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Some Aspects through Sedimentation Study on the Extremely Elongated Micelle Formed in Cationic Surfactant-Aromatic Additive Systems

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Sedimentation studies were carried out upon systems composed of HTAB or HPB, a cationic surfactant, and several aromatic additives which were accompanied by remarkable viscoelasticity in a solution in which the existence of extremely elongated gigantic rod-like micelles was previously established by the authors as images under an electron microscope. Those elongated rod-like micelle systems appeared to be separated into two components: one showed floatation and the other sedimentation under a 6×10^4 rpm force field, providing rather pertinent values of $S_{20\omega}$ in the order of 10^{-13}s, compared with several proteins or other polymeric substances. After attaining an equilibrium state during sedimentation, the micellar particle weight was deduced to be about 1.2×10^7 amu. The obtained values seemed to be considerably smaller than those expected from the electron microscope images where the length of the rod-like micelles were assumed to be infinitely elongated. The discrepancy is likely to have been brought about by a degradation of the micelle chain under a strong centrifugal force field.

Several cationic surfactants with appropriate chain lengths, such as hexadecyltrimethylammonium bromide (HTAB) and *N*-hexadecylpyridinium bromide (HPB), when added to various aromatic substances such phenolic derivatives like iodophenol and salicylic acid or its sodium salt, form infinitely elongated rod-like micelles. The occurrence of these extremely elongated rod-like micelles has been established through electron microscope studies[1,2] by the authors for a wide variety of pairs of surfactant-additive systems.[3] A solution composed of these substances possesses a remarkable viscoelasticity in solution, which reflects an entanglement of those extremely elongated rof-like micelles with each other.

These solution behaviors aroused the interest of several investigators who investigated the solution structure etc. in more detail through many field measurements of NMR,[4] light scattering,[5] neutron scattering,[6] flow[7] and electric birefringence[8] and dynamics.[9]

The values of the micelle length, obtained through these experiments are not very great, only several thousand Å at most. These values are far smaller than those which are suggested from observations of electron micrographs.

The reasons for this discrepancy are unknown. Whether it is caused by specimens being in a dry condition for electron microscopy, or in a wet condition for other measurements in solutions, is one of the most relevant problems that needs to be urgently solved. Hence, we intended to determine the micellar particle weights and selected a sedimentation measurement technique as an alternative direct method to approach this problem. A knowledge of the micellar particle weight is also a requisite in order to disclose the solution behavior as the remarkable viscoelasticity in these systems.

Experimental

Cationic surfactants, HTAB and HPB, were commercially available and used after one recrystallization from an acetone-methanol mixture. Aromatic additive substances were all of a special pure grade and used as purchased. Measurements of the sedimentation velocity and micellar particle weight in equilibrium were achieved by using a Hitachi Seisakusho Co. centrifugal separator attached to it with a UV scanner (ABS-7, Hitachi Co) under a controlled temperature of 20 °C. All analyses of the obtained data were automatically processed by a Hitachi data analyzer DA-7 online with the above apparatus. The progress of the sedimentation was detected by the UV absorption fitted to the appropriate absorption wavelength of the additive substances. The values of specific volume, $\bar{v}$, required to estimate the micellar particle weight which referred to $M=2RT/(1-\bar{v}\rho)\omega^2\cdot \mathrm{dln}\, C/\mathrm{d}r^2$ were measured as to the sediment deposited on the bottom of a centrifugal separation cell. The sediment was filled into a Lipkin-Devison type pycnometer held at 20 °C thermostat in which the densitometry deduced the values of $\bar{v}$.

The conductance measurement relied on a conductivity meter, CM-30ET (TOA Electronics Ltd.). Values were directly obtained by using a cell equipped with a meter for reading the specific conductivity in units of $\mathrm{S\,m^{-1}}$ ($\Omega^{-1}\,\mathrm{m^{-1}}$). Measurements were always carried out for solutions thermostated at 20 °C. For a frozen-dried sample of sediments prepared beforehand, an analysis of the surfactant content was carried out by a volumetric method in which any color change of congo red, an indicator, was detected as the end point by a wolframophosphoric acid solution of a known titer.

