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A Complex Generated in a Cationic Surfactant-Aromatic Additive System

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Aqueous binary solutions of hexadecyltrimethylammonium bromide (HTAB) and *o*-iodophenol (OIPh) exhibit remarkable viscoelasticity. From the centrifuged sediment of such a solution a *crystalline* product was isolated on long standing. Elementary analysis of the *crystals* for C, H, and N gave an estimated composition consistent with a one-to-one molar ratio of the two substances. Comparisons with DSC and IR measurements on the *crystal* and equimolar mechanical mixtures suggested that a *crystalline* complex was formed characterized by low thermal stability.

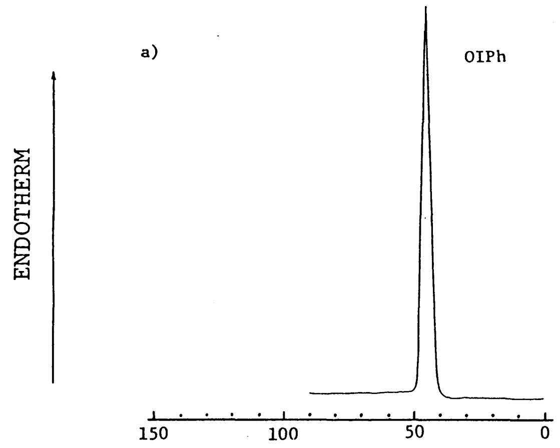
By electron microscopy we have recently identified elongated rod like micelles in several cationic surfactants such as HTAB or *N*-hexadecylpyridinium bromide on treatment with some aromatic derivatives.[1-3] These solutions often exhibit high viscoelasticity and spinnability. We have established that the viscoelasticity in solution arises from a cobweb-like entanglement of the elongated rod shaped micelles.[3]

Other investigators accumulated informations about the cause of the solution behaviors over the extensive areas,[4,5] but little is yet known about the condition suitable for the generation of such gigantic micelles in solution containing quaternary ammonium cationic surfactants and aromatic compounds, though there has been speculation about the interactions taking place in such systems.[6]

In the sediment centrifuged from HTAB/OIPh aqueous solutions after long standing we have isolated a *crystalline* product. This material exhibits strong viscoelasticity and spinnability when dissolved in water and appeared to be a complex of HTAB and OIPh. Elementary analysis, differential scanning calorimetry (DSC) and infrared spectroscopy (IR) of the *crystals* have been carried out.

Results and Discussion

The *crystals* are prismatic with average size about 1 mm×3mm. They exhibt lateral cleavage streaks and a granular structure.



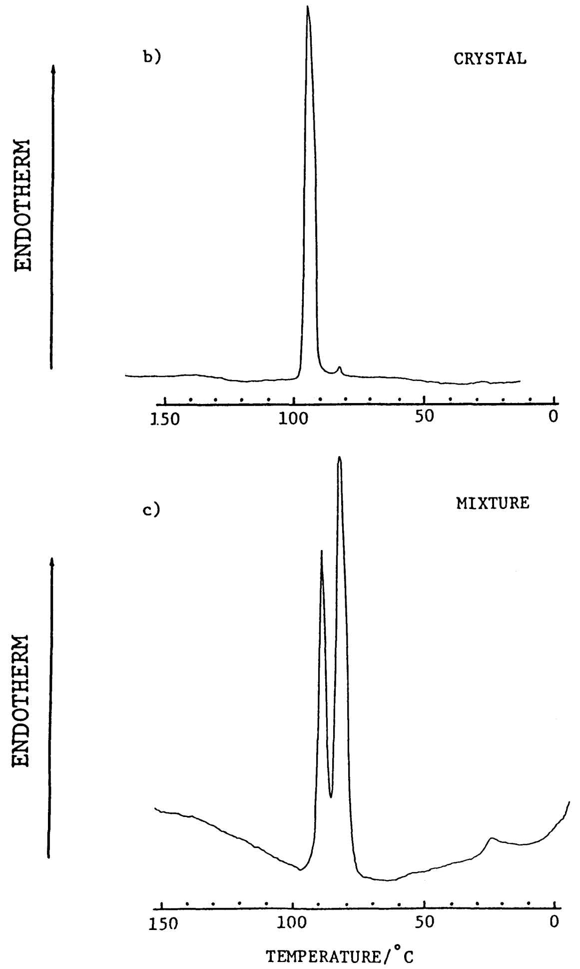


Fig. 1. The thermogram in DSC of a) OIPh, b) *crystal*, and c) the mechanical mixture of one-to-one molar ratio of HTAB and OIPh.

