Calorimetric Study of the Glassy State. XV.† Thermodynamic Study of Pinacol Hexahydrate and Pinacol-d_2 Hexadeuterate

Masaharu OGUNI, Takasuke MATSUO, Hiroshi SUGA,* and Syûzô SEKI
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560
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The heat capacities of pinacol hexahydrate and its deuterate analogue were measured in the temperature region between 13 and 260 K. A phase transition was found and the temperature of transition was determined to be 192.14 K for the hydrate and 191.17 K for the deuterate, respectively. The enthalpy and entropy of the transition were estimated to be 924 J mol^{-1} and 5.10 J K^{-1} mol^{-1} for the hydrate and 944 J mol^{-1} and 5.28 J K^{-1} mol^{-1} for the deuterate. The transition was interpreted as the order-disorder change of the orientations of the pinacol molecule. Besides the phase transitions, an additional anomaly was found around 150 K for the hydrate and two around 130 K and around 160 K for the deuterate, respectively. All of them are relaxational in their characteristics and interpreted as glass transitions due to freezing of reorientational motions of the water molecule and the pinacol molecule. The transition temperature and the activation enthalpy for the higher glass transition of the deuterate were estimated to be 167.2 K and (34±4) kJ mol^{-1}, respectively.

The existence of pinacol (2,3-dimethyl-2,3-butane diol) hexahydrate was first shown by Fittig[1] in 1859. The structural feature of the hydrate is that the crystal at room temperature involves two kinds of orientational disorder. X-Ray diffraction study by Kim and Jeffrey[2] revealed that the crystal has a three-dimensional hydrogen-bonded network composed of layers of water molecules and hydroxyl groups of the pinacol molecules. The diol molecules are entrapped in the voids in this framework with two-fold orientational disorder. Thus, the crystal is clathrate-like but not a genuine clathrate because the hydroxyl groups of the alcohol are incorporated in the host lattice.

The dielectric constants of the crystal were measured by Cook and Meakins[3] in the temperature range 240—290 K, and by Garrington and Williams,[4] who observed high values of ε'_0 exceeding 50. On the basis of the systematic measurements on partially dehydrated samples, they showed that the large value of ε'_0 is due to reorientational motions of the water molecules. It is noted in their work that the behaviour of dielectric dispersion and absorption is closely related to that in hexagonal ice crystal. Thus both the pinacol and the water molecules are in orientationally disordered states.

The present paper reports calorimetric studies on pinacol hexahydrate and its deuterate analogue and discusses the observed heat-capacity anomalies in terms of ordering and freezing of the different molecular disorders. This study was undertaken as an extension of the calorimetric investigation on the relaxational heat capacity anomalies observed in stable crystals,[5] including $SnCl_2 \cdot 2H_2O$, $SnCl_2 \cdot 2D_2O$,[6] H_2O,[7] D_2O,[8] H_3BO_3 and D_3BO_3.[9] A study on phase diagram of water-pinacol system is also reported.

Experimental

Pinacol (Aldrich Chem. Co.) was purified by vacuum-distillation at 50—60 °C. The water content of the purified crystal was analysed by use of Karl-Fischer's method to be 0.36 mg cm^{-3}. This crystal was used for the phase diagram study of the pinacol-water system. The hexahydrate crystal was prepared by recrystallization of the purified pinacol from the aqueous solution. The recrystallization was repeated three times for further purification. Excess water in the hexahydrate crystal was removed by equilibrating the crystal in a desiccator with the monohydrate.

Prior to the preparation of the hexadeuterate, the hydroxyl groups of the purified pinacol were deuterated by repeating alternately three times the dissolution of anhydrous pinacol into heavy water (99.75%) and the complete dehydration of the solution by the use of molecular sieve 3A. The anhydrous pinacol thus obtained was vacuum-distilled at 50—60 °C in order to remove the trace of molecular sieve. The hexadeuterate was recrystallized from the heavy water solution of the pinacol-d_2. The deuterated crystal was kept in a desiccator with the monodeuterate as in the case of the hexahydrate. The molecular formula of the deuterate crystal was $(CH_3)_2(OD)CC(OD)(CH_3)_2 \cdot 6D_2O$, and the deuteration level was estimated to be 99.5%.

