# Interactions of Some Aromatic Salts with Hexadecyltrimethylammonium Bromide Micelles. Viscosity, Counterion Binding, and Calorimetric Observations[1]

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*Received March 9, 1976*

The effect of disodium phenyl phosphate (PP), sodium benzenesulfonate (BS), sodium tosylate (TOS), sodium benzoate (BZ), and sodium *p*-toluate (Tol) on the viscosity of hexadecyltrimethylammonium bromide (CTAB) solutions was studied at low CTAB concentrations. A sharp viscosity increase was observed once a certain salt concentration of TOS or TOL was reached. In the absence of the *p*-methyl group, no effect was observed. Plots of bound bromide vs. [added salt] showed similar behavior for all salts. Apparently, introduction of a *p*-methyl group has a large effect on the size and/or shape of CTAB molecules while not affecting the counterion binding. The transfer of all salts except PP from water to the micelle is exothermic and for TOS depends on the micelle concentration.

In recent years the study of micelle catalyzed reactions has become an active area.[2,3] A chief factor preventing a clear understanding of these reactions is our ignorance of the mutual interactions between micelle and solubilizate. Many have studied the location of the solute in micelles.[4–16] Location of the solute is dependent on its chemical character as well as that of the micelle. A good example of this is the difference in location of pyrene, pyrenebutyric acid, and pyrenesulfonic acid in hexadecyltrimethylammonium bromide (CTAB) micelles.[4] Using a variety of techniques, progress is being made in locating solutes in micelles.

However, we have almost no understanding of the highly specific effects of various solutes on micelle structure. These effects are sometimes characterized by a large increase in the viscosity of a micellar solution caused by some solutes but not by others. The most thorough study of this effect was carried out by Wan, who investigated the effects of a variety of substituted benzoic acids on the viscosity of some cationic micellar solutions.[17] While salicylic acid and its salts increased the viscosity of dodecyl-, tetradecyl-, and cetyltrimethylammonium bromide solutions, *m*-hydroxybenzoic acid, *p*-hydroxybenzoic acid, as well as *o*-, *m*-, and *p*-amino-, chloro-, and nitrobenzoic acids caused no viscosity change.[17a] Larsen and co-workers reported a large viscosity increase for CTAB micellar solutions which was specific for both the organic solute and the inorganic anion present in the solution.[18] Bunton has observed a large viscosity for a CTAB solution containing sodium tosylate but not for one with sodium benzenesulfonate.[19] Stainsby and Alexander observed some time ago that chlorobenzene had pronounced effects on the viscosity of cetylpyridinium chloride in the presence of sodium chloride.[20] The effect of solubilized phenol on the viscosity of CTAB solutions was reported by Good and Milloy.[21] In these last three cases, there is a sharp increase in viscosity followed by a sharp decrease as the concentration of solute increases. This effect is absent with micelles formed from alkylsodium carboxylates.[17a,22] The high substrate specificity of these effects is fascinating. Much needs to be done to characterize the solute structural changes capable of inducing such effects and to determine to what extent all micellar properties are affected, so that plausible models for the structural change may be constructed. We report here a study of the highly specific effect of *p*-methyl substitution of sodium benzoate and sodium benzenesulfonate on the viscosity of CTAB solutions together with calorimetric and counterion binding studies of these systems.

## Results

In Figure 1, plots of the viscosity of 0.01 M CTAB solutions as a function of the concentration of sodium benzenesulfonate and sodium benzoate and their *p*-methyl derivatives are shown. A similar plot for disodium phenyl phosphate also is shown. The effect of the *p*-methyl substitution is startling. Without the methyl group, the solution viscosity is not dependent on the concentration of added salt. With the methyl group, there is a sharp increase in viscosity once a certain salt concentration has been reached.

The effect of the same salts on counterion binding is shown in Figures 2–4. The extent of counterion binding was measured using bromide ion selective electrodes as before.[23] A plot of bound bromide vs. salt concentration for all the salts shows two intersecting lines. The changes in slope in the counterion binding plots for the *p*-methyl derivatives occur close to, but at a higher concentration than, those concentrations at which the rapid increase in the viscosity plots begins. In both cases, the methyl group has only a small effect on the binding of bromide to the micelle.

