammonium bromide (CTAB) and 0.1 M KBr in aqueous solution. The effects of the addition of aliphatic *n*-amines ($C_4$, $C_6$, $C_7$ and $C_8$) and temperature on the shape of micelles were studied by viscosity measurements. The viscosity data show that transition of rod-shaped micelles to larger aggregates is induced by addition of higher amines ($\geqslant C_6$) up to a certain concentration; a further increase in concentration produced the opposite effect. Addition of $C_4$-amine induces only a rod-to-sphere transition. The data were interpreted in terms of solubilization/incorporation (decrease of micellar surface charge density) of amines inside the micelles and the nature of the effective solvent (water + amine). The latter effect dominated the change from larger aggregates to smaller micelles at higher concentrations of the added amine. Increasing the temperature produced effects similar to $C_4$-amine addition, namely, rod-to-sphere transition. Activation free energy ($\Delta G^*$) and enthalpy ($\Delta H^*$) were also computed from the temperature dependence of the viscosity. $\Delta G^*$ and $\Delta H^*$ values were higher for larger aggregates (long rods) than for smaller ones (spherical micelles) and $\Delta H^*$ covered almost the total contribution to $\Delta G^*$.**

KEY WORDS: Solubilization, structural transition, surfactant, viscosity.

In dilute solutions of water or brine, surfactant molecules associate reversibly to form aggregates of different morphologies. Among these, isotropic solutions of micelles have been extensively studied; at low concentrations, the micelles are generally globular (1), but they grow in certain systems when the surfactant concentration and/or the salt content (in case of ionic surfactant) is increased (2-4). Under these conditions micelles undergo a change from spheres to cylinders. This transition is important from both theoretical and practical view points. Theoretical importance can be sought, for example: (i) in predicting models for better understanding of organized media and (ii) in relating to classical DLVO theory and micellar growth and formation of biological structures and organized rod-shaped micelles. The presence of rod-shaped micelles results in increased solution viscosity, which is of practical importance because it enhances performance and customer appeal of surfactant formulations.

The effect of electrostatic charge on viscous flow has been investigated as the electroviscous effect (5). During the investigation of the relationship between the structure of micellar solution and its viscosity, it was discovered that a sharp increase in the viscosity of a concentrated surfactant solution relates to the formation of rod-like micelles, which can form a network in the solution (6).

Increasing attention is being devoted to the study of the incorporation or solubilization of neutral organic molecules (cosurfactant) into micelles in aqueous solution. Some of the most studied solubilizates are alcohols, because of their important role in preparation of microemulsions (7). Recently some linear medium-chain aliphatic amines have been getting more recognition as cosurfactants in microemulsion preparations (8-10). Despite the significance of amines in microemulsions, proper attention has not been paid so far to the contribution of medium-chain normal amines in micellar systems. It is generally accepted that the cosurfactants of medium chainlength bind to the micelle and intercalate between the surfactant ionic head groups to decrease the micellar surface charge density (11-14). This effect is correlated with a packing parameter, governed by the hydrophilic and hydrophobic groups of the surfactant. The ratio of the area per head group ($A_o$) to the average section of the hydrophobic part ($V_c/1_c$), namely, surfactant parameter Rp ($=V_c/A_o1_c$), is the fundamental geometric quantity for structural descriptions (15). This value should be kept in mind for structural investigation of any surfactant–solvent (additive) couple.

Visualizing the significance of micellar structure transitions and their dependence upon the nature of electrolytes (16,17), temperature, and, in some cases, the influence of organic additives (18), it was thought worthwhile to pursue a study of the effect of aliphatic amines on concentrated micellar solutions in aqueous potassium bromide (KBr). Compared with other techniques, the capillary viscometry method is simple and reliable and can provide a large body of important information with respect to the investigation of the increase in micelle size (19). Hence, in the present paper we submit the results of our preliminary studies on the effect of the addition of various aliphatic amines on the viscosity of 0.1 M cetyltrimethylammonium bromide (CTAB) + 0.1 M KBr solutions. From the temperature dependence of the viscosity, the activation free energies ($\Delta G^*$), enthalpies ($\Delta H^*$) and entropies ($\Delta S^*$) for viscous flow have been calculated.

## EXPERIMENTAL PROCEDURES

CTAB and KBr, obtained from Merck (Darmstadt, Germany), were "pro analysi" grade. The amines, *n*-hexylamine ($C_6NH_2$), *n*-hepthylamine ($C_7NH_2$) and *n*-octylamine ($C_8NH_2$) (all "Purum grade"), were obtained from Fluka (Buchs, Switzerland), and *n*- butylamine ($C_4NH_2$) was a Riedel-de-Häen product (Seelze, Hannover, Germany). All chemicals were used as supplied. Demineralized water, redistilled from alkaline potassium permanganate, was used.

