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The States of Water in Gel Cellophane Membranes

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Summary

The states of water in gel cellophane membranes were investigated by DSC measurements. An extra exothermic peak, which has not previously been reported, was observed at heating rates slower than 2.5K/min. The peak was ascribed to the crystallization of the liquid water in the heating process. The ratio of the nonfreezing water (often referred to as bound water) (g) to the dry membrane (g) was estimated to be 1.06. This value is far larger than the bound water contents reported for cellulose acetate membranes (FROMMER et al. 1972, TANIGUCHI et al. 1975).

Introduction

Gel membranes are widely used for desalination and biochemical separation processes (KELLER et al. 1976). The states of water in those materials, which are an important factor in interpreting the transport behaviour of solutes and solvents in the separation processes, are usually explained by two-state models (TOPRAK et al. 1979, BURGHOFF et al. 1979, FROMMER et al. 1972) or by three-state models (NAKAMURA et al. 1981, LEE et al. 1975, DROST-HANSEN 1969, AIZAWA et al. 1971, 1972, MIZUGUCHI et al. 1970, KRISHNAMURTHY et al. 1973), based on NMR, IR, DSC and other investigations. However, most workers (BURGHOFF et al. 1979, NAKAMURA et al. 1981, TANIGUCHI et al. 1975, YOON et al. 1982) have measured the states of water in gels at fixed cooling and heating rates in DSC. Although some workers made measurements at various heating rates, e.g. for poly(2-hydroxyethyl methacrylate) gels (LEE et al. 1975), they did not find a significant dependence of the DSC curves on the heating rate.

This report describes a detailed DSC analysis of water swollen gel cellophane membranes. The calorimetry was performed at cooling and heating rates of 0.31-10K/min, which revealed an extra exothermic signal in addition to the two endothermic peaks usually observed in the heating process.

Experimental

Water swollen gel cellophane membranes (GCM)(#500;Futamura

Co. Ltd) were used for the experiments. The thickness was about 100μm in the wet condition. The freezing and melting of pure water, and of water in GCM, were investigated with a DSC apparatus (Perkin Elmer Type II) equipped with a cooling cell. Before measurement, external water was carefully removed from the GCM by wiping with filter paper. The aluminum pans which were used to seal the samples were treated in boiling water for 1 hour before use. The sealed samples were cooled from 300 to 200K at cooling rates of 10, 5, 2.5, 1.25, 0.62 and 0.31K/min, and then heated to 300K at the same rates as in the cooling. The sample weights were about 2mg. The water content of the GCM was 3.3_3 g-H_2O/g-dry membrane at 25°C.

Results and discussion

During cooling, both the DSC curves of pure water, and those for the water in the GCM, gave only one sharp exothermic peak at all the cooling rates. The times needed for the freezing, which were independent of the cooling rates, were 19.5 sec and 22.5 sec respectively for pure water, and for water in the GCM. The freezing temperatures, which were assigned as the initial temperatures of the exothermic peaks, were 252.5 ± 0.5K and 256.5 ± 0.5K, respectively, and were independent of the cooling rates. Supercooling of the samples caused a depression of about 20 degrees in the freezing temperature.

The DSC curves in heating were found to be entirely independent of the cooling rate at which the samples were brought to the starting temperature. Fig. 1 shows the dependence of the DSC curves on the heating rate. When the heating rate becomes less than 2.5K/min, an exothermic peak appears in addition to the two endothermic peaks. Details of the DSC curves of the GCM, measured at heating rates of 10K/min and 0.31K/min, are given in Fig. 2. The former curve is an endothermic one composed of three overlapped peaks, but on the other hand, the latter curve consists of two endothermic peaks and one exothermic peak, which are designated as peaks 1, 2 and 3, respectively. Table 1 shows the maximum peak temperatures (T_1, T_2 and T_3), and the time intervals between the maxima of peak 1 and peak 2 (t_{12}). With a decrease of the heating rate from 10 to 0.31K/min, T_1, T_2 and T_3 were found to shift to lower temperatures, and T_2 approached 273K. This is due to the fact that the fast heating rate leads to the time lag of the response. Peak 2 is unequivocally assigned to the melting of the normal ice of free water (BURGHOFF et al. 1979, TANIGUCHI et al. 1975). The ice that melts at T_1 has been thought to be weakly perturbed by the polymer chain (TANIGUCHI et al. 1975), or to be condensed in the capillaries of membranes (BURGHOFF et al. 1979). Either mechanism is capable of causing a depression of the melting point of ice, of the order of a few degrees.

