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Thermal transition from viscoelastic to newtonian fluid in aqueous solution of 1 : 1 CTAB: o-iodophenol complex

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Abstract

Thermally induced transition in aqueous solution of 1 : 1 intermolecular complex formed between cetyltrimethylammonium bromide (CTAB) and o-iodophenol was studied by using a high-sensitive scanning microcalorimeter DASM 4 in the temperature range between 20 and 80°C. A heat capacity peak was observed at temperature around 55°C. The peak temperature depended strongly on the heating rate, indicating highly kinetic nature of the transition. The enthalpy change associated with the transition was found to depend significantly on stored period of the solution at room temperature. These observations were discussed in terms of possible structural change of micellar aggregates in association with the change in flow property of the solution during warming. Origin of slow kinetics of the self-assembly and disassembly processes of the complex in the solution is inferred.

Keywords: Calorimetry; Surfactant; Molecular complex; Viscoelasticity; Micellar aggregates

1. Introduction

Aqueous solutions of some amphiphilic molecules exhibit striking viscoelastic behavior. The viscoelasticity can be seen easily by simply swirling the solution and visually observing the recoil movement of air bubbles trapped in the solution after the swirling motion is stopped. The viscoelasticity of aqueous solutions of ionic surfactants is known to be enhanced if a third component is added to the solution [1]. The effects of additives on the fluidity of surfactant solutions were examined as a function of composition. Cetyltrimethylammonium bromide CTAB mixed with o-iodophenol is

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one example [2, 3]. In this system, the component crystals are found to produce a 1 : 1 intermolecular complex which can be separated from aqueous solution as a crystalline form [4]. The complex crystal undergoes a first-order phase transition at 95°C giving rise to a mesomorphic phase similar to some kinds of liquid crystalline material [2]. On the other hand, the aqueous solution of the complex shows a spectacular viscoelastic property at room temperature. The viscoelasticity of the solution seems to increase with time at room temperature. Microscopic observations shows that elongated rod-like micellar aggregates form in the aqueous solutions above some threshold concentration of the complex.

On heating, the solution changes its flow property over a narrow temperature range centered about 55°C, above which it becomes an ordinary viscous solution. The drastic change in fluidity with increasing temperature will reflect a change in micellar structure. Because of the cooperativity of the self-assembly or disassembly process and fairly high aggregation number of the micellar aggregates, the thermally induced transition may be detected by a scanning calorimeter possessing high stability and sensitivity. It is the purpose of this paper to describe briefly the calorimetric measurements on aqueous solution of the complex focussing their dependencies of the peak temperature on the heating rate and of the enthalpy change on the stored time of the solution at room temperature.

Experimental and Results

Commercial CTAB purchased from Wako Pure Chemical Industries Ltd. was purified by recrystallization from acetone/methanol mixture. o-Iodophenol of Kanto Chemical Co. Inc. was recrystallized from the same mixed solvent. An equimolar mixture of the purified components was dissolved into water through the conventional treatment of solubilization under a warmed condition. After attainment of the solubilization, the homogeneous solution was cooled down slowly to room temperature. Fairly large crystals were obtained during several days when kept at a cold state. The crystals were dried in a desiccator over silica gel. The molar composition of the crystalline complex was determined to be 1 : 1 by UV spectroscopy and elementary analysis.

An adiabatic differential scanning microcalorimeter DASM-4 originally developed by Privalov et al. [5] was used for the heat capacity measurements of solution with several heating rates ranging from 0.125 to 1 K min^{-1}. The calorimeter was operated under computer control for automatic data collection. Purified water was used as a reference substance. The calorimeter compared the heat capacities of water and a given aqueous solution. Each of the sample and reference volumes was about 0.45 cm^3. A sample solution of the 1 : 1 intermolecular complex CTAB: o-iodophenol with concentration of 1.42×10^{-2} mol kg^{-1} was prepared by dissolving the crystals into distilled water under stirring at 60°C. The sample was cooled down to room temperature. After storage of the aqueous solution for one week for the equilibration, the first series of measurements were carried out with the heating rate of 0.125, 0.25, 0.50 and 1 K min^{-1}, respectively. The enthalpy change associated with transition was estimated from each DSC tracing by the establishment of appropriate baselines according to conventional method.

