

THERMALLY-INDUCED TRANSITION IN AQUEOUS SOLUTION OF CATIONIC SURFACTANT CONTAINING AROMATIC RING

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Abstract

Heat capacities of aqueous solutions of cetyltrimethylammonium (CTA) salicylate, of CTA *m*-hydroxybenzoate and of CTA *p*-hydroxybenzoate were measured using a scanning microcalorimeter. Only the salicylate solution exhibited heat-capacity anomaly around 330 K, depending on the heating rate. The transition enthalpy was $3.5 \pm 0.2 \text{ kJ mol}^{-1}$, which was similar to that observed in solution of 1:1 intermolecular compound between CTA bromide (CTAB) and *o*-iodophenol (OIPh). The enthalpy of formation ΔH_f of the 1:1 intermolecular compound from CTAB and OIPh was determined by measuring the enthalpies of solution of the relevant crystals into ethanol. Positive value $\Delta_f H = 3.0 \pm 0.3 \text{ kJ mol}^{-1}$ was explained from a large difference between the heat capacities of the 1:1 compound and 1:1 mixture of the component crystals.

Keywords: enthalpy of formation, intermolecular compound, rod-like micelles, surfactant with additive, thermal transition

Introduction

It is well known that surfactant molecules in aqueous media form micelles at the region of what is called the critical micelle concentration, accompanying striking changes in various properties of the solution. With increasing surfactant concentration the micelles undergo a special set of structural transitions, transforming from a spherical into cylindrical and other shapes [1]. However, aqueous solutions of these surfactants usually behave as a Newtonian fluid.

The change in micellar structure can also be induced by adding some solutes to the solution [2]. The effect of solute on the solution properties depends strongly on the nature and concentration of the solute. The addition of some phenol derivatives to cationic surfactant is particularly interesting, because the additives sometimes induce spectacular changes in micellar structure giving rise to significant viscoelastic-

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ity characteristic of polymer solutions. Cetyltrimethylammonium bromide (CTAB) mixed with *o*-iodophenol (OIPh) provides a typical example, in which both the components are known to form 1:1 intermolecular compound [3]. Aqueous solution of the compound at room temperature is found to form gigantic rod-like micelles, as revealed by an electron microscope [4]. The solution was found to change its flow property on warming over a narrow temperature range around 330 K with a significant heat-capacity anomaly [5]. Similar situation can be expected for cetyltrimethylammonium salicylate (CTASAL), in which counter part of the cationic CTA^+ is *o*-hydroxybenzoate ion, as well as CTA *m*-(CTAMHB) and *p*-hydroxybenzoate (CTAPHB). A differential scanning microcalorimeter was used to detect a possible heat effect associated with the fluidity change in these aqueous solutions.

As a first step to understand the nature of intramolecular interaction, the enthalpy of formation of the 1:1 intermolecular compound from CTAB and OIPh crystals in the solid state was determined from measurements of the enthalpies of solution of the relevant crystals into ethanol at 298.15 K. The measurement of the enthalpy of solution was done using an LKB solution calorimeter. Molar heat capacities of CTAB, OIPh and the 1:1 compound were measured by using a Perkin Elmer DSC 7 in the temperature range between 260 and 305 K.

Experimental

CTAB and *o*-iodophenol purchased from Merck were purified by recrystallization from a methanol/acetone mixture solvent, respectively. The 1:1 intermolecular compound between them was newly prepared. An equimolar mixture of both crystals was dissolved into a hot water and kept at 330 K for a moment. The homogenized solution was cooled slowly and kept at room temperature until fairly long crystals were separated out. The composition of the crystals were examined by elementary analysis. In order to determine precisely the molar ratio between Br and I atoms, thermogravimetric measurement was carried out using Rigaku DTA-TG TAS300 system. This is because only OIPh crystal evaporates off from the 1:1 compound at temperatures as high as 330 K.