The partial molar heats of transfer of these salts from water to 0.01 M CTAB solution were measured and are reported in Table I. Independent data are available showing that at the soap and salt concentrations used, essentially all of the anionic salts are bound to the micelle.[24] Thus, the heats of transfer reported are heats of transfer from water to the micelle. Additionally, the dependence of the heat of transfer of sodium tosylate on the concentration of CTAB was measured. The effect of varying the soap concentration is significant as shown by the data in Table II.

## Discussion

**Viscosity.** A comparison of Figure 1 with Figures 2–4 leads to the conclusion that the effect of the solutes on the micelle structure and on the counterion binding to the micelle are independent. In all cases, counterion binding shows similar behavior; there is nothing to suggest that *p*-methyl benzoate is behaving any differently than benzoate or tosylate any differently than benzenesulfonate. Obviously the introduction of the methyl group has a profound effect on the structure of the micelle as evidenced from the plots of viscosity vs. solute concentration.

The viscosities of systems such as these are functions of the volume fraction and shape of the micelles in the solution.[25,26] It seems rather unlikely that a sudden change in the total volume of micellar material can be induced by a small change in salt concentration or by the introduction of a methyl group, so we are left with the other alternative. The methyl substituted salts are inducing a sudden change in the shape of the micelle. Solubilization near the micelle surface should result in a decrease in charge density leading to the formation of larger micelles and a change in the shape of the micelle.[27,28] Ellipsoids or rods are expected, both of which would lead to

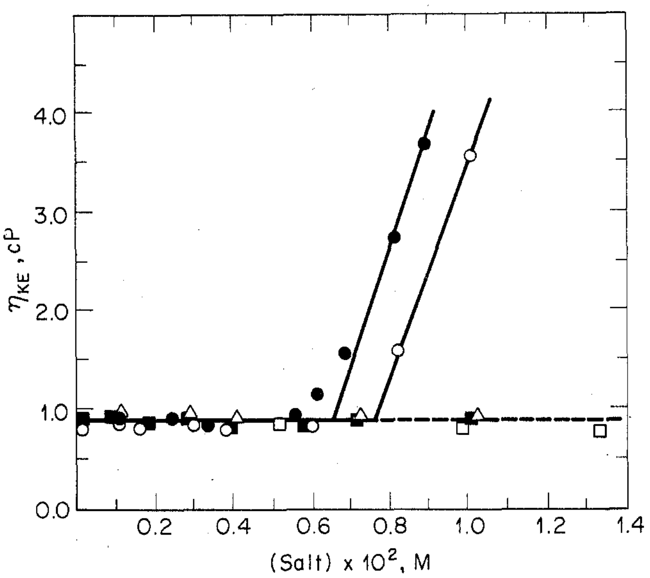

**Figure 1.** Viscosity of a 0.01 M CTAB solution containing sodium *p*-toluenesulfonate (●), sodium benzenesulfonate (■), sodium *p*-toluate (○), sodium benzoate (□), or disodium phenyl phosphate (△).

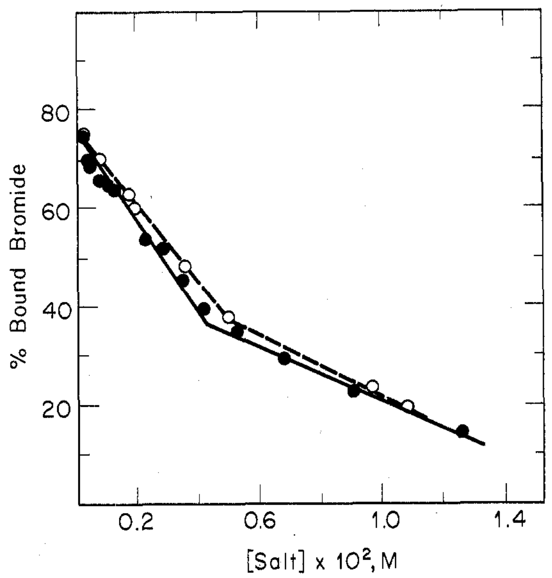

**Figure 2.** Bromide ion bound to the micelle in the presence of added sodium tosylate (●), or sodium benzenesulfonate (○).

