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NEW FINDING OF THE GLASS TRANSITION PHENOMENON IN SURFACTANT GEL PHASE: THE BINARY SYSTEM OF WATER AND DIOCTADECYLDIMETHYL-AMMONIUM CHLORIDE

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ABSTRACT: Differential scanning calorimetry on the two-component system of dioctadecyldimethylammonium chloride (DOAC) — water was carried out in the temperature region from 80 °C down to -100 °C. As the result, a new type of glassy state was found around at -40 °C for the supercooled complete gel phase.

In the binary system of water and dioctadecyldimethylammonium chloride (DOAC), the cationic surfactant having two long hydrocarbon chains, the bilayer-lamellar structure has been generally accepted as the standard model,[1,2] in analogy with the lipid—water system.[3,4]

In our previous study,[5] thermal analyses of DOAC—water systems in the temperature region down to -20 °C revealed that there occur the successive phase changes of coagel-to-gel and gel-to-liquid crystal due to the increasing structural disorders of the polar head groups and hydrocarbon chains, respectively. In addition, the gel phase prepared by the cooling of the liquid crystalline phase was allowed to be the supercooled state down to -20 °C. The perfect conversion to the coagel phase was attained only when the gel phase was annealed at the temperature of about 20 °C, at least for about 20 hours. After this treatment, the gel phase was obtained above 36 °C by the phase transition from the coagel phase and transformed into the liquid crystalline phase above 46 °C (= Krafft point). In the situation of the super-

cooled gel phase (below 36 °C), the interlamellar water incorporated between the bilayers of DOAC molecules did not crystallize. Thus, this fact indicated that the interlamellar water is composed of the structural bound and intermediate waters associated with the polar head groups of DOAC molecules [see ref.(5)]. When the limiting amount of the interlamellar water was accomplished by involving four molecules of the bound water and three molecules of the intermediate water per molecule of DOAC, the "complete gel phase", as named by us, came to appear. This gel phase coexisted with the excess free water on adding further water.

In the present study, additional thermal analyses of DOAC-water systems in the temperature region extending down to -100 °C are carried out with particular attentions to the thermal behaviors of non-freezable interlamellar water together with the supercooled state of the complete gel phase.

The procedures taken for the preparations of the completely dehydrated DOAC and the mixture of DOAC with water were the same as reported in our previous paper.[5] The differential scanning calorimetry (DSC) was performed by using Daini Seikosha SSC/560U equipment with the high-pressure-crucible made of silver.

Figure 1 shows the DSC heating curve (at the rate of 2 °C min^{-1}) for the specimen prepared by cooling (at the rate of ca. 5 °C min^{-1}) the liquid crystalline phase of DOAC-water mixture at the water content of 51 gram %. As is shown, the stepwise endothermic anomaly characteristic to the glass transition phenomenon is found around -40 °C. In this figure, the thermal behavior in the high temperature region is the same as the result reported in our previous work, i.e., the endothermic peak I at about 0 °C due to the ice-meltig of the excess free water appears first, followed by the broad exothermic peak II caused by the crystallization of the gel phase into the coagel phase and successively by the complex endothermic peak III attributed to the coagel—gel phase transition and finally by the sharp endothermic peak IV due to the gel—liquid crystalline phase transition. Based on these facts, it may be pointed out that the glass transition phenomenon observed around -40 °C is induced from the supercooled gel phase and the interlamellar water does not crystallize on