The heat capacity measurements were carried out by using the calorimetric apparatus described before.[9,10] The crystal was loaded into the calorimeter cell in a polyethylene bag where the water vapor pressure was adjusted in advance so as to prevent dehydration of the crystal. The loaded cell was cooled to liquid nitrogen temperature in a glass vessel, evacuated for twenty minutes, and filled with one-atmospheric pressure of helium gas. The cell was taken out of the vessel and tightly sealed by screwing a cap with a gold gasket. The mass of the sample was 38.970 g for the hydrate and 43.075 g for the deuterate, respectively. The inaccuracy of the heat capacity measurement is estimated to be 1% at liquid hydrogen temperature and less than 0.3% above 40 K.

Results and Discussion

Phase Equilibrium in Water–Pinacol System. The equilibrium phase diagram between water and pinacol was investigated by Pushin and Glagoleva in 1922.[11] They found existence of the stable monohydrate in addition to the hexahydrate. Their interest was concentrated on melting (and eutectic) phenomena, while ours is directed to the transitions in the crystalline state. Figure 1 shows the present results of the phase relation examined by DTA. The melting point of the hexahydrate was found to be 318.5 K, in agreement with Pushin and Glagoleva. Those of the anhydrous pinacol and of the monohydrate were higher by 1.0 K and 0.4 K respectively, than the values determined by them.

As shown in the figure, phase transitions were found

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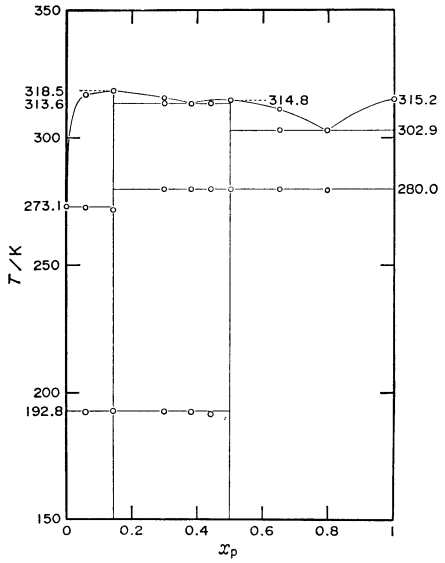

Fig. 1. Phase diagram of the system water–pinacol. x_p is the mole fraction of pinacol.

at 192.8 K and 280.0 K in the crystalline states of the hexahydrate and monohydrate, respectively. From the DTA curves the enthalpy of transition of the monohydrate was found to be larger by more than one order of magnitude than that of the hexahydrate. This is in good agreement with the observation that the room-temperature second moment[12] of the proton magnetic resonance of the monohydrate is considerably smaller than those of the hexahydrate and the anhydrous compound.

Heat Capacity. The heat capacities of the hexahydrate and the hexadeuterate were measured in the temperature region between 13 and 300 K. There appeared anomalies at 273 K and 277 K for the hydrate and the deuterate, respectively. These anomalies were interpreted as the melting of excess water contained in the crystal. Based on the assumption that this anomaly was attributed to melting of pure ice, the amount of excess water was estimated to be 127 mg for the hydrate and 69 mg for the deuterate corresponding to 0.33% and 0.16% of the sample masses,