The viscosities were measured with an Ubbelöhde viscometer (Aligarh Muslim University, Aligarh, India), fabricated by our own workshop at 30, 35, 40 and 45°C. The method of measurement of viscosities under Newtonian flow conditions was the same as described by other investigators (3). Density corrections were not made, as these have been found to be negligible (20). The solvent flow time was always longer than 200 s. At least four flow time measurements were made at each concentration, and

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a mean deviation from the mean of all measurements not exceeding 0.1 s was required. The temperature of the bath was controlled to an accuracy of ±0.01°C.

## RESULTS AND DISCUSSION

Figure 1 shows the effect of KBr on the relative viscosity ($\eta/\eta_0$) of 0.1 M CTAB solution at 303.16°K ($\eta$ and $\eta_0$ represent the viscosities of solution and solvent water, respectively). When a salt is added to a surfactant solution and its concentration reaches a threshold value, nonspherical micelles form because the presence of salt ions near the polar heads of the surfactant molecules decreases the repulsion force between the head groups. A reduction in the repulsion makes it possible for the surfactant molecules to approach each other more closely and form larger aggregates, which require much more space for the hydrophobic chains. This leads to a sharp rise in $\eta/\eta_0$; in the present system (of 0.1 M CTAB) it occurs around 0.1 M KBr, indicating the formation of larger aggregates (3,21) (rod-shaped micelles). This is the reason for choosing a 0.1 M CTAB + 0.1 M KBr system for the detailed study of the effect of *n*-alkylamines and temperature.

Figure 2 shows the variation of ln ($\eta/\eta_0$) with concentration of added amines at 303.16°K. Viscosity data for different amines at different temperatures are given in Table 1. Data in Table 1 and Figure 2 indicate that the addition of an amine may either decrease or increase the viscosity of the starting solution (0.1 M CTAB + 0.1 M KBr). It is further shown that the increase or decrease of viscosity depends upon the chainlength and the nature of added amine. With $C_6$, $C_7$ and $C_8$ amines, the viscosity rises abruptly, followed by a decrease. The effect is progressively more pronounced for higher amines. For $C_4NH_2$, viscosity decreases right from the beginning. The viscosity increments at low concentrations of higher amines ($C_6$–$C_8$) can be interpreted in terms of the formation of large micelles due to their solubilization/incorporation into the micelles. The decrease in the viscosity on further addition of these amines is a result of the breaking of larger micelles into small aggregates. Addition of $C_4NH_2$ results in breaking the initially present rod-shaped micelles into spherical micelles with a concomitant decrease to a viscosity value comparable to globular micellar solutions. The preceding discussion reflects that larger amines solubilize preferentially in micelles and lower the surface charge density, which is responsible for micellar growth. Further addition of the amine beyond the optimum concentration affects the water structure predominantly, resulting in the breaking up of giant aggregates to relatively smaller units; hence, a gradual decrease in viscosity is observed. The differing behavior of $C_4NH_2$ is due to the hydrophilic nature of this amine. It is partitioned more in the aqueous phase; hence, it affects the water structure and causes the breaking up of initially present large micelles in the solution (22). Such transitions from rod-to-sphere by the addition of lower alcohols to dodecyltrimethylammonium bromide–sodium salicylate micelles have been reported from light-scattering measurements (23).

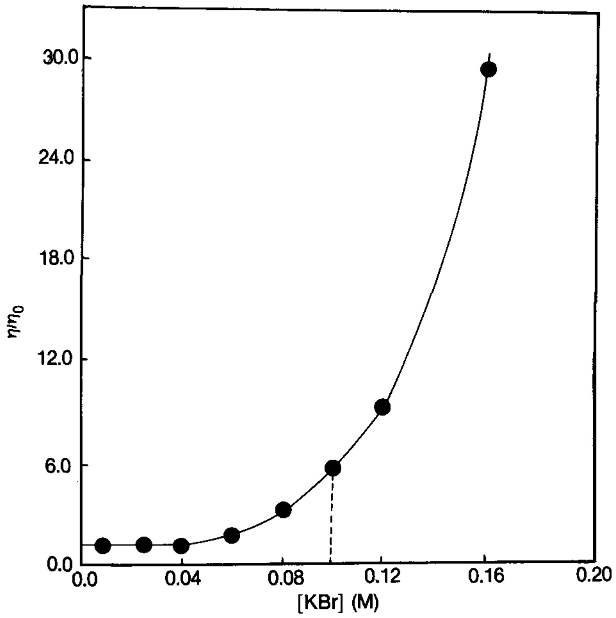

FIG. 1. Effect of potassium bromide (KBr) concentration on the relative viscosity of 0.1 M cetyltrimethylammonium bromide (CTAB) micellar solution at 303.16°K.