As expected, a fairly large heat-capacity peak appeared in the temperature range between 53 and 59°C, depending on the heating rate. The higher the scanning rate, the higher the peak temperature. The solution immediately cooled down to room temperature exhibited essentially the same phenomenon in the subsequent heating run, but the peak area was about 1/3 of the first run. This means that the recovery of the solution experienced temperatures above 60°C towards the initial state requires a long time. The solution was kept for one month at room temperature for further equilibration and the second series of measurements were started. In this measurements, the enthalpy change associated with the peak was found to increase significantly. The sample solution seemed to increase its viscosity with time at room temperature even after one month. Therefore the sample solution was stored for 11 months and the third series of measurements were done. The experimental results concerning the peak temperature and the enthalpy of transition are collected in Table 1 and the heat capacity curves for the third measurements are reproduced in Fig. 1. In this figure, only the top curve has correct scale for the differential heat capacity. The ordinate for the remaining curves is shifted downwards by 0.12 J g^{-1} K^{-1} step by step, respectively, for the sake of clarity. Here, the mole refers to the intermolecular compound $C_{16}H_{33}N(CH_3)_3Br{\cdot}C_6H_4(OH)I$ (molar mass 584.46 g mol^{-1}). The fairly large uncertainty in the determinations of the enthalpy of transition arises mainly from difficulty of estimating the baselines, because the transition occurs over a rather wide range of temperature compared to the case of the first-order transition. Dependence of the peak temperature on the heating rate is drawn in Fig. 2. It is rather surprising to see how the peak temperature of 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 changes arising from

Table 1
Thermodynamic quantities associated with thermal transition

$(dT/dt)/K\ min^{-1}$	$T_{max}/°C$	$\Delta_{trs}H/kJ\ mol^{-1}$
Series 1(1 week storage)		
0.125	53.3	1.8 ± 0.1
0.250	55.1	1.9 ± 0.1
0.500	56.4	1.9 ± 0.1
1.00	57.9	1.9 ± 0.1
Series 2(1 month storage)		
0.250	55.3	3.5 ± 0.2
0.500	56.8	3.6 ± 0.2
1.00	58.1	3.4 ± 0.2
Series 3(11 months storage)		
0.125	53.8	3.8 ± 0.2
0.250	55.2	3.7 ± 0.2
0.500	56.8	3.7 ± 0.2
1.00	58.5	4.0 ± 0.2

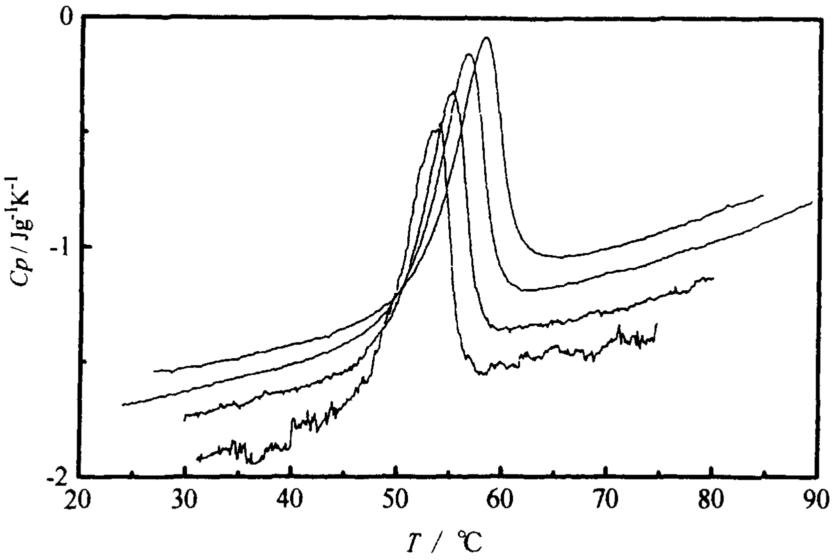

Fig. 1. Dependence of differential heat capacity for aqueous solution of CTAB : o-iodophenol complex on the scanning rate. The reference substance is pure water. Heating rate is 1.00, 0.50, 0.25 and 0.125 K min^{-1} from the top to bottom curve. Each sample was kept for 11 months at room temperature. The ordinate for each curve is shifted downwards by 0.12 $\mathrm{Jg}^{-1}\,\mathrm{K}^{-1}$ for the sake of clarity.

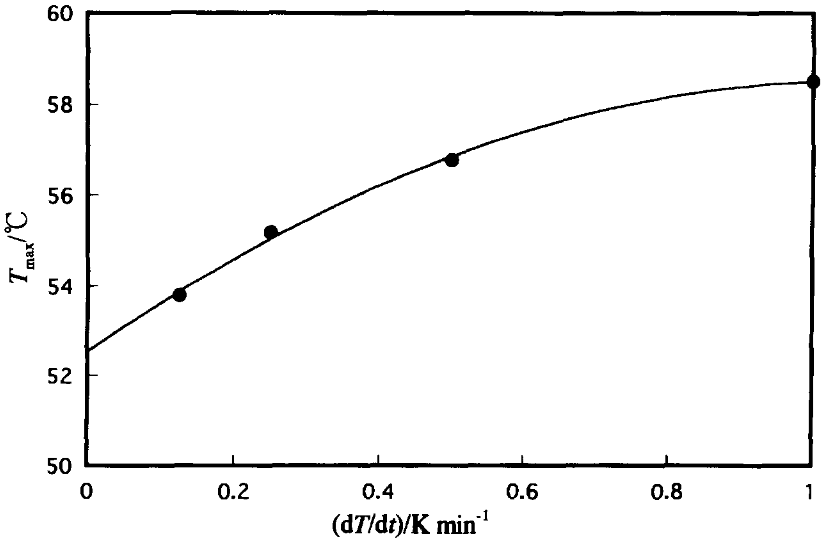

Fig. 2. Dependence of peak temperature for excess heat capacity on the scanning rate.

