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Phase behavior of CTAB: *o*-iodophenol binary system

K. Endoh, H. Suga*

Research Institute for Science and Technology, Kinki University, Kowakae, Higashi-Osaka 577-8502, Japan

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Abstract

The phase diagram of the binary system CTAB (cetyltrimethylammonium bromide): OIPh (*o*-iodophenol) was investigated by DSC and TG methods along with polarizing-microscopic and visual observations. It was found that CTAB and OIPh produced a 1 : 3 intermolecular complex in addition to the 1 : 1 complex already reported. Both complexes underwent incongruent melting at about 305 K and 365 K, respectively. Another complex of 2 : 1 ratio was observed in the high temperature region, which formed a solid solution of mesomorphic nature with the high-temperature metastable phase of CTAB over limited composition range. The thermodynamics of formation of the 1 : 1 complex in the crystalline state is discussed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Phase diagram; DSC; TG; Surfactant with additive; Intermolecular complex

1. Introduction

Aqueous micellar solutions containing various additives have many applications in detergency, enhanced oil recovery, pharmaceutical products, and so on. 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 ionic surfactants is particularly interesting, because the additives sometimes induce spectacular changes in micellar structures giving rise to strong viscoelasticity to the solution even in a dilute state.

Cetyltrimethylammonium bromide (CTAB) mixed with *o*-iodophenol (OIPh) provides a typical example, in which the component entities are known to form 1 : 1 intermolecular complex [1]. The aqueous solution of the complex at room temperature is found to form gigantic rod-like micelles, as revealed by electron microscopy [2]. On heating, the solution changes its flow property over a narrow temperature range around 330 K with an associated heat-capacity peak, and the solution becomes a Newtonian fluid [3]. The dramatic change in fluidity is surely related to the change in the micellar structure. A unique behavior of this thermally induced transition is that the peak temperature depends strongly on the heating rate even in the slow regime, suggesting a highly cooperative nature of the transition kinetically hindered.

As the first step to clarify the nature of intermolecular interactions, the phase behavior of the binary system CTAB–OIPh was investigated by DSC and TG techniques as well as polarizing-microscopic and visual observations in the present experiment.

2. Experimental

Commercial reagents of CTAB (Wako Chem.) and *o*-iodophenol (Merck) were purified by recrystalliza-

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*Corresponding author. Fax: +86-6-6721-8502
E-mail address: suga@cc.kindai.ac.jp (H. Suga)

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Table 1
Results of elementary analysis of the 1 : 1 complex of CATB, OIPh

Element	Content	
	Observed	Calculated
C	51.37%	51.38%
H	8.07	8.11
N	2.38	2.40
X(Br + l)	35.26	35.38

tions from an ethanol–acetone mixture, respectively, and each sample was stored in a desiccator over silica gel. An equimolar mixture of the purified components was dissolved in water through the conventional treatment of solubilization under a warm condition. The homogeneous solution was cooled slowly to obtain fairly large crystals of the 1 : 1 complex, which was carefully dried over silica gel in a desiccator. Results of elementary analyses of the complex are given in Table 1. The agreement between the values observed and calculated as 1 : 1 molar ratio is satisfactory. Only total content of the halogen atoms could be determined by the analyses. The ratio Br/I was obviously crucial for the determination of the composition. Fortunately, the ratio was determined by the TG method to be 1.002, as described later.

A DSC (Rigaku Denki 8240D) was used for the study of the phase behavior. A sample of a definite composition was prepared by mixing gravimetrically the component crystals and put into an aluminum sealed-sample pan. The DSC measurements, were carried out with a constant heating rate of 2 K min^{-1} for all the samples. For a CTAB-rich sample, reproducible results were not obtained until each sample was subjected to several thermal cycles between 300 K and 380 K for homogenization of the composition.

