

THE EFFECT OF SOLUBILIZATION ON COUNTER ION BINDING TO MICELLES

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Solutions of hexadecyltrimethylammonium bromide (CTAB) micelles have been used as catalysts for numerous reactions.³⁻⁶ This catalytic effect is thought to arise, at least in part, from the electrostatic stabilization of a charged transition state by the charged micellar surface.^{5,6} Since the net charge on the micelle surface is determined by the degree of counterion binding, a study of this effect is important in clarifying the role of counterions in the mechanism of micelle catalysis. Moreover, many ions that inhibit micelle catalysts also inhibit enzymes.^{7,8} Thus, micelles may prove useful as models for enzymatic systems. The purpose of this study is to investigate the effect of added organic solutes on the amount of halide bound in micelle systems of hexadecyltrimethylammonium chloride (CTACl) and bromide (CTAB). Specifically, we wished to determine whether the solubilization of an organic solute by the micelle is competitive or cooperative with counterion binding.

The physical properties of CTAB micelle systems are rather well characterized.⁹⁻¹⁹ The following observations are of particular relevance to the present study: (1) The micellar molecular weight of CTAB increases greatly upon addition of bromide ion. For example, the micellar molecular weight of 1% CTAB is 22,200.¹⁷ In 0.178 M KBr, the molecular weight has increased to 795,000.¹⁸ (2) Micelles of CTACl and CTAB, in the presence of added bromide ion, must undergo a drastic change of structure upon addition of a very small amount of certain organic solutes.⁹ For example, the addition of 0.025 M benzene to 0.1 N CTAB containing 0.1 M NaBr changes the relative viscosity from 4.9₄ to 585. The micelles increase in molecular weight and elongate in shape. (3) NMR chemical shifts indicate that nonpolar hydrocarbons and aromatics containing hydrocarbon side chains are solubilized within the micelle, while polar aromatics (e.g., benzoic acid) are solubilized on the surface.¹⁹

For this study, selected organic molecules (in a concentration range from 0.0 - 0.1 N, or

until gellation or phase separation took place) were added to CTAB alone and in the presence of bromide, chloride, or nitrate. The organic solutes were selected to (1) include examples of both "interior" and "surface" solubilized solutes; and (2) to include several solutes which markedly increase the viscosity and one example (n-hexane) of a species which has little effect on the viscosity. It will be shown that, surprisingly, the degree of counterion binding is not significantly altered by any of the organic solutes studied.

CTAB was recrystallized from carbon tetrachloride. CTACl, 50% aqueous solution, was used as received (City Chemical Corp.). All other chemicals were reagent grade and used without further purification. Small portions of the organic liquids, about 0.02 ml each, were added to 50 ml of the surfactant and salt with a 5 ml microburet. Benzoic acid was added in small weighed portions. Measurements were made up to, but not beyond the point at which phase separation occurred. Electromotive force (EMF) measurements were used to estimate the concentration of free (i.e., unbound) halide ions at 25°C. The appropriate Orion solid state ion-selective electrode and an orion double junction reference electrode (Model 90-02) were placed in the micelle system, and the EMF was measured by a Keithley microvolt null detector driving a 10 m.v. recorder. Immediately before and after a series of measurements on micelle systems, EMF values were determined for several aqueous NaCl or NaBr "standard" solutions. The free halide ion concentration in a micelle system was taken as the standard sodium halide concentration which gave the same EMF reading as the micelle system. Adopting the usual approximation that liquid junction potentials are negligible, a straightforward thermodynamic analysis²⁰ reveals that the basic assumption in our method is that the Henry's Law activity coefficient of a free halide ion at concentration C' in the micelle systems is equal to the activity coefficient of the halide ion at concentration C' in the standard. We also, of course, adopt the convention that the halide ions may be distinctly classified as either free or bound. One would not expect our procedure to be in error by more than a few percent. In fact, our value of 0.077 N (Table 1) for bound halogen in both 0.1 N CTAB and 0.1 CTACl (without added salt) is in good agreement with the literature value of 0.075 - 0.080 N.¹² Our results are compiled in Table 1. Based upon reproducibility and the assumptions in our procedure, we estimate the uncertainty in bound halide concentration at ~0.003 N.

Upon the addition of 0.1 N NaNO₃, the amount of bound bromide dropped to 0.04 N. It is interesting to note that nitrate ion increases the viscosity of the solution,⁹ and is reported to be an effective inhibitor in micelle catalyzed reactions such as ester hydrolysis where it

Table 1
The Effect of Salts and Organic Molecules on Unbound Bromide
and Chloride at 25°C

No.	Surfactant, 0.1 N	Salt, 0.1 N	Maximum Organic, N	Bound Br ⁻ or Cl ⁻ , N
1	CTAC	0	0	0.076
2	CTAB	0	0	0.077
3	CTAB	NaBr	0	0.067
4	CTAC	NaCl	0	0.082
5	CTAC	0	0.1 CCl ₄	0.076
6	CTAB	0	0.1 CCl ₄	0.077
7	CTAB	NaNO ₃	0.1 CCl ₄ *	0.040
8	CTAC	NaCl	0.03 CCl ₄ **	0.082
9	CTAB	NaBr	0.1 CCl ₄ *	0.067
10	CTAB	NaBr	0.02 C ₆ H ₅ COOH*	0.067
11	CTAB	NaBr	0.05 n-C ₆ H ₁₃ OH**	0.067
12	CTAB	NaBr	0.1 n-C ₆ H ₁₄ **	0.065

*Solution gelled.

**Solution had phase separation.

competes with hydroxide ion in the Stern layer.^{3,4} It is also reported to increase the aggregation number of micelles of dodecyltrimethylammonium bromide.²¹ Further studies of the competition between salts for the micelle have been completed and will be the subject of another paper.

It is curious that the addition of NaBr to the CTAB system results in a decrease in the amount of Br⁻ ion bound to the micelle. This effect, although small, is believed to be real. Moreover, this result seems to be independent of the nature of the added organic solute in all the solutions studied. This result can be rationalized since the addition of NaBr is known to increase the micelle size.²¹ If this results in a reduction of the charge density of the micelle decreased association should result.

The most striking feature of the data in Table 1 is that, within our experimental precision, none of the organic additives studied altered the concentration of bound halide in any of the micelle systems studied. Obviously there is no competition between the organic solute and the counterion for the micelle. This is particularly surprising in the case of benzoic acid which is thought to be solubilized at the surface of the micelle. The inhibiting effect of various anions, in particular bromide, on micelle catalysis is conventionally explained in terms of competitive binding of organic substrate and counterions.^{3,4} For example, the inhibition of

aromatic phosphate ester hydrolysis is most effectively done with added salts having large low charged anions such as arene sulfonates and bulky carboxylates.³ Inhibition increases in the order $\text{Cl}^- < \text{NO}_3^- \approx \text{Br}^- < \text{OTs}^-$.⁴ In general, our results are consistent with the inhibition order observed by Bunton, *et. al.*³ and his interpretation of it, provided that the organic substrate is an anion. We observed that added uncharged organic solutes did not alter the amount of halide ion bound to the micelle. The effect of large charged anions on bound halide is under investigation.

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