**Table I. Heat of Transfer ($\Delta H_T$) of a Series of Salts from Water to Aqueous CTAB (0.01 M) at 25 °C**

| Salt | $\Delta H_{s(\mathrm{CTAB})}$, kcal/mol | $\Delta H_{s(\mathrm{H_2O})}$, kcal/mol | $\Delta H_{\mathrm{trans}}$, kcal/mol |
|---|---|---|---|
| PP | −0.550 ± 0.131 | −3.82 ± 0.21 | 3.27 ± 0.25 |
| TOL | −1.64 ± 0.14 | −1.17 ± 0.11 | −0.47 ± 0.18 |
| BS | 0.445 ± 0.173 | 1.70 ± 0.18 | −1.25 ± 0.25 |
| TOS | 1.17 ± 0.23 | 2.54 ± 0.60 | −1.37 ± 0.64 |

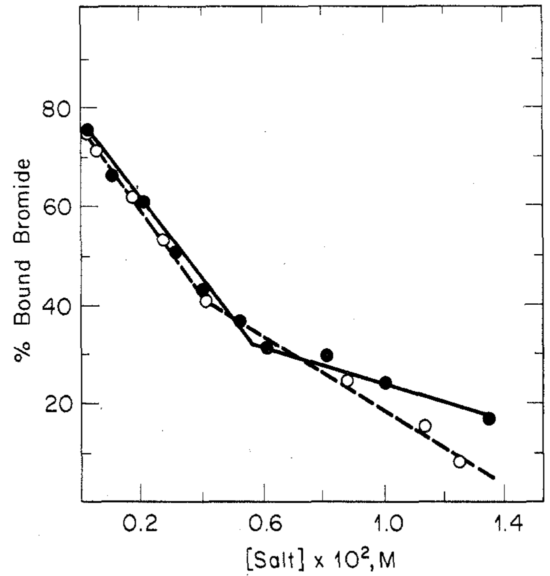

**Figure 3.** Bromide ion bound to the micelle in the presence of added sodium *p*-toluate (○), or sodium benzoate (●).

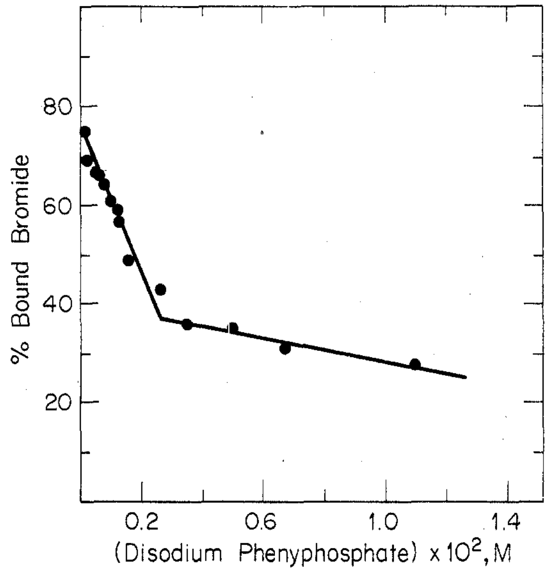

**Figure 4.** Bromide ion bound to the micelle in the presence of added disodium phenyl phosphate.

**Table II. Heat of Transfer ($\Delta H_T$) of Sodium Tosylate to CTAB Solutions at 25 °C**

| [CTAB], M | $\Delta H_{s(\mathrm{CTAB})}$, kcal/mol | $\Delta H_{\mathrm{trans}}$,[a] kcal/mol |
|---|---|---|
| 0.100 | 0.564 ± 0.232 | −1.98 ± 0.64 |
| 0.060 | 0.316 ± 0.380 | −2.22 ± 0.71 |
| 0.030 | 0.654 ± 0.133 | −1.89 ± 0.61 |
| 0.010 | 1.17 ± 0.23 | −1.37 ± 0.63 |

[a] $\Delta H_{s(\mathrm{H_2O})}$ = 2.54 ± 0.60 kcal/mol.

higher viscosity. However, any change in charge density at the micelle surface is expected to result in a change in counterion binding—and we have pointed out that the viscosity and bromide binding seem to be independent. It is possible that the size and shape changes are caused by changes in charge density too small to be detected by our selective ion electrode measurements. Or possibly the changes are due to alterations of the internal structure of the micelle caused by the methyl group, alterations which have little effect on the surface charge density. It seems of little use to speculate on the origin of the effect until more systems have been studied and data on the size and shape of the micelle together with information on the location of the solute ions in the micelle are available. At this point it is obvious that small solute structural changes can cause pronounced alterations in micelles, a factor which may be of some importance to groups studying micellar catalysis.