The intermolecular complex of the 1 : 1 composition melts incongruently to yield an isotropic liquid solution coexisting with anisotropic solid, as is shown later. In order to determine the solubility curve of the solid, the sample was placed into glass-tubing of 6 mm i.d. with a cap and placed into a thermostatted copper block with a temperature constant to within ±0.3 K. The phase boundary between the anisotropic solid and isotropic solution was determined by changing the composition of the sample until either a homogeneous solution or solid phase is obtained through visual observation. Volatility or thermal stability of the neat and the 1 : 1 complex samples was examined by TG–DTA system (Rigaku Denki 8101 D) with the same heating rate of 1 K min^{-1} under the flow of N_2 gas at the rate of 50 $\mathrm{cm}^3\ \mathrm{min}^{-1}$. Microscopic observation was carried out by a polarizing microscope (Olympus BHA 751-P) equipped with a hot stage (Union Optics CMS-2), whose temperature was controlled manually within ±2 K. The infrared spectra of CTAB crystal were measured by a spectrometer (Hitachi, JASCO FT/IR 3) with a variable temperature cell. The spectra were recorded at 300 K for the low-temperature phase and at 400 K for the high-temperature phase.

For the determination of enthalpy of formation of the 1 : 1 complex from the component crystals, the enthalpy of solution of each crystalline sample was measured using an LKB solution calorimeter (LKB 8700-1 Precision Calorimetric System). The calorimetric temperature was measured by a thermistor for its high sensitivity. The measurement has been done manually by a built-in Wheatstone bridge which includes the thermistor in one arm. The resistance measurement was automated by use of a digital voltmeter (Keithley 2000) with precision of ±4 mΩ, which corresponds approximately to ±0.1 mK at 298.15 K. Molar heat capacities of each crystalline sample were measured by DSC (Perkin Elmer 7) in the temperature range 260 and 310 K.

3. Results and discussion

3.1. Thermal behavior of CTAB, OIPH and 1 : 1 complex

Figs. 1 and 2 show the DSC and TG curves of CTAB, OlPh and 1 : 1 complex, respectively. A sharp endothermic peak observed at 315 K in OlPh sample corresponds to the melting temperature. The TG measurement shows that the rate of mass reduction due to the sublimation and vaporization is very rapid in this substance, so that all the sample evaporates from the TG pan before the boiling temperature (460 K accompanied by some decomposition) is reached.

The solid–solid phase transition of pure CTAB crystal has already been examined by DSC and X-ray powder diffraction methods [4,5]. The crystal at room temperature belongs to the monoclinic system, being optically anisotropic. Microscopic observation

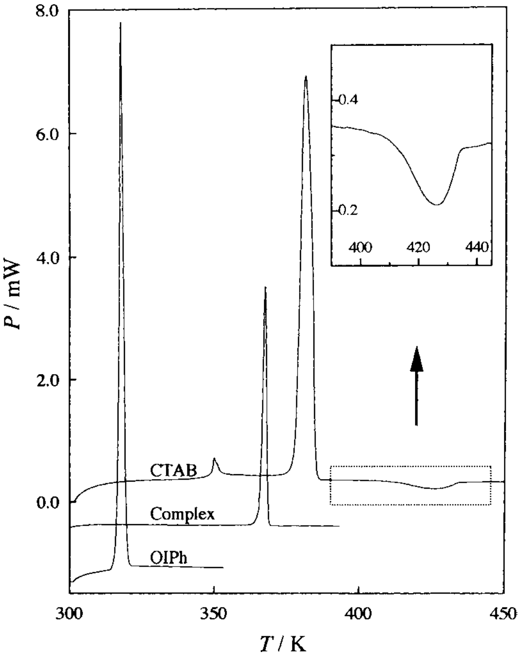

Fig. 1. DSC curves of CTAB, 1 : 1 complex, and OlPh. The high temperature part of the CTAB crystal is reproduced in the inset on a magnified scale.

of the crystal above the transition temperature shows that many wrinkles appear in the crystals, which are almost isotropic: the plate-like crystals extinguish for practically all orientations at crossed polaroids. There appear sporadically some anisotropic crystals coexisting with the isotropic mother phase. This puzzling problem will be discussed later. Another small endothermic peak appears in the DSC curve at about 347 K, which reminds us of similar peaks observed in some long-chain *n*-alkanes [6] and *n*-alkylhalides [7]. The crystal starts to decompose above ca. 450 K and all the sample crystals disappear above 530 K. There exists a broad exothermic peak just before the signal of decomposition of the crystal appears. This exothermic effect is discussed later in relation to the coexistence of the two different kinds of high-temperature phase in CTAB crystal.

