New Phase Transition Phenomena of DL-2-Amino Butanoic Acid-Water System and DL-Norleucine-Water System

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DSC measurements of transition of DL-2-amino butanoic acid(DL-ABA) and of DL-norleucine(DL-NL) containing water were made. It was found that peak temperature obtained in transition of DL-ABA-water system was independent of water content and was 359 K compared with the B-A transition temperature, 506 K, whereas the peak temperature of DL-NL-water system was nearly equal to 390 K in solid-solid phase transition.

In the course of thermoanalytical and calorimetric studies on polymorphic behaviors of crystalline modifications for aliphatic α-amino acids with normal alkylchains[1-3], we have found that the α-form DL-NL is transformed into the γ-form DL-NL at 390 K with the enthalpy of transition of 4.4 kJ/mol by DSC[1-3], and values of transition temperature and enthalpy are in good agreement with those of Grunenberg et al.[4], and that the B-A transition in DL-ABA occurs in the wide range of temperature near its decomposition temperature, and the transition pattern is similar to that of γ-α transition in glycine[2]. From the measurements of partial molar heat capacities, it was recognized that the phase transitions of DL-ABA and DL-NL were of the first order[2].

It seems that thermal analysis on transitions of amino acid-water systems brings about suggestive information on transition phenomena of biological systems, especially of biomembranes, or of proteins.

In a process obtaining the B-form of DL-ABA crystals from aqueous solution by recrystallization, a sample containing small amount of water was heated at about 100 °C after filtration. The sample obtained was pure A-form[5]. Accordingly, it is suggested from the result that the B-form of DL-ABA containing water is converted into the A-form at lower temperature than its transition temperature, 506 K.

In this work, to confirm phase transition phenomena in amino acid-water systems, and to take account into the role of water molecules, thermal analysis of DL-ABA-water system was made in comparison with that of DL-NL-water system.

DL-2-amino butanoic acid (DL-ABA) and DL-Norleucine (DL-NL) were purchased from Sigma Chemical Co. The samples used were the purest reagents commercially available : the purity of the compounds was guaranteed to be more than 98%. These samples were further purified by crystallization, and then the B-form of DL-ABA was obtained from aqueous solution, and was identified as the B-form by IR absorption.

Differential Scanning Calorimeter (DSC) used in this experiment is a Model DSC-3100 Smade by MAC Science Co. About ten mg of sample and water was sealed in a Ag-Au seal pan, and the sample and the blank pans were set in each respective holders. DSC measurements were made at heating rate of 5 K min^{-1}.

DSC curve obtained for DL-ABA-water system is shown in Figure 1. As is shown in Figure 1, there are two peaks, the one

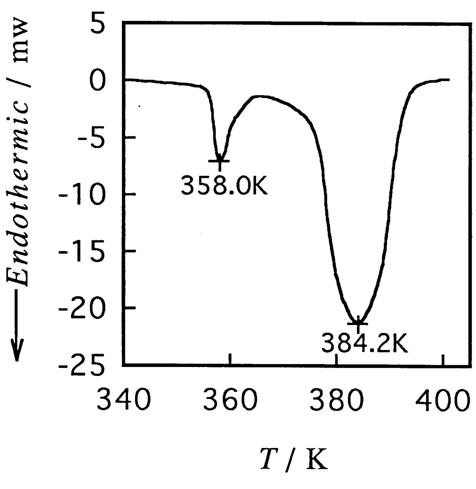

Figure1. DSC curve of DL-ABA containing water (24.4%) .

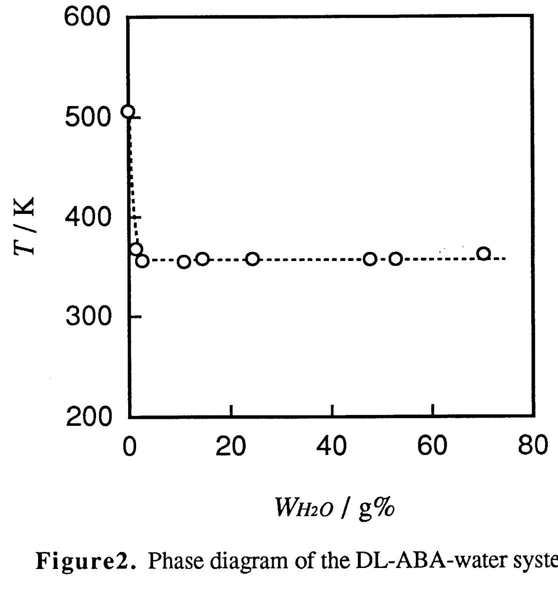

Figure2. Phase diagram of the DL-ABA-water system.

at a temperature of 358 K is associated with a transition of DL-ABA-water system and the other with the boiling point (384 K) of water. To confirm the transition, I.R. measurements were made. Different samples with about 60g% water content (WC) were heated at 353, 383 K, and dried *in vacuo* at room temperature. Samples after transition (353, 383 K) were identical with the A-form of DL-ABA obtained by Tsuboi et al[5]. It was found as a new transition phenomenon that the B-A transition temperature (Tt) is shifted from 506 K in the solid to a low temperature of 358 K only in the existence of water. Figure 2 indicates phase diagram. Tt decreased steeply at a very low WC of 1.4% and then remained unchanged around *ca.* 360 K. The resulting transition phenomenon led us to the suggestion that water plays a important role of an appreciable decrease in Gibbs energy of the A-form DL-ABA in comparison with the B-form.

It should be noted that similar phase transition behavior induced by water to that for DL-ABA was presented by Kodama et al.[6,7] for main (liquid crystal-gel) transition in L-dipalmitoylphosphatidylcholine-water system, in which water is involved as incorporated water.

Figure 3 shows apparent enthalpy change (ΔHt) for the B-A transition at Tt as a function of WC, where the ΔHt values were calculated using the weight of whole DL-ABA for each WC. The ΔHt value was decreased from *ca.* 5 kJ/mol to *ca.* 3.5 kJ/mol gradually with WC up to *ca.* 50 %, and then depressed abruptly to nearly zero kJ/mol. The decrease in the ΔHt value was ascribed to the dissolution of DL-ABA crystal and the overestimation of the weight of DL-ABA involved in the actual transition.

On the other hand, for DL-NL-water system the γ-α transition temperature was independent of WC and is nearly equal to 390 K in solid phase transition. This is probably because DL-NL is of higher hydrophobicity and is hard to be interacted with water in comparison with DL-ABA.

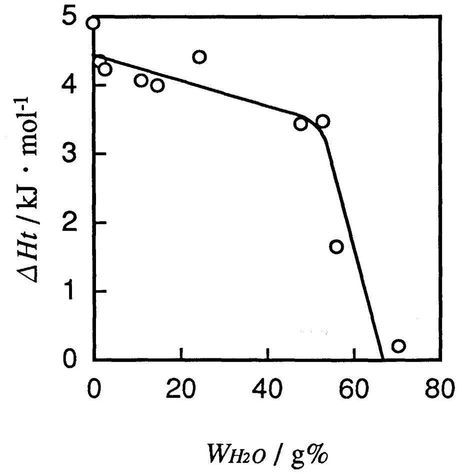

Figure3. Apparent enthalpy change of DL–ABA–water system *vs.* water content.

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