There is one other possible explanation. As pointed out by

Tanford,[28] the surface area/volume ratio is larger for a prolate ellipsoid than for an oblate ellipsoid. Thus, it is possible to increase the volume of a micelle at constant surface charge density by moving from a prolate to an oblate ellipsoid. Unfortunately, Tanford also predicts that for a given charge density, oblate ellipsoids will be smaller (lower aggregation number). This is in conflict with the observed viscosity increase. Finally, at large aggregation numbers, especially for prolate ellipsoids, the dependence of charge density on micelle volume is quite shallow, and significant changes in micelle size may occur without large changes in the charge density.

The last topic to be discussed is the heats of transfer from water to the micelle. From Sepulveda's data for all the salts except sodium benzoate, we know that at the concentrations used, all of the salts are essentially completely bound to the micelle.[24] Sepulveda calculated an equilibrium constant for binding to the micelle using a model based on a finite number of binding sites per micelle. Such a model should be consistent with a Langmuir isotherm[29] and his data do not appear to be consistent with one. At low soap concentrations, as the salt concentration increases, the moles of salt bound first increase, then decrease. This contradiction raises doubts about Sepulveda's analysis of his binding data and we do not choose to make quantitative use of them.

The heat of transfer of disodium phenyl phosphate is endothermic while the transfer of the other three salts is exothermic. There is not enough data to ascribe these results to any particular effect. The small enthalpic driving force for the transfer of the aromatic carboxylates and sulfonates might have an electrostatic origin or might be due to the known favorable interactions between aromatics and tetralkylammonium salts.[30]

The heats of transfer of sodium tosylate are dependent on the concentration of CTAB as shown by the data in Table II. It seems most reasonable to associate this with changes in micelle size and structure which occur with changes in the CTAB concentration, although there is no compelling evidence for this interpretation.

## Experimental Section

The calorimetric techniques[31] and the methods for measuring bound counterions[23] have been described. Hexadecyltrimethylammonium bromide purchased from City Chemical Corp. was recrystallized from carbon tetrachloride and dried in vacuo at 55 °C. It showed no minimum in a plot of surface tension vs. concentration and titration with $AgNO_3$ gave a molecular weight of 364.7 ± 1.3 (actual 364.5). Doubly distilled water was used for all experiments.

**Viscometry.** The viscosity of the soap solutions was measured using Ostwald capillary viscometers which had been rinsed several times with distilled water and dried in an oven. To each viscometer was added 5.5 ml of the solution to be run, and the solutions were allowed to equilibrate in a constant temperature bath for at least 30 min. In measuring flow times, the solution was drawn up into the bulb of the viscometer using a rubber squeeze bulb attached to a piece of Tygon tubing into which a small wad of cotton had been inserted. Flow times were obtained using a Haydon electronic stop clock and recorded to the nearest tenth of a second. At least five determinations were made on each solution and the average calculated.

Equation 1, which takes kinetic energy into account, was used to calculate the viscosities ($\eta_{KE}$). $A$ and $B$ are constants, $\rho$ is the solution density, and $t$ is the flow time in seconds.

$$\eta_{KE} = A\rho t - B\rho/t \qquad (1)$$

$A$ and $B$ were determined by measuring the flow times and densities of carbon tetrachloride, distilled water, benzene, and methanol and using their viscosities at 25 °C obtained from the Handbook of Chemistry.[32] The constants for each viscometer were calculated from the resulting four simultaneous equations. $A$ was the same in all cases while $B$ varied. Only the standard deviation in the flow time was used in the final calculations since those associated with $A$ and $B$ were relatively insignificant. Densities were determined using a 25-ml jacketed pycnometer after equilibration of the solution for 30 min in the constant temperature bath.

**Acknowledgment.** The very helpful comments and criticisms of Professors Linda Magid and Luis Sepulveda are gratefully acknowledged.

**Registry No.**—CTAB, 57-09-0; sodium *p*-toluenesulfonate, 657-84-1; sodium benzenesulfonate, 515-42-4; sodium *p*-toluate, 17264-54-9; sodium benzoate, 532-32-1; disodium phenyl phosphate, 3279-54-7.

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