Results and Discussion

Measurements were mainly carried out upon systems containing HTAB-iodophenols, which showed rather clearer sedimentation profiles on diagrams for any analysis (Fig. 1), whereas HTAB-salicylic acid, the most typical viscoelastic system, showed no clear profiles of sedimentation under a 6×10^4 rpm centrifugal force field for an hour or so. In Fig. 1 it is obviously shown that these systems are composed of two entities, one of which moves to the upper part and the other to

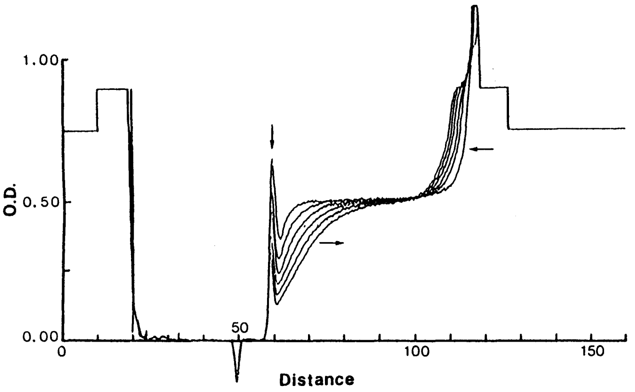

Fig. 1. Concentration traces observed for each ten minutes lapse in a system of HTAB-*o*-iodophenol under a 6×10^4 rpm centrifugal force field. HTAB concentration was 5×10^{-3} mol l^{-1} and the mixing molar ratio was unity. O. D. values were from 305 nm absorption of *o*-iodophenol. Arrows show the direction of the shift of the concentration traces with the lapse of time.

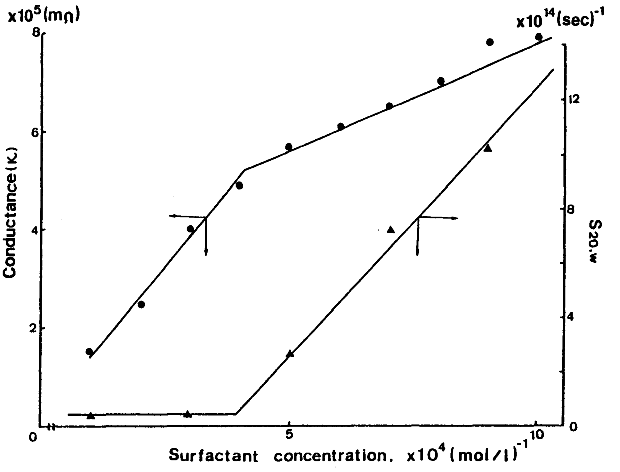

Fig. 2. The relation of conductance and $S_{20,\omega}$ vs. surfactant (CPB) concentration.

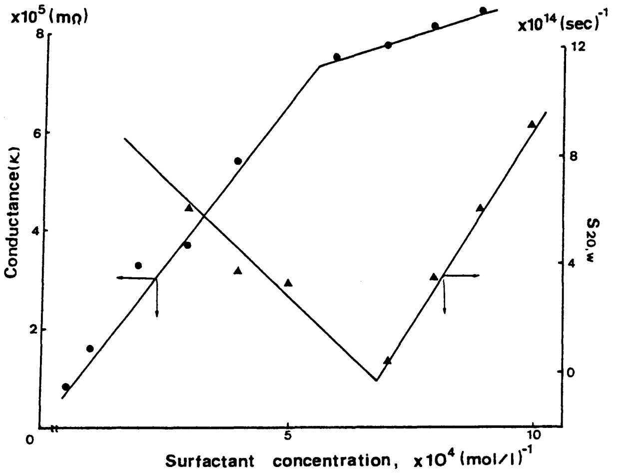

Fig. 3. The relation of conductance and $S_{20,\omega}$ vs. surfactant (CTAB) concentration.

the bottom side of a cell as time passes. The sedimentation coefficients, $S_{20\omega}$, obtained from each separated part in several systems, are summarized in Table 1; values having either a plus or minus sign show the sedimentation or the floatation, respectively. In ionic surfactants such values as $S_{20\omega}$, which indirectly suggest a state of surfactant aggregation, are sensitively affected by any surface charge. In order to avoid those effects arising from an electric charge which cause interactions between micellar particles, a supporting electrolyte is generally added to the systems to be studied. However, in our systems a special electrolyte was not added at all so as not to cause any inevitable changes in the aggregation states (shapes, degrees, or numbers etc.) due to the electrolyte added. Because viscoelastic extremely elongated gigantic micelles are also very sensitive to the coexistence of any other substance, such as electrolytes. The values of $S_{20\omega}$ appear, however, to fit the generally accepted magnitude, nearly of 10^{-13} s,[11] in their order.