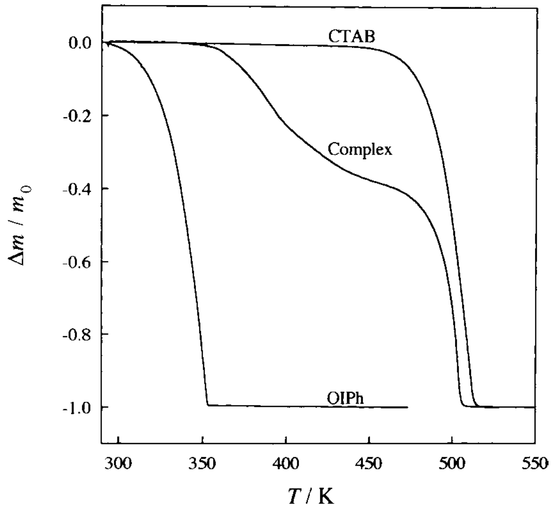

Fig. 2. TG curves of CTAB, 1 : 1 complex, and OlPh.

The peak observed at 365 K in the 1 : 1 complex was reported [1] to be due to a phase transition from room-temperature phase to a smectic phase. The explanation seems to be reasonable, as one component crystal CTAB undergoes a phase transition at 376 K into an isotropic mesophase on heating [4,5]. Careful examination of the anisotropic solid by the polarizing microscope, however, showed coexistence with isotropic liquid solution. Thus the peak is not associated with the phase transition but with an incongruent melting of the complex, giving rise to a mixture of the anisotropic solid and the isotropic solution. The composition of the anisotropic solid is 2 : 1 in the mole fraction. Texture of the polarizing-microscopic pattern of the anisotropic solid is really similar to those of some liquid crystalline materials [8].

Once the incongruent melting takes place, recovery of the initial homogeneous complex will take a long time at room temperature. This explains why the previous authors [1] could not obtain the same DSC curve for the second run as that for the first one. They reported that the single peak observed in the first heating run split into two peaks at 356 and 361 K for the second run, and the double peaks remained to exist for the third and fourth runs.

The TG curve of the 1 : 1 complex shows a strong depression of vapor pressure of OlPh in the complex from that in the pure sample. Mass reduction due to evaporation of OlPh is retarded by about 50 K for the complex than for that of OlPh crystal, indicating a lowering of chemical potential of OlPh by the formation of the complex with CTAB. The difference in volatilities between the complex and OlPh was used to determine the molar ratio of the complex sample. If the TG cell is kept at about 350 K, only the OlPh component escapes from the complex until pure CTAB crystal is left behind in the pan without undergoing thermal decomposition. From the mass reduction, the molar ratio of CTAB/OIPh was determined to be 1.002.

3.2. Nature of disorder in CTAB crystal

Some crystals transform into mesophases on warming, either orientationally disordered crystals (ODC) or liquid crystals (LC) [9] before they ultimately melt to give rise isotropic liquids. In the ODC phase, molecules reorient dynamically along many directions while keeping the translational periodicity with respect to the centers-of-masses of the molecules. The motion will surely enhance the time-averaged molecular symmetry and therefore most of the ODC belong to the cubic system, being generally fcc or bcc. They are mechanically soft in relation to the orientational disorder. For that very reason, these crystals are also called as "plastic crystals" or "isotropic crystals". In contrast, molecules in LC phase align approximately along a particular direction but the translational invariance is broken to some extent. Thus the LC have optically anisotropic property.

Crystal structure of CTAB at room temperature [5] is such that the cetyltrimethylammonium cations and bromide anions extend bidimensionally to form an ionic layer which is sandwiched between the hydrocarbon chain layers with trans zig-zag conformations. The Coulomb force in the ionic layers is much stronger than the van der Waals forces in the hydrocarbon layers. It is this ionic bonding which raises the melting temperature of this crystal. The melting temperature will be so high that thermal decomposition actually precedes the process. The crystal transforms into the high-temperature phase with a large entropy of transition amounting to 150 J K^{-1} mol^{-1}. This indicates that a great deal of orientational and conformational disorder exist in the high-temperature cubic phase. Iwamoto et al. [5] have suggested a "quasi-liquid" structure for the hydrocarbon chains in the cubic phase based on the fact that the X-ray diffraction peaks arising mainly from hydrocarbon chains at room temperature are replaced by a diffuse halo above the transition temperature.