Table 1. The Results of the Elementary Analysis of the *Crystal* Obtained from the Sediment Solution of the HTAB/OIPh System

	Content	
	Observed	Calculated[a]
C (%)	51.28	51.37
H (%)	8.10	8.05
N (%)	2.48	2.40

a) The values are those which supposed to be composed of HTAB and OIPh in the molar ratio of unity.

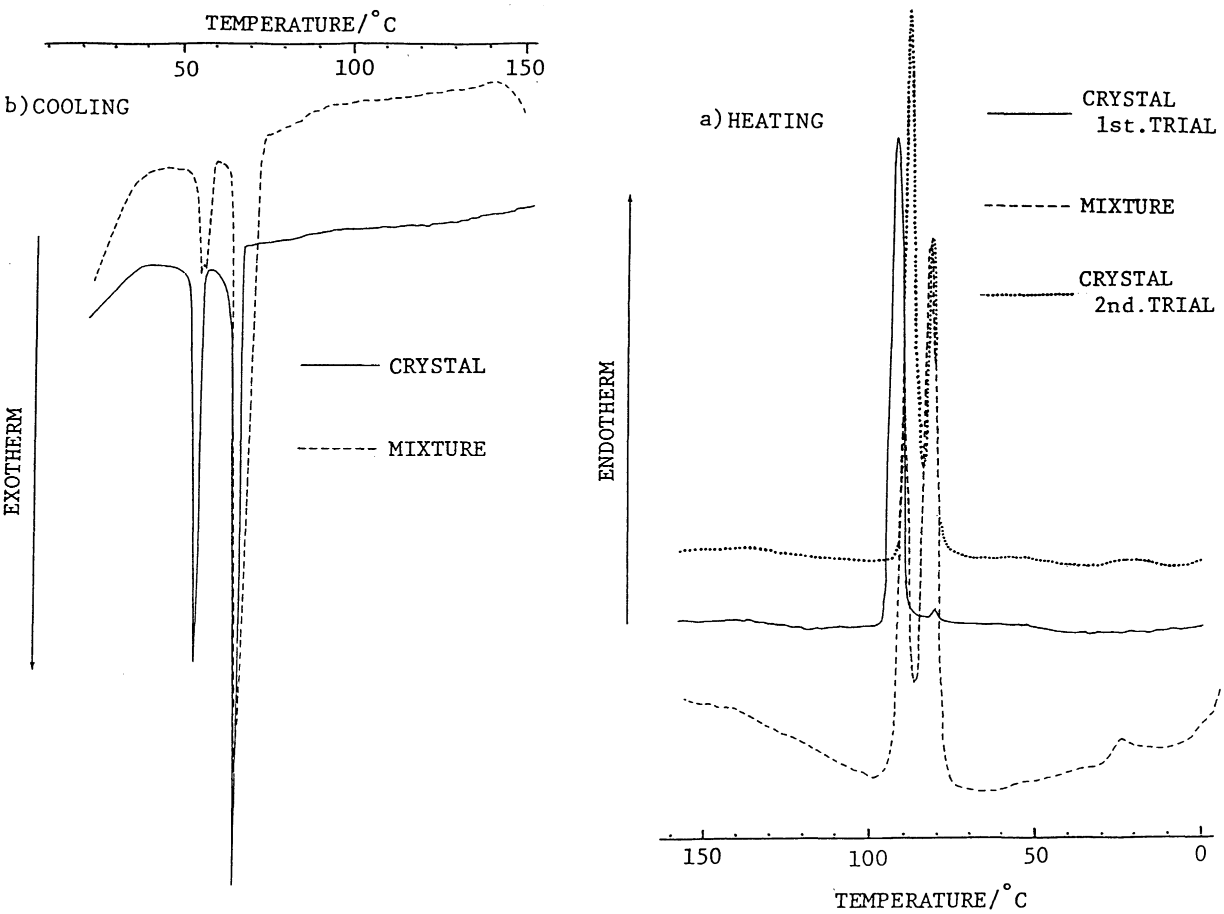


Fig. 2. The thermograms in DSC of the *crystal* and the mechanical mixture in one-to-one molar ratio, a) a comparison of the profiles in the repeated trial upon the first heating of the *crystal* with the second one and with the profile of the mixture. In the mixture the profile was not changed depending on the repetition, b) a comparison of the cooling profile of the *crystal* with that of the mechanical mixture.

Elementary analyses of the washed and dried material for C, H, and N are given in Table 1. These are in good accord with the values expected for each component and suggest a one-to-one molar complex formation. From the elementary analysis some anticipation of containing water hydrated was denied after a treatment of a one overnight drying before analysis. But it appeared for the *crystals* to occlude some water in the initial stage of having just been taken out of the sediment solution, because the *crystals* decreased their weight by about 20% during a one ovenight evacuation at room temperature. The fact was also supported in the thermal analyses (see below).