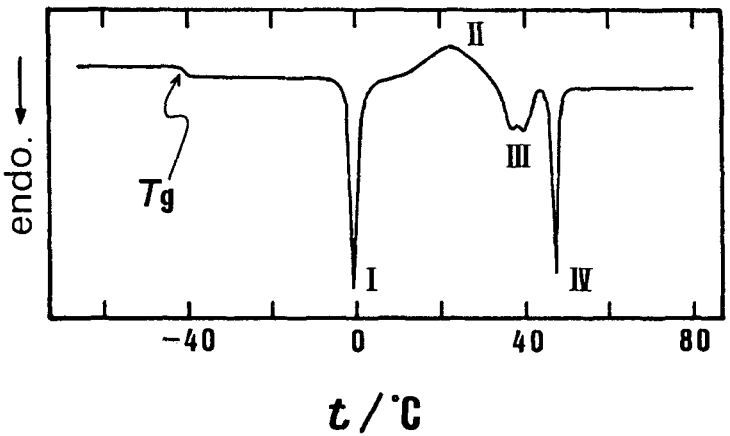

FIGURE 1 Typical DSC heating curve with the rate of 2 °C / min for DOAC-water system 51 gram % water content. T_g represents the glass transition temperature around 40 °C. Peaks I ~ IV correspond to the following phase changes, respectively ;

Peak I : from crystallized free water (ice) to liquid water,
Peak II : from supercooled gel to coagel,
Peak III : from coagel to gel (irreversible process),
Peak IV :from gel to liquid crystal.

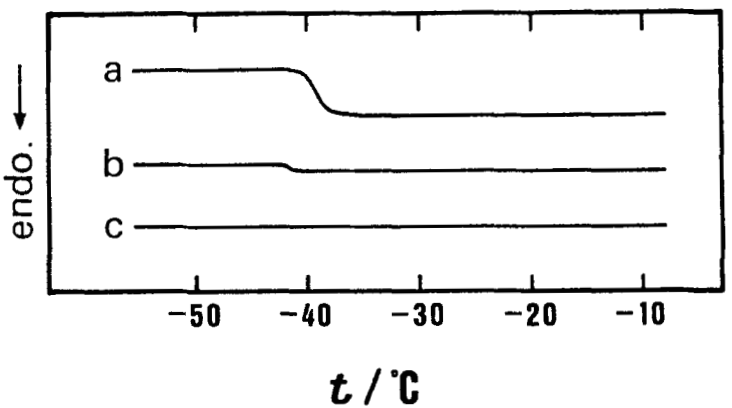

FIGURE 2 Dependence of the glass transition phenomenon of DOAC-water system on the heating rate and the water content. Curve a, reproduced from Fig. 1, is compared with curve b taken at the heating rate of 0.2 °C / min and curve c for the anhydrous DOAC.

cooling down to -100 °C. Figure 2 indicates the enlarged DSC curves around the glass transition temperature under various experimental conditions. Curve a, showing a marked endothermic anomaly, reproduces the result given in Figure 1. When the heating rate of 0.5 °C min^{-1} instead of 2 °C min^{-1} is used, the glass transition becomes less prominent, as shown by curve b. In the one component system of the completely dehydrated DOAC, the glass transition is no longer observed (curve c).

Based on these facts, we should like to discuss, hereon, the nature of liquid water in general,[6,7] in order to clarify the glass transition phenomenon found in this study from the viewpoint of the not-crystallized interlamellar water in the supercooled gel phase.

One of the present authors (S. S.) succeeded in obtaining the glassy state of pure water by use of the vapor condensation calorimeter,[6] indicating that pure liquid water cannot be brought into its glassy state by the supercooling process. On the other hand, the glassy state of the water enclosed into the pores of zeolite, different from pure water, has been reported.[8] As revealed in our previous paper, the polar head groups in the gel phase exist in the partly fused state which is brought about by three molecules of the intermediate water,[5] while two long hydrocarbon chains are arranged in the ordered crystalline state. That is, the gel phase lies in the state of the semi-crystalline mesophase.[9,10] Accordingly, we presume, it is difficult to admit the possibility that the source of the glass transition phenomenon found here is confined exclusively to the not-crystallized interlamellar water, though the anhydrous DOAC shows no this phenomenon. Anyhow, the glass transition phenomenon of the supercooled gel phase found in the present work is attributed to the cooperative interaction between the structural interlamellar water and the partly fused polar head groups. On this respects, we should like to propose here the new type of glassy state, i.e., "the glassy gel state", in addition to the glassy liquids, glassy liquid crystals and glassy crystals.[11,12]

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