kinetic hindrance of nucleation and growth of a new phase [6]. Even in these cases, strong dependence of the transition temperature on the heating rate as observed in the present system occurs scarcely.

Discussion

The aqueous solution of pure CTAB forms an isotropic phase in the concentration range between 0 and 0.7 mol L^{-1} at 25°C. From the critical micelle concentration (about 9×10^{-4} mol L^{-1}) up to approximately 0.3 mol L^{-1}, the solution contains small spherical micelles with 2.6 nm in radius. As the concentration of CTAB is increased further, the micelles start to grow and become thread-like in shape. Shikata et al. [3] examined the effect of additive on the formation of gigantic micellar aggregates by measuring dynamic moduli and loss in a CTAB aqueous solution of 0.1 mol L^{-1}. As the concentration of sodium salicylate (Sal) as an additive is increased, viscoelastic property of the solution changed at some concentration range of Sal, indicating formation of thread-like micellar aggregates. Clausen et al. [7] also confirmed these behavior in the solution of $CTA^{+}Sal^{-}$ system.

Essentially the same phenomena were observed by Sakaiguchi et al. [8] in CTAB or cetylpyridinium bromide when some aromatic compounds such as iodophenol, salicyclic acid are added. They succeeded to find out the existence of extremely elongated rod-like micelles in electron micrographs [9]. Small angle X-ray scattering measurement [10] on one-dimensionally arrayed cylindrical micelles gave a considerably sharp diffraction peak corresponding probably to the diameter of the long micelles. The situation is the same in the present o-iodophenol and CTAB system. In each case, formation of the intermolecular compound was confirmed by X-ray and DSC measurements. The aqueous solution exhibited a spectacular viscoelasticity even in very diluted state. The rod-like micelle is so elongated that terminals of each rod are difficult to find out even by intentional observation [3]. The chemical affinity between o-iodophenol and CTAB is rather large. When both the component crystals are mixed at 17°C, a part of the sample is found to liquefy immediately at the interfaces. A large exothermic formation energy causes to raise the sample temperature above 22°C : a eutectic temperature between o-iodophenol and 1 : 1 molecular complex [11]. It is worthy to measure quantitatively the enthalpy of formation between them by a solution calorimetry. However, an experimental difficulty arising from extremely poor solubility of o-iodophenol into water must be overcome by an appropriate ways.

Although some models for explaining the growth in length of the rod-like micelles have been proposed, the nature of binding is not fully understood. For such elongated rod-like micelles, mechanical flow causes an orientation of the micelles, resulting in storage of elastic energy by a mechanism similar to polymer solutions exhibiting viscoelasticity [12]. However, the binding energy in the micellar aggregates will be overcome by an entropic factor that induces dissociation of the giant micelles into spherical ones when the temperature is raised. The entropy of systems always tends to randomize self-associating assembly at high temperatures, resulting in formation of normal viscous solution consisting of spherical micelles. The strong dependence of the peak temperature on the heating rate shows that the dissociation process is of highly kinetic nature. The reverse process, the restoration of the original rod-like micelles, obviously takes much longer time. As is evident from Table 1, the enthlapy change associated with the thermal transition from viscoelastic to Newtonian solution increases as the storage of the solution at room temperature is prolonged. It is evident that the formation of gigantic micellar aggregates takes an extremely long period.

Most probably, a freshly prepared solution involves rather short pieces of rod-like micelles. Isrelachvili et al. [13] have discussed the thermodynamics of formation of micelles in general and derived the following equation.

$$\mu_{\mathrm{N}}^{0} = \mu_{\infty}^{0} + \frac{\alpha R T}{N},$$

where μ_{∞}^{0} is the chemical potential per amphiphilic molecule for an infinite cylinder, μ_{N}^{0} for an aggregate composed of N molecules. The quantity α is a temperature independent parameter characteristic for a particular system. The term $\alpha RT/N$ arises because the change in chemical potential with aggregate size will be determined by the unfavorable packing of the molecules at the ends of aggregate. As far as the α value is small irrespective of positive or negative in sign, the micelles stay essentially spherical. On the other hand, large positive values for α imply a rapid increase in micelle size [12]. In such a system, the driving force to elongate the energetically favored rod-like micelles increases as the growth proceeds. While, the probability for encountering the terminal members of each rod with spherical micelles or amphiphilic molecules decreases rapidly during the formation of rod-like micelles in a dilute solution. This will be one reason for slow kinetics of the formation of micellar aggregates particularly at the final stage. There is, however, no consideration in this discussion concerning the roles played by additives in the favorable formation of the rod-like micelles.