The samples of CTASAL, CTAMHB and CTAPHB were supplied through the courtesy of Hirata. Each sample was prepared by the reaction of CTAB and *o*-, *m*-, or *p*-hydroxybenzoic acid in aqueous solution, respectively. The obtained crystals were purified by recrystallization and washing well with cold water until Br^- ions are unable to detect by addition of silver ions. The sample crystals were dried over silica gel in a desiccator separately. Aqueous solution of each sample of about 6 mmol kg^{-1} concentration was prepared gravimetrically for the calorimetric measurement by use of a high-sensitive microcalorimeter DASM-4. The solution of CTASAL exhibited a remarkable viscoelasticity even in this dilute solution. The heating curves were recorded one week after the preparation of solutions with occasional stirring for the equilibration.

Enthalpy of solution was measured by using an LKB 8700 precision solution calorimeter with a modification for temperature measurement. The calorimetric ves-

sel is enclosed in a metal jacket and immersed in a thermostatted bath controllable within ± 1 mK. The vessel of 100 cm^3 capacity is equipped with a thermistor for temperature measurement, a heater for electric calibration, and a stirrer with a holder for glass-ampoule of 1 cm^3 capacity. The resistance of the thermometer has been measured hitherto manually in conjunction with a built-in Wheatstone bridge. Owing to the high-sensitive value $d\Omega/dT$ of the thermometer (roughly $40\ \Omega\ \text{K}^{-1}$ at $298.15\ \text{K}$), the resistance changes rapidly during a reaction as well as a heating period. This situation makes difficult to measure frequently the resistance value during these periods. The Wheatstone bridge was replaced by a digital multimeter (Keithley 2010). Ten readings of the resistance value collected during 1 s were smoothed and the average value was fed into a personal computer every 10 s. In this way, manual operation for the temperature measurement was fully automated without loss of precision (within $\pm 4\ \text{m}\Omega$ or equivalently $\pm 0.1\ \text{mK}$).

Microscopic observation was carried out with a polarizing microscope (Olympus BHA 751-P) equipped with a hot stage (Union Optics CMS-2), whose temperature was controlled within $\pm 2\ \text{K}$. Molar heat capacities of CTAB, OIPh and the 1:1 compound were measured by Perkin Elmer DSC 7 with a low-temperature mode. The temperature scale and the heat effect were calibrated by use of standard reference materials including cyclohexane, water, benzoic acid and indium. The heat capacity data are believed to be reliable with inaccuracy of $\pm 2\%$.

Results and discussion

The results for the heat-capacity measurement of CTASAL aqueous solution with a concentration of $6.594\ \text{mmol kg}^{-1}$ are drawn in Fig. 1, along with the results for aqueous solution of CTAB:OIPh 1:1 compound [5] with a concentration of $14.13\ \text{mmol kg}^{-1}$ for the sake of comparison. The curves give the specific heat capacity c_p of the solution referred to that of pure water. Only the uppermost curve has correct scale for the differential heat capacity. The ordinate for the remaining curves is shifted downwards by $0.12\ \text{J K}^{-1}\text{g}^{-1}$ step by step for the sake of clarity. As expected, a fairly large heat-capacity peak appeared in the CTASAL solution at temperature in the range between 330 and 350 K, depending strongly on the heating rate employed in the range 0.25 and $2\ \text{K min}^{-1}$.

The effect of heating rate on the peak temperature for the excess heat capacity is drawn in Fig. 2. The full line is only a guide for eyes. We have no idea about the functional form of this dependence and the number of data points are too small to carry out the least-squares' fitting. It is surprising to see how the peak temperature of the excess heat capacity depends on the scanning rate even in the slow heating regime. This kind of sluggish transition can be observed in some solid-solid phase transitions arising from kinetic hindrance for nucleation and growth of a new phase, but probably not in polymer solutions arising from conformational changes of dissolved species. The transition in a synthetic polypeptide poly (ϵ -carbobenzyl-*L*-lysine) due to a helix-coil transition of the main chain takes place almost reversibly [6].