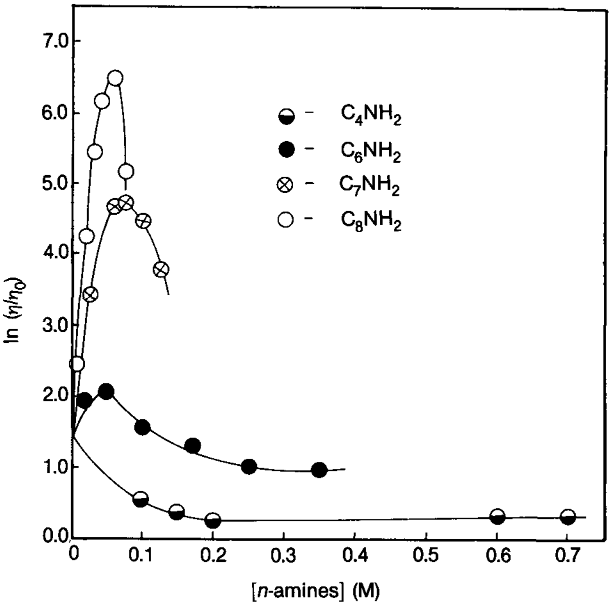

FIG. 2. Logarithms of relative viscosities of 0.1 M CTAB + 0.1 M KBr solutions as a function of added *n*-amines at 303.16°K. Abbreviations as in Figure 1.

Alternatively, the phenomenon of micellar growth of CTAB-amine systems could be understood by considering variation in the surfactant parameter. Because length ($l_c$) and volume ($V_c$) remain the same for a typical surfactant, amine addition decreases the area per head group ($A_0$) of a surfactant molecule. Consequently, the Mitchell–Ninham parameter (15), which, in principle, decides the aggregate shape, increases with concomitant micellar growth. The CTAB-amine couple could be regarded as a single surfactant with the Mitchell–Ninham parameter increasing progressively for higher amines. Accordingly, CTAB-octylamine should show micellar growth earlier than CTAB with lower-chain amines. This is indeed reflected in viscosity results (Fig. 2).

Figure 3 shows the ln ($\eta/\eta_0$) vs. 1/T plots for different concentrations of $C_7NH_2$ (similar types of plots were obtained for other amines). The observed linearity of the

TABLE 1

**Relative Viscosities, Activation Free Energies and Enthalpies for the Viscous Flow of 0.1 M CTAB + 0.1 M KBr Solutions in the Presence of Amines**[a]