In each system of HPB- and HTAB-*o*-iodophenol the dependence of $S_{20\omega}$ on the surfactant concentrations are shown in Figs. 2 and 3, respectively, in which the conductance behaviors are also exhibited in order to show the distinct relation of $S_{20\omega}$ or κ to the surfactant concentration. As is common knowledge, a conductivity measurement is one of the most reliable methods for estimating the cmc of any surfactant, which is represented as a sharp break point in a κ vs. concentration diagram. In both systems the curves of

Table 1. $S_{20,\mathrm{w}}$ Values of Several Surfactant/Additive Systems

System surfactant/additive[a]	Concentration mol l^{-1}	$S_{20,\mathrm{w}}$/s	
HTAB/*o*-iodophenol	1×10^{-3}	1.01×10^{-13}	-2.76×10^{-14}
	5×10^{-3}	1.13×10^{-13}	-5.47×10^{-14}
	1×10^{-2}	1.99×10^{-13}	
HTAB/*p*-iodophenol	5×10^{-3}	1.01×10^{-13}	-2.84×10^{-14}
	1×10^{-2}	1.89×10^{-13}	
HTAB/salicylic acid	1×10^{-3}		-2.16×10^{-13}
HTAB/sodium salicylate	1×10^{-2}	0.13×10^{-13}	
HTAB/sodium biphthalate	1×10^{-2}		-0.03×10^{-13}
HPB/*o*-iodophenol	5×10^{-3}	1.04×10^{-13}	-1.34×10^{-13}

a) Mixing molar ratios of each surfactant/additive systems are equal to unity.

conductance vs. surfactant concentration had clear break points which were assumed to be the cmc's of each surfactant-additive system, above which concentration the micelles were formed in those composed solutions. The values of the composed systems were a little smaller, but in good coincidence, compared with those for each single surfactant system of HPB[12] and HTAB[13] reported hitherto. Some lack of uniformity concerning $S_{20\omega}$ values was found over the low concentration range in an HTAB-*o*-iodophenol system, whereas no lack in HPB-*o*-iodophenol; this seems to be due to a difficulty in the appraisal of the sedimentation distance on a diagram of the former system necessary to determine the $S_{20\omega}$ value. Thus, we were provided with a good correspondence of aggregation states with $S_{20\omega}$ under a support of gradual increase of the micellar weight with an increase in the surfactant concentration above cmc, though it is imposed with several assumptions that micelle structure, say its form and density etc., is left unchanged during micelle growth. The same behavior of succeeding aggregation with an increase in the surfactant concentration in those viscoelastic systems has been reported by some investigators in various studies.[9,14]

The results of an analysis on the sediments deposited at the cell bottom under a 6×10^4 rpm centrifugal force for 1 h are presented in Table 2. It should be noted that the above-mentioned sediments do not refer to some crystalline or other materials. The sediments gathered at cell bottom were, of course, clear and appeared something like jelly in a test tube, being kept without flowing down in its up-side-down state. The sediments were a little enriched in iodophenol compared with those of the initial component ratio, increasing with an increase in the molar ratio of the surfactant/iodophenol until a level off at a ratio of 1.0. The values, however, suggest that in those systems the elongated micelles comprise two components of surfactant and iodophenol in a nearly unity composition at optimum states. This idea has been supported from many facts: e.g. the viscoelasticity[3,15] is most remarkably induced at a mixing molar ratio of unity with both components.

Table 2. Analyses of Sediments of HTAB/*o*-Iodophenol Systems

Original mixing molar ratio (HTAB/*o*-iodophenol)	HTAB	*o*-Iodophenol	Assayed value in molar ratio of HTAB/*o*-iodophenol
	weight %[a]	weight %[a]	
1/0.5	73.2	26.8	1/0.6
1/1	57.7	42.3	1/1.2
1/2	56.8	43.2	1/1.3

a) Water contents of the sediments were nearly the same to be given as averaged 97.1% in weight, values shown were referred to the frozen-dried samples as total materials.