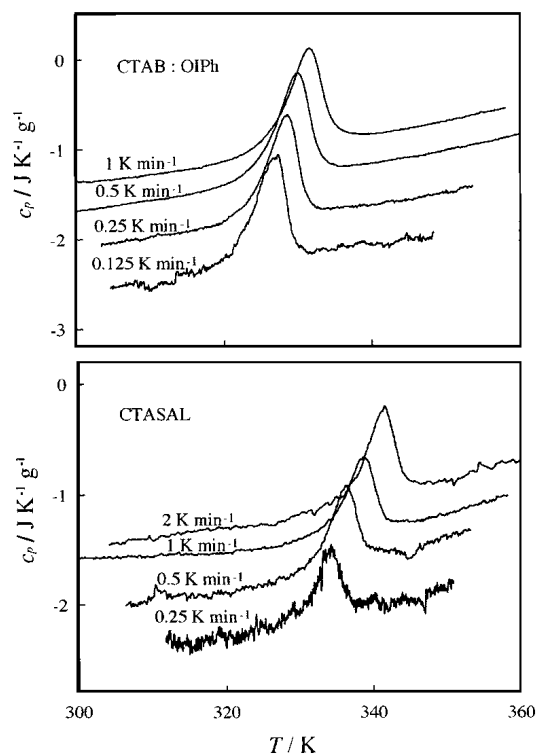


Fig. 1 Specific heat capacity of aqueous solution of CTASAL and CTAB:OIPh as a function of temperature

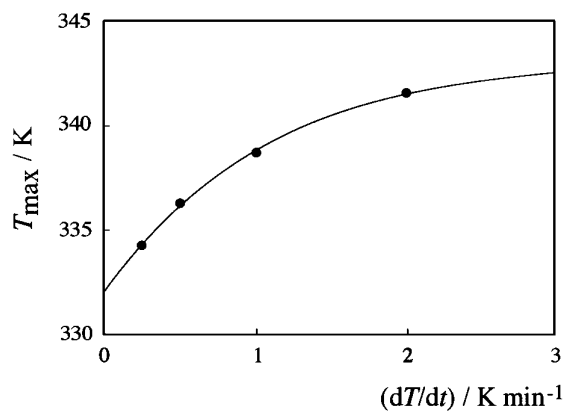


Fig. 2 Temperature for heat-capacity maximum T_{max} associated with thermal transition of CTASAL solution as a function of heating rate

The reversible nature is similar in thermal transition of schizophyllan solution due to changes in orientations of side chains attached to the backbone of triply helical structure [7]. The sluggish nature of the transition in the present solutions will be associated with a very high polymeric nature of the rod-like micelles. The entropy-decreasing process for recovering the initial rod-like micelles will require obviously much longer time. The longer the retaining time of the solution at room temperature, the larger the enthalpy change for the subsequent heating run. In fact, almost one month was necessary to obtain the saturated value for the thermally-induced transition in the case of the solution of CTAB:OIPh 1:1 compound [5].

The saturated value of the enthalpy change associated with the transition was $3.8 \pm 0.2 \text{ kJ mol}^{-1}$ for CTASAL and $3.5 \pm 0.2 \text{ kJ mol}^{-1}$ for the 1:1 CTAB-OIPh compound. The results are summarized in Table 1 along with the peak temperature for the excess heat capacity. The fairly large uncertainty in the determination of the enthalpy change arises mainly from difficulty of estimating their base lines, particularly for the slow heating rate. Since the solutions above the transition region exhibit normal Newtonian behavior, they are considered to be composed of spherical micelles. Kalus *et al.* [8] have proposed a structural model for the gigantic rod-like micelle of cetylpyridinium salicylate based on a neutron diffraction experiment. In their model, salicylate ions are intercalated between the pyridinium rings at the periphery of the micelle with its plane perpendicular to the rod direction. In such spatial arrangements, $\pi - \pi$ interaction among the benzene rings will be an important ingredient of the intramicellar forces along the cylindrical axis.