Peak 3, which was observed in the heating process, has not previously been reported for such membrane-water systems. However similar calorimetric observations i.e., the appearance of two endothermic peaks and one exothermic peak were reported

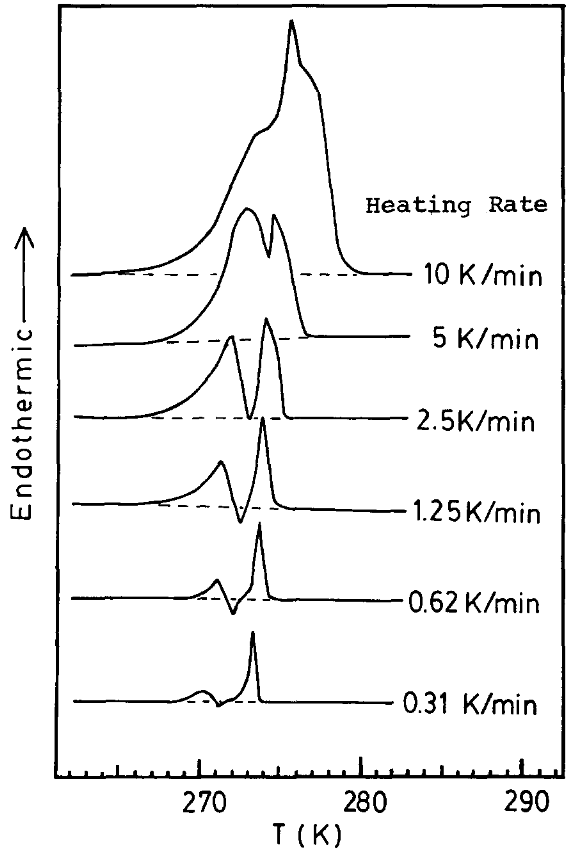

Fig. 1 Heating Rate Dependence of DSC Curves, Water-swollen Gel Cellophane.

TABLE I

Heating Rate Dependence of DSC Peak Temperatures and Time Interval between Peak 1 and Peak 2.

Heating Rate (K/min)	10	5	2.5	1.25	0.62	0.31
T_1 (Peak 1) (K)	273.0	272.8	271.6	271.2	270.8	270.2
T_2 (Peak 2) (K)	275.2	274.2	273.8	273.6	273.5	273.3
T_3 (Peak 3) (K)	-	-	272.8	272.4	271.6	271.2
t_{12} (sec)	13.2	16.8	52.8	115.0	261.3	600.0

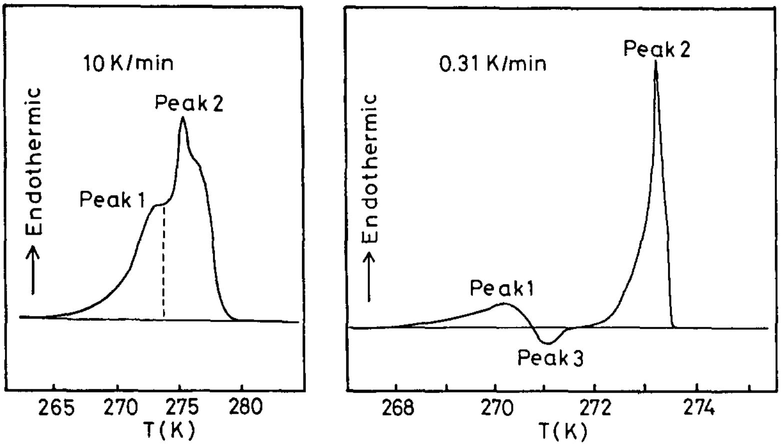

Fig. 2 DSC Heating Curves of Water-swollen Gel Cellophane.

for the polymorphism of ethynylestradiol (AGUIAR et al. 1967) and for the mesophase of poly(ethylenetetraphthalate-co-p-oxybenzoate)(MEESIRI et al. 1982). In both cases the exothermic peaks found at 393K or 380-431K were ascribed to crystallization of the liquid produced by the melting at the endothermic peak in the heating process.