Microscopic examination at ×40 of a small *crystal* immersed in water showed a swollen profile domain surrounding the *crystal.* On touching the swollen region with a needle tip the region changed abruptly to a heavy viscoelastic solution. This observation seems to be very important to deduce the molecular weight of the *crystalline* species and the relation of the solution behaviors to the gigantic micellar figures observed in the electron micrographs.

In Fig. 1 the DSC's of the *crystals* and the equimolar simple mechanical mixtures of the single component constituents are compared. In this respect the behavior of the *crystal* and the equimolar mixture both differ from each other, i.e. OIPh only shows a characteristic endotherm at 42.3 °C corresponding to its solid to liquid phase transition. HTAB was assumed to have a very high temperature transition near 235—237 °C.7)

All thermal behaviors can be compared with the observations under a polarizing microscope. The single endotherm of the *crystal* at 94.5 °C corresponds to a solid-smectic phase change observed as the disappearance of the sharp crystal edge seen under the microscope. The as yet uncharacterized smectic phase persists to considerably higher temperatures in accord with that no other peaks are observed in the DSC above 94.5 °C. Microscope image changes are also observed at temperatures consistent with the endothermal peaks in the DSC diagrams. Judged from their fluidity the phase transitions would appear to be due to smectic changes.

On subsequent cyclic thermal changes the endothermal peak profile of the *crystal* separated into a doublet at 83.0 °C and 88.0 °C (Fig. 2a) after the first cycle, but subsequent cycles produced no further change. In the cooling stage the exothermal profile for the *crystal* was identical with that of the equimolar mixture. (Fig. 2b) This would suggest that there is a thermally induced dissociation of the complex. On the contrary, on a second heating cycle of the mixture changes occur in the thermogram which approaches that of the *crystal*. No restoration of the initial peak profile of the *crystal* DSC may also be explained by the fact that the *crystal* is a high molecular weight entity which would be difficult to restore the original crystal lattice during such a rapid cooling. From this we infer that the HTAB/OIPh *crystalline* complex has an equilibrium point towards the components. In reversal a system of components readily deviates to the complex side.

Some effects of moisture are observed in the thermogram of the *crystal*. After several DSC cycles a specimen left overnight in moist air exhibited other peaks in the low temperature region (Fig. 3). These can be attributed to water retained in the crystal lattice. Exposure to moisture increased the *crystal* weight by about 1% and restored the initial state after several DSC cycles with decrease of those peaks of the moisture origin. This suggests that the HTAB/OIPh complex can accomodate some water of hydration.

Figure 4 shows the IR spectra of the *crystal* and the equimolar mixture. There are significant differences between 1400 and 700 cm^{-1} due to additional bands in