Table 1 Thermodynamic quantities associated with thermal transition of CTASAL and CTAB:OIPh aqueous solutions

$(dT/dt)/\text{K min}^{-1}$	T_{max}/K	$\Delta_{\text{trs}}H/\text{kJ mol}^{-1}$
CTASAL (1 week storage)		
0.25	337.27	3.8 ± 0.2
0.50	336.28	3.8 ± 0.2
1.00	338.71	3.9 ± 0.2
2.00	341.55	3.7 ± 0.2
CTAB:OIPh (1 month storage)		
0.25	328.5	3.5 ± 0.2
0.50	333.0	3.6 ± 0.2
1.00	331.3	3.4 ± 0.2

Thus we can propose a model for a possible change in micellar structure in these solutions, as shown schematically in Fig. 3. At room temperatures, the aqueous solutions behave like a polymer solution by forming multimolecular aggregates of highly polymeric nature. At high temperatures, they behave like a solution containing small solute entities. It is important to note, however, that aqueous solution of

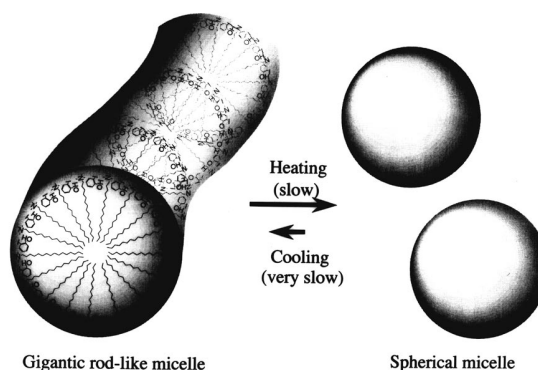


Fig. 3 Possible model of change in micellar structure at thermally-induced transition

CTA *m*- or *p*-hydroxybenzoate does exhibit neither viscoelastic property at room temperature nor the thermally-induced transition on warming. The heat capacity curve for CTAMHB is given in Fig. 4. In this way, subtle difference in their steric hindrance of the substituent groups are considered to affect seriously the stability of the gigantic rod-like micelles. As has been suggested by Israelachivili *et al.* [9], geometrical constraint is one of the determining factor in self-assembly problem. Relative orientations of respective counterions in their micelles are, however, not clear at the present moment.

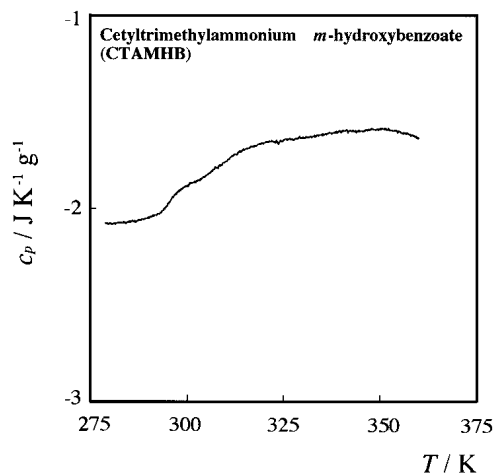


Fig. 4 Specific heat capacity of aqueous solution of CTAMHB as a function of temperature

As a first step to understand the intramicellar interactions, the enthalpy of formation of the 1:1 intermolecular compound from CTAB and OIPh crystals in the solid state was determined through the measurements of the enthalpy of solution of the relevant crystals into a common solvent. Water is not suitable for the purpose, be-

cause OIPh is almost insoluble. Also growth of the gigantic micelles will be followed immediately after the solution process of CTAB:OIPh crystal in water. After several trying, ethanol was chosen ultimately as a common good solvent.

Before the measurements, sample characterization is unavoidable. Table 2 lists the result of elemental analysis of the present 1:1 compound. Total amount of Br and I was determined by the chemical method. The ratio between them, Br/I, was determined by a separate TG analysis, since OIPh component is able to evaporate off from the compound when it is kept at temperatures around 330 K. From the change in mass of the initial sample, the ratio Br/I was determined to be 1:1.002. Thus the composition of the 1:1 compound can be regarded as satisfactory. The thermogravimetric method has demonstrated its effectiveness in quantitative determination of the molar ratio if one of the component crystals is volatile.