| Concentration of amines (M) | Relative viscosity ($\eta/n_o$) 30°C | 35°C | 40°C | 45°C | ΔG* (kcal/mol) | ΔH* (kcal/mol) | Correlation coefficient (r)[b] |
|---|---|---|---|---|---|---|---|
| 0 | 4.77 | 2.82 | 1.94 | 1.48 | 14.88 | 14.88 | 0.9981 |
| *n*-Butylamine | | | | | | | |
| 0.100 | 1.79 | 1.43 | 1.31 | 1.22 | 4.77 | 4.78 | 0.9943 |
| 0.150 | 1.56 | 1.38 | 1.28 | 1.20 | 3.04 | 3.04 | 0.9987 |
| 0.200 | 1.31 | 1.23 | 1.22 | 1.19 | 0.89 | 0.89 | 0.9873 |
| 0.600 | 1.39 | 1.36 | 1.35 | 1.34 | 0.53 | 0.53 | 0.9972 |
| 0.700 | 1.40 | 1.38 | 1.37 | 1.35 | 0.41 | 0.41 | 0.9919 |
| *n*-Hexylamine | | | | | | | |
| 0.020 | 6.69 | 3.76 | 1.81 | 1.64 | 18.99 | 18.99 | 0.9995 |
| 0.050 | 8.07 | 4.29 | 2.67 | 1.91 | 18.37 | 18.37 | 0.9928 |
| 0.100 | 5.29 | 3.75 | 2.67 | 2.04 | 12.22 | 12.22 | 0.9992 |
| 0.175 | 3.65 | 2.73 | 2.50 | 2.09 | 6.75 | 6.75 | 0.9892 |
| 0.250 | 3.18 | 2.79 | 2.54 | 2.34 | 3.87 | 3.88 | 0.9958 |
| 0.350 | 2.97 | 2.89 | 2.72 | 2.57 | 1.47 | 1.47 | 0.9976 |
| *n*-Heptylamine | | | | | | | |
| 0.025 | 31.60 | 12.80 | 5.91 | 3.33 | 28.56 | 28.56 | 0.9949 |
| 0.060 | 115.02 | 46.09 | 16.49 | 7.64 | 34.98 | 34.98 | 0.9990 |
| 0.075 | 117.20 | 48.85 | 22.13 | 10.69 | 30.45 | 30.45 | 0.9970 |
| 0.100 | 97.14 | 47.91 | 23.84 | 10.99 | 27.72 | 27.71 | 0.9991 |
| 0.125 | 45.10 | 17.36 | 11.96 | 7.90 | 21.45 | 21.45 | 0.9847 |
| *n*-Octylamine | | | | | | | |
| 0.010 | 11.85 | 5.10 | 2.77 | 1.91 | 23.34 | 23.34 | 0.9980 |
| 0.020 | 73.52 | 20.70 | 8.74 | 4.26 | 35.93 | 35.93 | 0.9934 |
| 0.030 | 259.99 | 30.86 | 10.33 | 4.18 | 51.70 | 51.70 | 0.9814 |
| 0.040 | 532.84 | 131.78 | 35.90 | 13.05 | 47.52 | 47.52 | 0.9985 |
| 0.060 | 678.58 | 251.47 | 89.90 | 37.82 | 37.04 | 37.04 | 0.9977 |
| 0.075 | 190.69 | 175.86 | 135.83 | 84.94 | 10.22 | 10.22 | 0.9896 |

[a] CTAB, cetyltrimethylammonium bromide; KBr, potassium bromide.
[b] From the linear variation of ln ($\eta/\eta_0$) with 1/T.

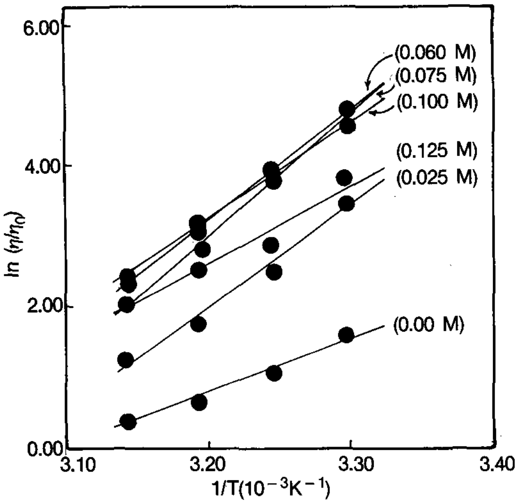

**FIG. 3. Variation of ln ($\eta/\eta_0$) with 1/T for 0.1 M CTAB + 0.1 M KBr solutions in the presence of various concentrations of *n*-heptylamine (noted in parentheses). Abbreviations as in Figure 1.**

plots shown in Figure 3 is interpreted in terms of the relation (24):

$$\ln \eta/\eta_0 = \ln A + \Delta G^*/RT \qquad [1]$$

where A is a constant and ΔG* is the activation free energy for viscous flow. As densities of the solutions were close to the density of water, kinematic corrections were neglected, and values of ΔG* were calculated from the slopes of these straight line plots (Fig. 3). As stated earlier, $\eta/\eta_0$ values were obtained only at four temperatures in the range of 30–45°C. The lack of more experimental data points does not preclude obtaining good correlation coefficients (r). Estimation of activation parameters is, therefore, sufficiently adequate. The r and calculated ΔG* values are also shown in Table 1. Using the Gibbs-Helmholtz equation:

$$\delta(\Delta G^*/T)/\delta(1/T) = \Delta H^* \qquad [2]$$

along with the dependence of ΔG* on T (Fig. 4), the activation enthalpy (ΔH*) for the viscous flow was calculated. The ΔH* values reflect the energy used in the rod-to-sphere transition. When the temperature is increased by a small value, dT, the total energy added to the system is $C_p$dT, where $C_p$ is the heat capacity at constant pressure. This amount of energy will be spent partially on "evaporating" some of the amphiphiles previously attached to the micelles. At high temperature, these evaporated surfactant molecules are unable to remain in solution, so it is a necessary consequence that they form new micelles that consist of a smaller number of monomers. This mechanism is involved in the transition of rod-shaped micelles to spherical ones at elevated temperatures.