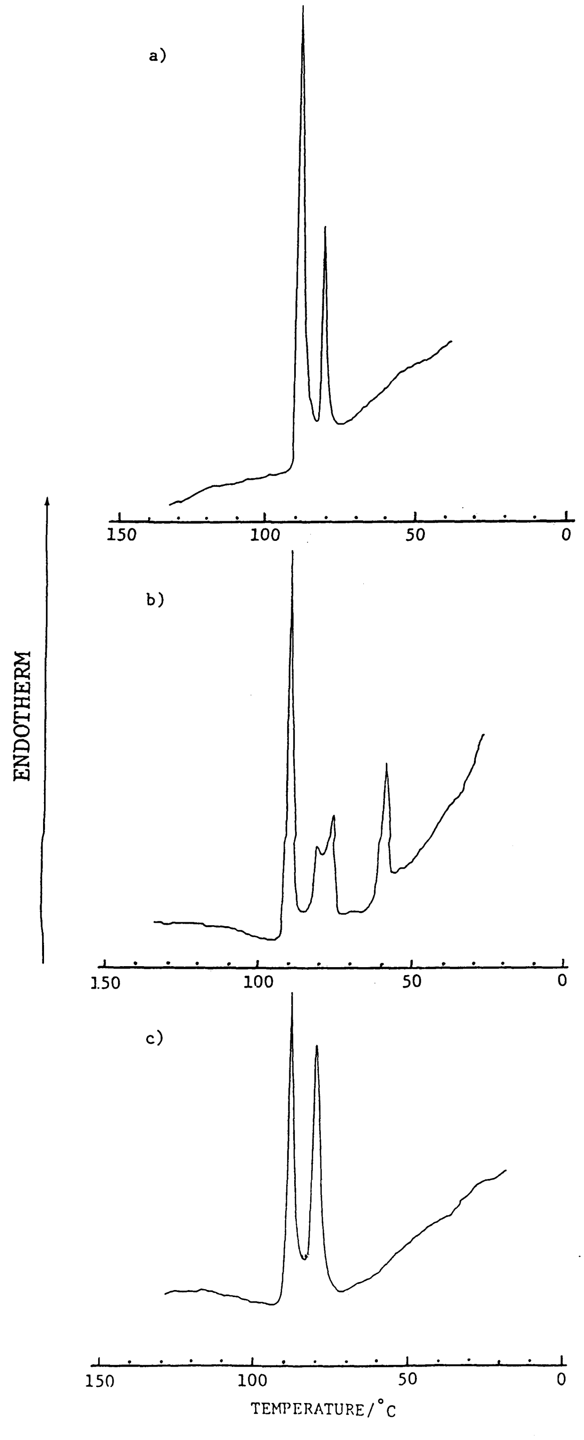


Fig. 3. The effect of the water hydrated on the *crystal* DSC, a) before moistened after several repeated trials, b) one-over-night moistened specimen, and c) after the second trial of the moistened specimen. In the succesive trials the profiles were almost not changed any more.

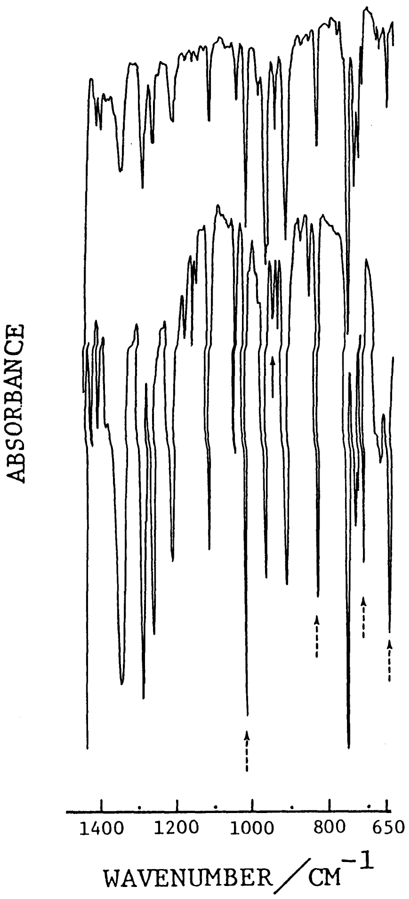


Fig. 4. The IR absorption spectra of the *crystal* (below) and the mechanical mixture in one-to-one molar ratio (above). ↑ shows a newly splitted doublet band, observed in the *crystal*, from a singlet band of the mechanical mixture. ⇡ shows the remarkably increased bands in the *crystal* compared with those of the mechanical mixture.

the spectrum of the *crystal*. There are also some notable intensity reversals. New bands occur at 931 cm^{-1} and 938 cm^{-1}; these would appear to result from a splitting of the 938 cm^{-1} band. Intensity reversals are noted in four regions (Fig. 4). These would appear to involve a nearly 4-fold enhancement in the intensity for the *crystal*. From these we infer that there are changes on the skeletal motions of the benzene nucleus of OIPh. This may be associated with a difference of the surrounding field in the *crystal* and the equimolar mixture.

From these differences in the DSC's and IR spectra of the *crystal* and the equimolar mixture we may deduce that the interactions between the aromatic and quaternary ammonium groups is not very great and that the complex formation and dissociation can easily be induced by heat.

X-Ray analysis of the *crystalline* species is currently in progress revealing the crystal structure is $Pnn2$ orthorhombic with lattice constants a=8.722 Å, b=39.954 Å, c=8.404 Å, $\alpha=\beta=\gamma=90°$ with a unit cell volume of V=2928.6 $Å^3$. Some structural aspects of the *crystal* have also been known.[8] Further work is under way to refine these data to ascertain the exact structure of the complex *crystal* with particular consideration to the interaction of the materials, the large elongated micelle structure and the behavior of the solutions.

We are indebted for the elementary analysis to the members of the Assay Laboratory of the Protein Research Institute of Osaka University.

Experimental

HTAB was used after one recrystallization of commercially available material from an acetone-methanol mixture. OIPh was of pure reagent grade, used as purchased. The sediment solutions of HTAB/OIPh were obtained by centrifugal separation at 60000 rpm for 1 h. using a Hitachi SPC85H centrifuge. The DSC measurements were carried out using a Rigaku Denki Co. Low Temperature Differential Scanning Calorimeter. Since the profile shift of the thermogram was considerable in repeated runs, especially following the initial heating, the cycles were always repeated on a way of a heating-after-cooling cycle. The rate of temperature scan was maintained at 10 $K\,m^{-1}$ in both directions. IR measurements were made on a Hitachi 260-10 Infrared Spectrometer. The spectra were measured as KBr disks.

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