Table 2 Results of elementary analysis of 1:1 compound

Element	Amount	
	observed/%	calculated/%
C	51.37	51.38
H	8.07	8.11
N	2.38	2.40
X(Br+I)	35.26	35.38

The 1:1 compound was reported to transform at 368 K into a smectic phase [3]. Careful examination of the crystal by DSC and polarizing microscope clarified, however, that the crystal exhibits an incongruent melting at 368 K, giving rise to a mixture of optically isotropic solution and anisotropic solid. As OIPh component progressively evaporates from the system, the remaining solid part was found to be

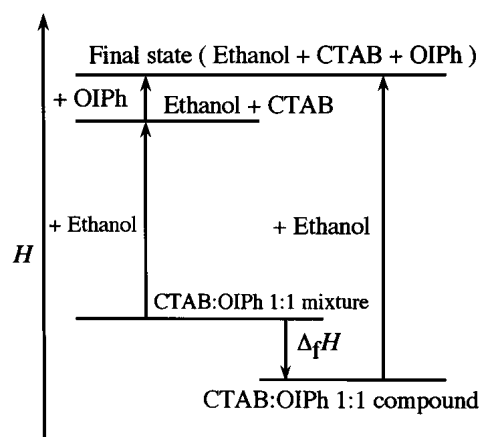


Fig. 5 Schematic energy diagram in relation to the formation of 1:1 compound from CTAB and OIPh crystals in the solid state

a new intermolecular compound with the composition of 2:1. A polarizing-microscopic photograph showed that the 2:1 compound had really a smectic-like texture.

The principle of the experimental determination for the enthalpy of formation of the 1:1 compound from the component crystals is as follows. About 1 mmol of CTAB crystal is dissolved into ethanol at 298.15 K, and then the same amount of OIPh crystal is added to the solution. The same solution can be prepared independently by dissolving the same amount of the 1:1 compound into the same solvent. The heat effect associated with each process can be measured by using a solution calorimeter. The difference in enthalpies between the former and the latter processes gives directly the enthalpy of formation of the compound in the solid state. The principle is drawn in Fig. 5 as a schematic energy diagram.

Figure 6 shows one example of actual measurement for the enthalpy of solution by the modified LKB solution calorimeter. The initial endothermic (resistance-increasing) process is associated with the solution of a crystal and the subsequent exothermic one is due to supply of an electrical energy for the calibration. The automatic measurement exceeds conventional manual operations by collecting many data points with smoothing procedure. Table 3 summarizes the results of the three determinations for the enthalpy of solution of each crystal and the resulting value for the enthalpy of formation $\Delta_f H$.

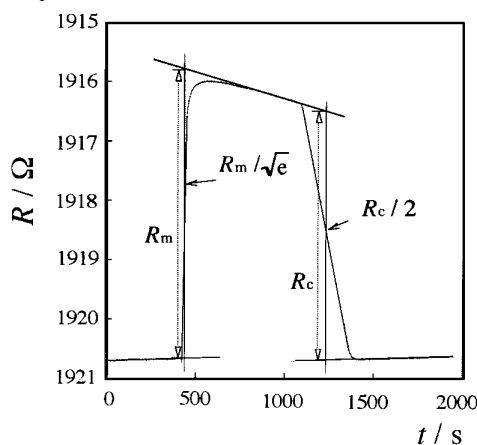


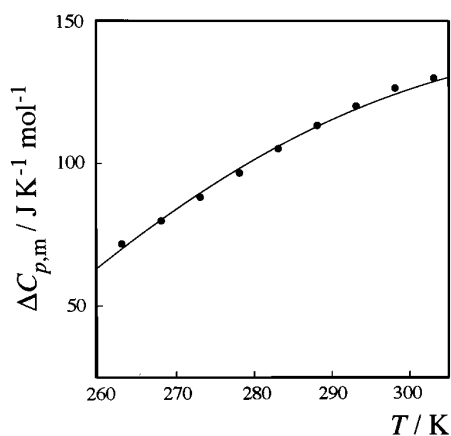
Fig. 6 Typical example for temperature change of calorimetric vessel due to dissolution (endothermic) followed by heating (exothermic) processes