This picture is supported by the IR spectra of the crystal reproduced in Fig. 3. The IR spectra taken at 300 K exhibit progression bands [10,11] characteristic of the trans zig-zag conformation of the hydrocarbon chains. The bands are significant in the wave-number region between 900 and 1100 cm^{-1}. The progression bands disappear in the cubic phase owing to the onset of conformational disorder. If the trans and gauche conformers are realized equi-energetically in the cubic phase, the corresponding entropy gain is $R\ln 3^n$, where n is the number of carbon atoms capable to create new conformers through internal rotation. If the number n is chosen to be 15, the calculated conformational entropy 137.0 J K^{-1} mol^{-1} accounts for essentially the total entropy of transition experimentally observed. Random formation of conformers, however, is not possible in the cubic lattice owing to strong intra- and inter-molecular repulsive interactions.

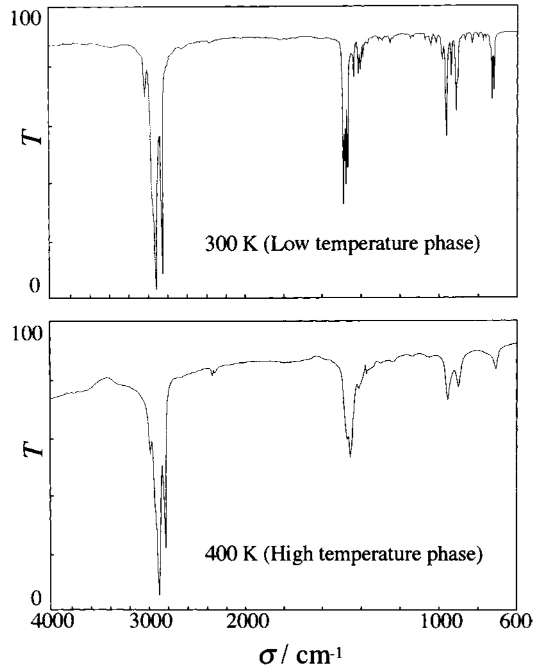

Fig. 3. IR spectra of CTAB crystal taken at 300 K (low-temperature phase) and 400 K (high-temperature phase).

It is obvious that the conformational disorder of the molecules alone does not give any isotropic nature to the high-temperature phase. Orientational disorder of molecules must take place synchronously with the conformational disorder [12]. Thus each molecule will take random conformers within a limited space, giving rise to enhanced molecular symmetry in the part of the hydrocarbon chain. Then the molecule undergoes orientational disordering among several directions to acquire a cubic site symmetry at each lattice point. All the IR band in the high-temperature phase are extremely broad, reflecting highly disordered nature of the constituting molecule. It is highly desirable to determine the molecular structure and their dynamics in this intriguing cubic phase.

3.3. Phase diagram

The phase diagram determined by DSC and visual observation is drawn in Fig. 4. Samples with more than 20 compositions were used for this purpose. The construction of the phase diagram is mostly based on the enthalpy change associated with each process, which is plotted in Fig. 5 as a function of mole fraction of CTAB. A new intermolecular complex with 1 : 3 molar ratio was found to exist in addition to the 1 : 1 complex already known. The 1 : 3 complex exhibits an incongruent melting at 305 K. The eutectic temperature between the new complex and OIPh is 298 K. The formation of a complex was hinted when samples of CTAB and OIPh were mixed at room temperature kept at 290 K. A part of the contacted samples melted immediately at the interface, indicating that an exothermic process occurred on mixing. Thus the formation of 1 : 3 complex is accompanied by an enthalpy decrease which induces spontaneous heating of the sample above the eutectic temperature.