In addition to the analyses of sediments, the densities of the sediments were measured by using a Lipkin-Devison type pycnometer, being determined at 20 °C to be 1.0035 $cm^{-3}g^{-1}$ for HTAB-iodophenol system referred to water at 20 °C. In our systems composed of HTAB or HPB and aromatics such as iodophenol, the values appeared to be much smaller compared with those of single surfactants reported concerning their micellar form, though the available data were very few, especially regarding cationics.

Studies of sedimentation equilibrium based on the Archibald method provided the particle weight of the elongated rod-like micelle by introducing the above obtained specific volume of the sedimentating micellar particle. An equilibrium state for those micellar systems was presumed to be attained after 30 h operation of the apparatus under 6000 rpm force. An averaged value of the micellar particle weight in several times trials resulted in 1.2×10^7 amu; this seemed to be very much smaller than that expected from the electron microscopic images.

It seems that there's no decisive conclusion about the variation of micellization under a centrifugal force field, especially in an electrically perturbed state of ionic surfactants: various effects concerning the concentration gradient on the micellar size, structure and/or a shift of aggregation equilibrium. While in our systems of HTAB- or HPB-aromatic additives, which provide an extremely elongated gigantic micelle, the circumstances are presumably very much similar to those explained by the concept of the Phase Separation Model. In other words, in the Mass Action Law Model or the Mutiple Equilibrium Model, the gigantic micelles are very stable and almost undissociable in solution: that is, equilibrium deviates extremely to the side of gigantic micelle formation having a large equilibrium constant. It cannot easily be moved to produce shorter, smaller aggregates or to be dissociated to single surfactant molecules with only a little change in the micellar and monomer concentrations. A smooth shift of the concentration traces (Fig. 1) with the centrifugation time lapses seems to prove this view point to be reasonable.

The apparent discrepancies between the obtained values and the expected one from the electron microscopic images might be due to some degradation effect of a long micellar chain into smaller fragments under a strong force field. Those micellar chains of infinite length are evidently in firmly entangled states, also as shown in the electron micrographs.[3] They can form a gigantic tight network structure all over the whole system. We were not able to obtain a sedimentation profile in HTAB-salicylic acid systems which showed the most typical viscoelastic behavior with some gel-like appearance. These micellar chains of HTAB-salicylic acid system seem to form too firm a frame-work in structure to suffer from fragmentation. The elongated micellar chain in a HTAB-iodophenol system is perhaps easier than the micellar chain of HTAB–salicylic acid to be broken into fragments to become shorter chains of which micellar particle weight might be so reasonably decreased, as has been obtained as the above value. In electron micrographs the thickness of the micellar chain was evidently different from each other between these two systems, it being thinner in HTAB–iodophenol than in HTAB–salicylic acid.[3)] The experimental fact support the result of sedimentation.

At any rate, the value was, however, not so much different from those which had been reported by several authors concerning several analogous viscoelastic systems by many different method.[4,13)] Moreover, it was approximately one order larger compared with values[16)] measured in these cationic surfactant systems added with a simple salt, such as NaBr etc. The particle weight obtained here implies that the micellar chain has a length of about 1710 nm from the following consideration and results based on a treatment[17)] of a contour length estimation etc.: A rod-like micellar chain is cylindrically constructed by surfactant molecules accompanied by phenolic derivatives as ionic counterparts in about a one-to-one ratio, which are arranged with a hydrocarbon core surrounded by hydrophilic groups. The cylindrical micelle is assumed to be a stack of thin elementary discs composed of fewer surfactant molecules than twenty in a disc.[16)] The molecular weight of the thin elementary disc is nearly 7×10^3 nm^{-1}, it being postulated that the additives are localized only at a micelle surface. Through this consideration, therefore, the stacking number of discs can be deduced to about 1940 by dividing the averaged micellar chain molecular weight by the elementary disc molecular weight; the micellar chain length can subsequently be derived, as described above, to be about 17100 Å through an appraisal of the disc thickness to be ca. 9 Å.[16)]

Whether such a length of micellar chain is suitable for explaining the viscoelastic solution behavior is now yet ambiguous because of insufficiency of directly comparable data of both in qualities and in quantities. We are undertaking a more reasonable elucidation of the viscoelastic solution behavior, which might be reflected by the micellar structure etc. through more extensive and detailed data.

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