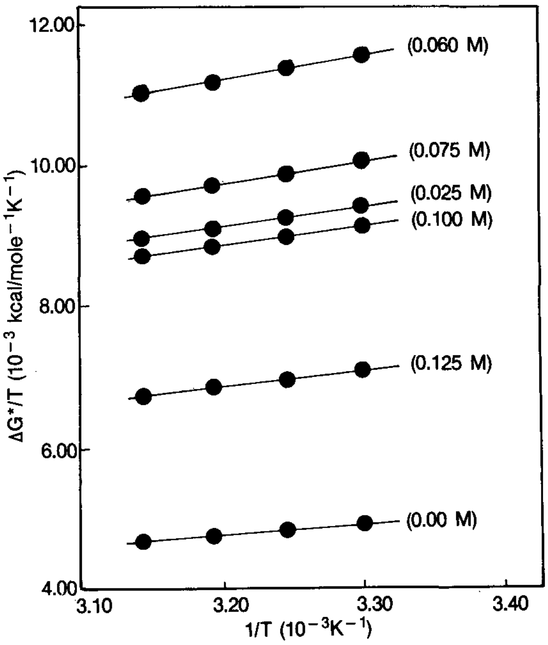

**FIG. 4. Gibbs-Helmholtz plots for 0.1 M CTAB + 0.1 M KBr in the presence of various concentrations of *n*-heptylamine (noted in parentheses). Abbreviations as in Figure 1.**

The obtained ΔH* values (from Fig. 4) are also tabulated in Table 1. The values of ΔG* and ΔH* show that ΔH* covers the total contribution to ΔG* and, therefore, the entropic contribution is negligible. The observed linearity in the ln $\eta/\eta_0$ vs. 1/T plots (Fig. 3) indicates that the enthalpic contribution to ΔG* is independent of temperature.

Figure 5 shows the variation of ΔH* with concentration of added amines. Table 1 and Figure 5 show that ΔG* and ΔH* values are highly dependent on the nature and concentration of added amines. The higher values of ΔH* correspond to the formation of larger aggregates (elongated rods), and low values to the smaller aggregates (spherical micelles). The magnitudes of ΔG* and ΔH* for different amines indicate that higher-chainlength amines are capable of inducing the growth process of micelles up to an optimum concentration, beyond which change in solvent structure plays a dominant role. While the low values of ΔH* for $C_4NH_2$ show that water structure factors play an important role with hydrophilic additives with a concomitant breaking up of larger aggregates. The behavior of these amines is due to the combined effect of two opposite effects, partitioning in the micellar phase and partitioning in the bulk solvent. At higher concentrations, the latter effect plays an important role in breaking up the larger aggregates.

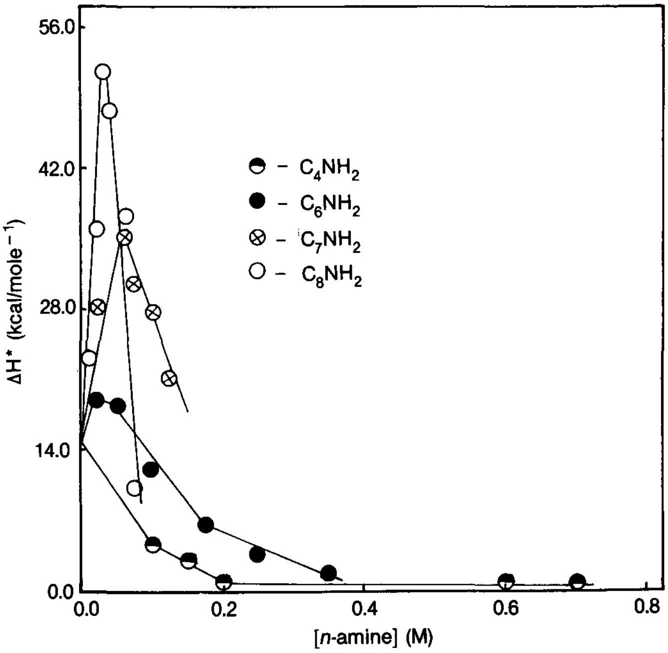

**FIG. 5. Variation of activation enthalpy (ΔH*) for the viscous flow of 0.1 M CTAB + 0.1 M KBr solutions as a function of added *n*-amines. Abbreviations as in Figure 1.**

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