If the heating rate is slow, there will be enough time for water melted at peak 1 to recrystallize again near the surrounding ice that provides nuclei for the growth of additional ice at below 273K. Hence an exothermic peak, peak 3, can appear if the heating rate is sufficiently low. It is found that peak 3 becomes observable when t_{12} is longer than about 50 sec (see Table 1).

The weights of water, W, corresponding to each peak were estimated from the following relation.

$$W = K \cdot R \cdot A \,/ \Delta H \cdot S$$

where ΔH is the transition enthalpy of water, K is the calibration constant (0.0476 for the instrument used), R is the range sensitivity in mcal/sec·cm, A is the peak area in cm^2, W is the weight of H_2O in mg and S is the chart speed of the recorder in cm/sec. Since the three peaks observed in the heating process appear at temperatures near 273.15K, the ΔH value at 273.15K, 79.4 mcal/mg, was used in the calculation of W. The weights of water for each peak thus obtained are summarized in Tables 2 and 3. It can be seen from Table 2 that when the heating rate was lowered from 5K/min to 0.31K/min, the water associated with peak 1 (W_1) decreased gradually to ca. 1/3 of the original amount. In contrast to this, the weight W_2 for peak 2 increased gradually, and W_3 for peak 3 gave a maximum at 0.62K/min. The decrease of W_1 is due to the fact that the exothermic heat for the recrystallization of the liquid H_2O is gradually included in peak 1. On the other hand, the increase of W_2 is caused by increasing amounts of the recrystallizing ice. The increasing time for recrystallization of the H_2O brings about an increase in W_3 when the heating rate is lowered to 0.62K/min. On the other hand, given sufficient time, there will be a decrease of W_3 as most of the exothermic heat will have been included in peak 1. Therefore a maximum in W_3 can be observed. According to these arguments, the sum of the weights $W_1+W_2-W_3$ should give the total freezing water in GCM. In fact, as seen in Table 2, the values are independent of the heating rate. These values agree with the amount of freezing water estimated from the data for the cooling process (table 3).

The amount of unfrozen water can be estimated by subtracting the freezing water from the total amount of water in GCM. The ratio of unfrozen water (g) to dry membrane (g), was calculated to be 1.06. The unfrozen water ratio of cellulose acetate membranes (CA) was reported to be 0.4 by TANIGUCHI et al. (1975), for a total water ratio 2.5 g-H_2O/g-dry membrane, and to be 0.4-0.7 by FROMMER et al. (1972), for total water ratios of 1.0-3.1 g-H_2O/g-dry membrane. The unfrozen water

TABLE II

Heating Rate Dependence of DSC Peaks of Gel Cellophane. dry membrane 0.46mg, water content 3.3_3 g-H_2O/g-dry membrane.

Heating Rate (K/min)	10	5	2.5	1.25	0.62	0.31
W_1 (Peak 1) (mg)	(0.400)	0.729	0.649	0.549	0.484	0.248
W_2 (Peak 2) (mg)	(0.669)	0.315	0.387	0.536	0.736	0.819
W_3 (Peak 3) (mg)	-	-	0.001	0.066	0.116	0.048
$W_1+W_2-W_3$ (mg)	1.069	1.044	1.035	1.019	1.104	1.019
Unfrozen Water (mg)	0.461	0.486	0.495	0.511	0.426	0.511

TABLE III

Cooling Rate Dependence of DSC Peaks of Gel Cellophane. dry membrane 0.46mg, water content 3.3_3 g-H_2O/g-dry membrane.

Cooling Rate (K/min)	10	5	2.5	1.25	0.62	0.31
W (mg)	1.03	1.06	1.01	1.03	0.993	1.08
Unfrozen Water (mg)	0.500	0.472	0.518	0.505	0.537	0.446

ratio in GCM obtained in this work is far larger than the values in CA. This difference may be ascribed to the larger amounts of OH groups in GCM. On the other hand, the unfrozen water ratio of cellulose with 30%-70% crystallinity is reported to be 0.11-0.23 g-H_2O/g-dry polymer (NAKAMURA et al. 1981), which is far smaller than the values for GCM and CA. Therefore it is supposed that the amounts of unfrozen water may be affected by the morphology of the polymer (FROMMER et al. 1972).

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