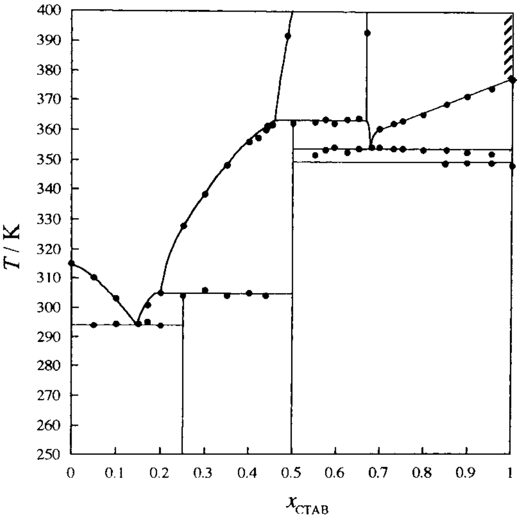

Fig. 4. Phase diagram of the CTAB–OIPh binary system.

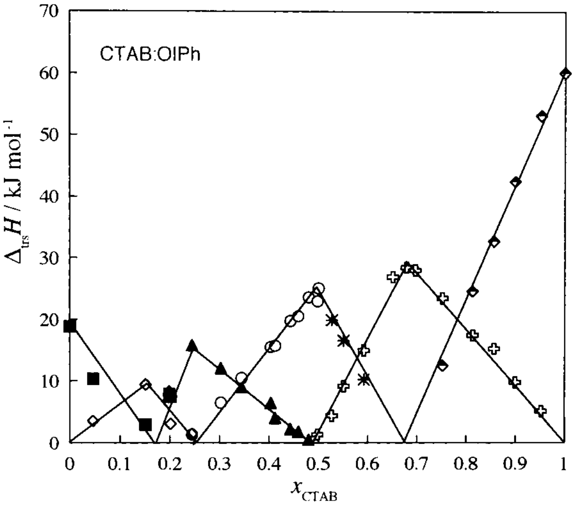

Fig. 5. Enthalpy change associated with each phase change.

As reported in Section 3.1, the 1 : 1 complex also exhibits an incongruent melting at 365 K, giving rise to a mixture of isotropic OIPh-rich solution and anisotropic CTAB-rich solid. The solubility curve of the solid into OIPh liquid was determined visually by changing the composition until either a single solution phase or a single solid phase was obtained. The composition of the solid side was always 0.667 and this result strongly suggests the formation of 2 : 1 complex at high temperatures. The 2 : 1 complex forms a solid solution with the cubic phase of CTAB crystal over a narrow composition range. On lowering the temperature, the solid solution exhibits a phase separation into pure CTAB and the 1 : 1 complex at about 353 K, the eutectoid temperature.

Thus the 1 : 1 complex gives a mixture of the anisotropic 2 : 1 complex and the OIPh-rich isotropic solution in the first heating run. The amount of each phase in the mixture can be given by the lever rule [13]. One of the split DSC peaks observed in the second run [1] corresponds to the eutectoid temperature, and the other probably to a melting point of OIPh-rich solid sample.

An important question might be raised at this stage. Why the optically isotropic CTAB phase can produce a series of solid solution with the anisotropic 2 : 1 complex at high temperatures? As has been described above, the high-temperature phase of CTAB crystal is composed of two different kinds of phase; the main ingredient of the phase is cubic and the remaining minority is optically anisotropic. This observation clearly contradicts the phase rules [13] which state that only a single phase should exist thermodynamically over a range of temperature and pressure in any crystals of single component. The major part of phase is considered to be the stable phase and the remaining metastable phase. In fact, the anisotropic part of the phase diminishes the amount irreversibly on heating with an exothermic effect until all the phase becomes isotropic. The anisotropic phase never recovers on recooling. Thus the isotropic phase is the stable high-temperature form of CTAB crystal. The exothermic effect associated with the irreversible transformation is shown in Fig. 1 on a magnified scale.