The value $\Delta_f H$ was determined to be $3.0 \pm 0.3 \text{ kJ mol}^{-1}$. The positive value was really unexpected, as the entropy of formation for the 1:1 compound will be obviously negative. The evaporation rate observed in TG experiment, being in proportional to the vapor pressure of OIPh, is more than 100 times smaller for the compound than for pure OIPh crystal. From these experimental findings, it is evident that the component OIPh is stabilized by the formation of compound. It follows naturally a negative value for the Gibbs energy of formation $\Delta_f G$. Thus, the value $\Delta_f H$ should be negative.

Table 3 Enthalpies of solution of the system of CTAB+OIPh in ethanol

Solute	$\Delta_{\text{sol}}H/\text{kJ mol}^{-1}$		
CTAB in ethanol	66.5	66.7	66.4
OIPh in (CTAB+ethanol)	2.74	2.71	2.70
CTAB+OIPh+ethanol	69.2	69.4	69.1
CTAB: OIPh in ethanol	66.0	66.4	66.4
$\Delta_f H$	3.2	3.0	2.7

This conjecture should, however, be valid only at 0 K. The positive value of $\Delta_f H$ at 298.15 K can happen if the heat capacity of the intermolecular compound is larger than the sum of those of the component crystals. The molar heat capacities of the relevant crystals were measured using a Perkin Elmer DSC 7 in the temperature range between 260 and 305 K, and the results are drawn in Fig. 7 as a function of temperature. It turned out that the heat capacity of the 1:1 compound was about $125 \text{ J K}^{-1} \text{ mol}^{-1}$ larger than that of a hypothetical mixture of both component crystals at 298.15 K. This amount of the excess heat capacity corresponds to 23% of that of the mixture at the same temperature.

**Fig. 7** Excess heat capacity of 1:1 compound over 1:1 mixture of CTAB and OIPh plotted as a function of temperature

This fact results in an intriguing consequence, since the heat capacity is closely related to the entropy. Thermodynamic data of the relevant crystals lack fully in literature. Let us suppose that the entropy of the 1:1 mixture (sum of the entropies of CTAB and OIPh) be $400 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298.15 K. Multiplying 1.23 to this value, the corresponding entropy of the 1:1 compound becomes $492 \text{ J K}^{-1} \text{ mol}^{-1}$ at the same temperature. Then the $-T\Delta_f S$ term in the Gibbs energy of formation, $-27.4 \text{ kJ mol}^{-1}$ at 298.15 K, surmounts greatly the positive value of $\Delta_f H$. Thus the formation of the

1:1 compound turns out to be driven entropically at least at 298.15 K. It is important and interesting to ask why such a large difference in heat capacities, and hence in entropies exist between the mixture and the compound.

OIPh is known to be a hydrogen-bonded crystal at room temperature [10]. The phenolic hydroxyl group can act as a proton donor as well as a proton acceptor and links each molecule to two others to form one-dimensional hydrogen-bonded crystal. This situation makes each molecule to be bound rather rigidly and the molecular motion will be suppressed in the neat crystal. The constraints will be lessened to some extent by the formation of 1:1 compound, in which OIPh molecules will be separated and isolated by the hydrocarbon chains of CTA molecular ions. This will result in enhancement of the vibrational degrees of freedom in the compound, leading to a larger entropy as a whole. In any way, X-ray structural analyses of the 1:1 compound as well as CTAB crystals are highly desiderative for further discussion on the thermodynamic aspect of formation of the compound.

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