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A HIGHLY SPECIFIC EFFECT OR ORGANIC SOLUTES AT LOW CONCENTRATIONS ON THE STRUCTURE OF CTAB MICELLES

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The study of micelle catalyzed reactions is an area of increasing activity and growing interest. The effect of both electrolytes and organic molecules on the structure of micelles is an important factor in micellar catalysis. We wish to report that a variety of organic molecules present in very low concentrations can cause pronounced changes in the structure of micelles. Furthermore, this change is highly specific, depending both on the organic solute and on the electrolytes present in the system.

That changes in micelle structure can have pronounced effects on micellar catalysis has been demonstrated recently by Bunton.[3] A large effect of sodium tosylate on the structure of cetyltrimethylammonium bromide (CTAB) micelles and on the catalysis of the decarboxylation of 6-nitrobenzisoxazole-3-carboxylate has been observed. The structural change occurring is almost certainly the conversion of spherical or elipsoidal micelles to larger rod-like micelles. This structural change is detected most easily by the large increase in the viscosity of the solution caused by the rod-like micelles.

Large effects of aromatic solutes on the structure of micelles have been reported[4,5] and it has been suggested that there exists a special interaction between aromatic molecules and cationic micelles.[3,6] As is clear from the data in Table 1, such large viscosity increases are not limited to aromatic molecules, but are induced by a number of organic molecules of varying type.

Several reports on the structures of micelles of cetyltrimethylammonium bromide (CTAB) have recently appeared,[7-10] and this micelle has been used to catalyze a variety of reactions.[3,11,12] Using small angle x-ray scattering a complete study as been made of CTAB micelles as a function of soap concentration in aqueous solution.[13] At low concentrations the micelle

Table 1. Viscosity[a] of Aqueous Solutions Containing 0.1 M CTAB,[b] 0.1 M NaBr, and Added Solute at 25° Relative to Water at 25°.

Group 1			Group 2		
Solute	[Solute]	n_{rel}^{e}	Solute	[Solute]	n_{rel}
None	0.0	4.94±.01	naphthalene[c]	<0.0099	8.73± .19
n-hexane	0.0079	5.57±.03	Benzene	0.0097	19.5 ±2.8(32.2)[d]
Ethanol	0.0123	4.81±.13		0.0253	346.[d]
Sucrose	0.0087	4.88±.04	n-Hexanol	0.0088	19.2 ± .7
Ethyl Acetate	0.0061	4.90±.05		0.0290	644[d]
Acetic Acid	0.0130	4.68±.10	Benzoic Acid	0.0087	42.2 ± .3
dl-Alanine	0.0165	4.93±.09		0.0250	585.[d]
l(-)-Tyrosine	0.0020	4.63±.12	Carbon tetrachloride	0.01844	345.[d]
Urea	0.0335	4.68±.02	Chloroform	0.01579	177.[d]
			Methylene chloride	0.03179	118.[d]

[a] For all Newtonian Fluids, capillary Ostwald viscometers were used in a constant temperature bath. The measurements on non-Newtonian fluids were made with a Haake-Rotovisco and are reported at a speed of 18 rpm, rate of shear 25.3 sec^{-1}.

[b] Purified by recrystallization from CCl_4.

[c] Not complete dissolved.

[d] Non-Newtonian Liquid.

[e] Kinetic energy corrections not applied.

Table 2. Intrinsic Viscosities [n], Specific Volumes (V), and Axial Ratios (α) for Some Micellar Solutions.

Temp.	Soap	[Salt]	[Solute]	[n] (ml/g)	V(ml/g)	α[b]
25°	CTAB	----	----	11.2[a]	4.39[a]	1.0[a]
25°	CTAB	.1000	----	9.1±1.5	.995	7.5
25°	CTAB	.1000	.025 PhCOOH	828	.995	146
30°	CTAB	.178	----	15.8±0.4	.991	16.5[c]

[a] From ref. 7.

[b] Calculated assuming a rod-like micelle with the diameter of the micelle equal to twice the chain length of the soap.

[c] Lit. 18.1, ref. 10.

is spherical; it becomes rod shaped as the concentration increases. The addition of sodium bromide to solutions of n-dodecyltrimethylammonium bromide or CTAB causes the size of the micelles to increase.[14,15,16] In the presence of NaBr the micelles are apparently rod shaped. In the absence of added salt, the addition of organic solutes such as benzene increases the micelle size slightly.[17,18]

As shown by the data in Table 1, many organic solutes added to CTAB in the presence of sodium bromide have no effect on the viscosity of the solution. However, small amounts of a variety of solutes have a pronounced effect on the viscosity, indicating large changes in the structure of the micelle are occurring. In addition to aromatic molcules, both alkyl halides and alkanes can cause dramatic changes in the micelle structure. It is especially noteworthy that while both ethanol and hexane have little or no effect, n-hexanol causes a pronounced change. The nature of the electrolytes present is also of great importance and the effects are highly specific. In the absence of added sodium bromide, the effects of <u>all</u> of the solutes in Table 1 on the viscosity of CTAB solutions are small. Also, no viscosity increases were observed with cetyltrimethylammonium chloride, while the nitrate salt showed large structural changes caused by organic solutes.[19] A full discussion of these observations is deferred to a full paper.

By measuring the specific volume and intrinsic viscosity of a colloidal system, the shape of the particles can be estimated.[20] A series of solutions of varying concentrations in CTAB, also containing salt and organic solute where appropriate, were prepared. The CTAB was recrystallized from CCl_4, and the solutions prepared using deionized water, redistilled in glass apparatus. Densities of the solutions were obtained using 25 ml jacketed specific gravity bottles. The intrinsic viscosity was obtained graphically, by plotting n_{sp}/C_m vs. C_m. The relationship between specific viscosity n_{sp} and the intrinsic viscosity $[n]$ is given by $n_{sp}/C_m = [n] + \alpha C_m$. C_m is defined as $[CTAB] - [CTAB]_{Cmc}$, both in g/ml; n_{sp} is the viscosity relative to that of the system at its c.m.c., minus 1.0, i.e. $n_{sp} = n_{rel} - 1$. The relevant data are given in Table 2. The necessary Cmc values were obtained by surface tension measurements.

It is clear from the data presented here that electrolytes and a variety of organic molecules can have cooperative, high specific, and large effects on the structure of cationic micelles. A full understanding of these effects is necessary in order to understand the catalysis of organic reactions by micelles.

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