This kind of coexistence of the stable and metastable phases can be encountered in some crystals. Cubic modification of KCN at room temperature undergoes a phase transition at 168.3 K into an orthorhombic phase on cooling [14]. Special thermal treatment of the crystal around 168.3 K produces a metastable monoclinic phase coexisting with the stable phase [15,16]. The monoclinic phase transforms irreversibly into the stable orthorhombic phase on cooling and never appears until the same special treatment is repeated. Interestingly, this metastable phase can be stabilized by addition of a second component. Thus there is a stability-reversal composition region in KCN–KBr binary system. Above a certain critical KBr concentration, only the monoclinic phase appears at temperatures below the transition temperature.

A similar situation can be observed in thiophene–benzene binary system. In contrast to benzene, thiophene crystals exhibit a richness polymorphs composed of seven modifications [18]. They appear either in the stable phase sequence or in the metastable phase sequence. Addition of benzene to thiophene above the mole fraction of $x = 0.05$ realizes only the metastable phase sequence [19,20]. It is not clear at this moment as to whether the stability-reversal phenomena are of thermodynamic origin or of kinetic origin.

Turning to the present system, the isotropic and anisotropic high-temperature phases of CTAB crystal will have chemical potentials of similar magnitude. The metastable anisotropic phase will be stabilized by addition of an appropriate amount of OIPh. The chemical potential of the metastable phase is more affected than that of the stable phase by the added OIPh to induce the stability reversal at some concentration, and the anisotropic phase thus stabilized can form the solid solution with the anisotropic 2 : 1 complex over a limited composition range. The shaded area drawn in Fig. 4 represents schematically the stability-reversal region. The determination of the exact location of the range requires necessarily a structural study on a series of the solid solutions.

3.4. Thermodynamics of 1 : 1 complex formation

It is interesting to know the interaction energy that produces the 1 : 1 complex between CTAB and OIPh crystals. This will be possible by measuring the enthalpies of solution of the 1 : 1 complex and of a hypothetical 1 : 1 mechanical mixture. Ethanol was chosen as one of the best solvents for all the relevant crystals. Each crystal of the amount of 0.100 m mol was packed into a thin-glass ampule, and the dissolution was started by breaking the ampule inside a calorimetric cell containing 100 cm^3 of ethanol at 298.15 K. First, the enthalpy of solution $\Delta_{\mathrm{sol}}H$ of CTAB crystal was measured. The resulting solution was used as the solvent for the subsequent measurement of $\Delta_{\mathrm{sol}}H$ of OIPh. Thus the final solution is composed of 100 cm^3 ethanol and equimolar amount of CIAB and OIPh. The same solution can be obtained by dissolving the same amount of 1 : 1 complex into the same amount of ethanol. The difference between the enthalpies of solution for the 1 : 1 complex and hypothetical 1 : 1 mechanical mixture gives directly the enthalpy of formation of the 1 : 1 complex from the component crystals in the solid state.

$$\begin{aligned}&\mathrm{CTAB\,(cr)} + \mathrm{OIPh\,(cr)}\\&\quad = 1 : 1\ \mathrm{complex}\ (\mathrm{cr})\Delta_{\mathrm{f}}H_{298.15\,\mathrm{K}}\end{aligned}$$

Three series of measurements gave the following result: $\Delta_{\mathrm{f}}H_{298.15\ \mathrm{K}} = +(3.0\pm0.3)\ \mathrm{kJ\ mol}^{-1}$. The positive value was really an unexpected result. The expectation was, however, not based on a serious consideration.

The vapor–pressure depression qualitatively observed in the TG measurement shows clearly that the Gibbs energy of formation $\Delta_{\mathrm{f}}G$ is negative. The

Table 2
Molar heat capacities of CATB, OIPh, and their 1 : 1 complex

T/K	$C_{p,m}$/J K^{-1} mol^{-1}		
	CTAB	OIPh	1 : 1 Complex
263.15	450	131	653
268.15	454	133	667
273.15	462	135	685
278.15	470	137	703
283.15	480	139	724
288.15	489	142	744
293.15	499	144	763
298.15	509	147	782
303.15	519	150	800
308.15	532	160	822

rate of vaporization, being assumed to be proportional to the vapor pressure of OIPh, is reduced by more than two orders of magnitude for the 1 : 1 complex than for the neat crystal. The necessary consequence of these facts is that the entropy of formation $\Delta_f S$ should be positive. Unfortunately, there is no literature reference that lists the entropy values of the relevant compounds. Since the entropy of any substance is directly related to the heat capacity of the substance, the molar heat capacities of the three crystals were measured by DSC. The results are tabulated in Table 2. It turns out that the heat capacity of the system increases greatly due to the complex formation. The heat-capacity difference between the 1 : 1 complex and a hypothetical mixture reaches almost 125 J K^{-1} mol^{-1} at 298.15 K, as shown in Fig. 6. This amount of excess heat capacity of the complex corresponds to 23% of that of the mixture at the same temperature.