The role of additives was reported to be somewhat complex to analyze. Ulmius et al. [12] suggested that an aliphatic compound such as cyclohexane is solubilized in the interior of the micelles. While aromatic compounds are solubilized closed to the polar surface of the rod-like micelles at moderate concentrations of additives. Kalus et al. [14] also suggested from a neutron diffraction experiment the existence of additives at the polar surface in the case of cetylpyridinium salicylate. In their suggested model, salicylate ions are intercalated between the pyridinium rings at the periphery of the micelle with its plane perpendicular to the rod. In such spatial arrangements, π-π interactions among the benzene rings will be an important ingredient of the intramicellar forces along the rod axis. These conjectures, however, require sophisticated proofs.

A similar thermally-induced transition was observed in aqueous solution of pure CTAB over a small concentration range in the 10^{-2} mol kg^{-1} region [15], which alone did not exhibit viscoelasticity. Effects of some additives on the anomalous heat capacity were examined and possible mechanism of the anomalous behavior was discussed in details. It has been concluded that the transition observed around 45°C is quite reproducible and arises from subtle changes in spherical micelles. Therefore the mechanism of thermally-induced transition in the present intermolecular complex system will be different from that in pure surfactant system.

This is the first calorimetric study on thermally-induced transition from viscoelastic to Newtonian fluid in a dilute aqueous solution of 1 : 1 complex formed between CTAB and o-iodophenol. At low temperatures, the aqueous solution behaves like a polymer solution by making multimolecular aggregates. At high temperatures, they bahave like a solution containing small solute entities. In this way, the present molecular complex bridges the worlds between low- and high-molecular-weight compounds. It has been known that the molecular complex formation widely developed over a series of phenol derivatives coupled with cationic surfactants including CTAB and its homologues. It is our intention to enlarge the objects exhibiting more or less similar behavior in order to clarify the nature of energetic as well as entropic aspects of the complex formation and to clarify the role of additive played in the formation of the gigantic micelles.

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References

[1] S. Gravsholt, J. Colloid Interface Sci., 57 (1976) pp. 575–578.
[2] H. Hirata, H. Kanda and Y. Sakaguchi, Bull. Chem. Soc. Jpn., 62 (1989) pp. 2461–2464.
[3] T. Shikata, H. Hirata and T. Kotaka, Langmuir 3 (1987) pp. 1081–1086.
[4] H. Hirata, Y. Kanda and S. Ohashi, Colloid Polym. Sci., 270 (1992) pp. 781–784.
[5] P.L. Privalov, V.V. Plotnikov and V.V. Filimonov, J. Chem. Thermodyn., 7 (1975) pp. 41–50.
[6] N.G. Parsonage and L.A.K. Staveley, Disorder in Crystals, Clarendon Press, Oxford, 1978.
[7] T.M. Clausen, P.K. Vinson, J.R. Minter, H.T. Davis, Y. Talmon and W.G. Miller, J. Phys. Chem., 96 (1992) pp. 474–484.
[8] Y. Sakaiguchi, T. Shikata, H. Tamura and H. Hirata, J. Electron Microsc., 36 (1987) pp. 168–176.
[9] Y. Sakaiguchi, Y. Shikata H. Urakami and H. Hirata, Colloid Polym. Sci., 265 (1987) pp. 750–753.
[10] H. Hirata, M. Sato, Y. Sakaiguchi and Y. Katsube, Colloid Polym. Sci., 262 (1988) pp. 862–864.
[11] K. Endoh and H. Suga, Unpublished results.
[12] J. Ulmius, H. Wennerstrom, L.B.-A. Lindblom and S. Gravsholt, J. Phys. Chem., 83 (1979) pp. 2232–2236.
[13] J.N. Israelachivili, D.J. Mitchell and B.W. Ninham, J. Chem. Soc., Faraday Trans. II, 72 (1976) pp. 1525–1568
[14] J. Kalus, H. Hoffmann, K. Reizlein, W. Ulbrich and K. Ibel, Ber. Bunsenges. Phys. Chem., 86 (1992) pp. 37–42.
[15] M.J. Blandamer, B. Briggs, J. Burgess, P.M. Cullis and G. Eaton, J. Chem. Soc. Faraday Trans. II, 87 (1991) pp. 1169–1175 : 88 (1992) pp. 2871–2874.