If the entropy of the 1 : 1 mixture (sum of the entropies of CTAB and OIPh) were 400 J K^{-1} mol^{-1} at 298.15 K, the entropy of formation becomes +92 J $K^{-1}mol^{-1}$ at the same temperature. Then the $-T\Delta_f S$ term in the Gibbs energy change, −27.4 kJ mol^{-1} at 298.15 K, surmounts greatly the positive $\Delta_f H$ value. Thus the formation of the complex turns out to be driven entropically. It was suspected that the large heat capacity of the complex at room temperature arises from a polymorphic phase transition occurring at low temperatures. Examination of the 1 : 1 complex by DSC showed absence of any thermal anomaly in the complex down to 100 K. From where does this large excess heat capacity, hence a large excess entropy, of the complex originate?

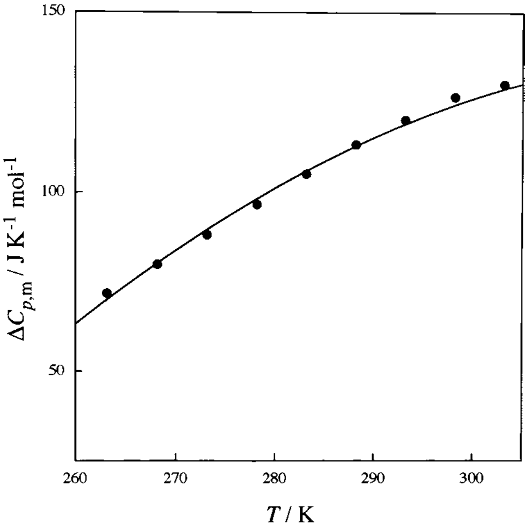

Fig. 6. Excess heat capacity of the 1 : 1 complex over that of the 1 : 1 mechanical mixture.

According to the X-ray structural analysis, the *o*-iodophenol crystal belongs to monoclinic system and has a hydrogen-bonded structure at room temperature [21]. The phenolic hydroxy group capable of forming hydrogen bonds can act as a proton donor as well as a proton acceptor. The hydroxy group links each molecule to two others to construct an one-dimensional hydrogen-bonded chain. Thus each molecule is bound rather rigidly by the O–H· · ·O hydrogen bonds and the molecular motion will be suppressed more or less in the neat crystal. The constraints in the motion will be relaxed to some extent by the formation of complex, in which *o*-iodophenol molecules will be separated and isolated by the hydrocarbon chains of CTAB. Thus the vibrational degrees of freedom of the complex will be greatly enhanced in the crystal, leading to the entropy increase. This conjecture, however, should be tested by an X-ray structural analysis of the 1 : 1 complex in a future study.

4. Concluding remarks

In relation to the experimental determination of the phase diagram of CTAB:OIPh binary system, many important and interesting problems were pointed out without clear answers. Among other things, the nature of disorder in the high-temperature phase of CTAB crystal seems to be very important. This is because the topic is closely related to the controversial problem as to whether the so-called smectic-D (cubic) phase observed in some thermotropic liquid–crystalline materials is really a kind of LC phase or of ODC phase. Some workers [22] proposed an ODC-like structure with primitive cubic space group. The others [23,24] suggested higher-order structural models in which rod-like micelles with axial symmetry are arranged spatially with 3-fold symmetry. Convincing evidence has not been given to these proposed structural models. The only indisputable aspect is that the phase is cubic and it is not appropriate to call it smectic. Clarification of the nature of disorder in mesogenic compounds will deepen our understanding of the state of aggregation of molecules [17].

Acknowledgements

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