Table 1. Molar heat capacity of pinacol hexahydrate

T_{av}/K	C_p/J K^{-1} mol^{-1}	T_{av}/K	C_p/J K^{-1} mol^{-1}	T_{av}/K	C_p/J K^{-1} mol^{-1}	T_{av}/K	C_p/J K^{-1} mol^{-1}	T_{av}/K	C_p/J K^{-1} mol^{-1}
13.07	8.458	65.76	107.6	(quenched)		(annealed)		192.37	979.7
14.09	10.01	67.49	110.8					192.57	859.6
15.11	11.59	69.22	114.0	125.98	207.9	126.35	208.6	192.86	425.9
16.14	13.21	70.97	117.2	127.93	211.0	128.83	212.5	193.29	309.8
17.20	14.95	69.73	114.9	129.89	214.2	131.31	216.2	194.21	306.0
18.28	16.77	71.50	118.2	131.78	216.9	133.75	220.1	196.06	309.1
19.39	18.81	73.32	121.4	133.61	219.7	136.16	223.9	197.90	311.2
20.58	20.82	75.15	124.7	135.45	222.7	138.57	227.8	199.72	312.5
21.83	23.13	76.95	127.9	137.31	225.3	141.00	232.4	201.54	316.1
23.01	25.39	78.76	131.1	139.18	228.2	143.43	237.2	203.37	318.3
24.23	27.75	80.55	134.4	141.03	231.1	145.87	242.7	205.22	321.0
25.51	30.19	82.34	137.5	142.87	233.6	148.27	247.3	207.16	323.3
26.75	32.68	84.14	140.7	144.68	236.7	150.62	251.3	209.27	326.3
28.07	35.20	85.95	143.8	146.47	239.4	152.95	254.8	211.45	329.1
29.58	38.18	87.76	146.9	147.73	241.5	155.25	258.5	213.62	332.2
31.19	41.36	89.60	150.1	148.54	242.7	157.52	262.1	215.76	335.2
32.74	44.48	91.45	153.1	150.08	247.7	160.43	266.4	217.90	337.9
34.29	47.58	93.26	156.2	152.23	252.1	163.31	270.7	220.01	340.7
35.85	50.64	95.07	159.2	154.34	256.0	165.22	273.4	222.77	344.5
37.46	53.85	96.96	162.3	156.42	259.5	167.30	276.8	224.85	347.4
39.08	56.91	98.89	165.5	158.48	263.3	169.38	280.2	226.92	350.1
40.65	59.98	100.84	168.5	160.52	266.4	171.46	283.6	228.97	353.2
42.27	63.10	102.79	171.8	162.54	269.2	173.56	287.3	231.01	356.0
43.93	66.29	104.73	174.9	164.49	272.6	175.68	291.0	233.04	358.7
45.58	69.44	106.67	178.0	166.52	275.4	177.77	294.9	235.07	361.4
47.23	72.69	108.61	181.2	168.51	279.1	179.85	298.8	237.05	364.0
48.87	75.81	110.54	184.3	170.52	282.2	181.90	303.1	238.80	366.5
50.47	78.91	112.48	187.1	172.57	285.3	183.93	307.2	241.02	369.8
52.11	82.03	114.42	190.3	174.59	288.7	185.93	312.2	243.39	372.8
53.78	85.28	116.34	193.1	176.50	292.9	187.88	318.0	245.75	376.3
55.45	88.41	118.25	196.2	178.49	296.3	189.42	322.9	248.09	379.3
57.12	91.55	120.18	199.0	180.40	300.2	190.34	326.9	250.42	382.7
58.80	94.70	122.10	202.3	182.29	303.9	190.90	330.2	252.72	385.6
60.51	97.98	124.04	204.3	184.16	307.9	191.35	333.7	255.02	389.1
62.27	101.23					191.80	336.8	257.29	392.3
64.04	104.49					192.15	754.1	259.55	395.6

Table 2. Molar heat capacity of pinacol hexadeuterate

T_{av}/K	C_p/J K^{-1} mol^{-1}	T_{av}/K	C_p/J K^{-1} mol^{-1}	T_{av}/K	C_p/J K^{-1} mol^{-1}	T_{av}/K	C_p/J K^{-1} mol^{-1}	T_{av}/K	C_p/J K^{-1} mol^{-1}
16.41	14.08	68.90	117.3	121.41	217.2	123.10	221.2	191.30	1263.5
17.27	15.60	70.57	120.5	123.70	221.1	125.19	225.4	191.47	997.8
18.16	17.13	70.79	120.9	125.98	225.9	127.25	229.1	191.72	517.3
19.13	18.97	72.44	124.1	128.27	229.9	129.61	233.6	192.08	354.1
20.18	20.89	74.01	127.1	130.53	234.9	131.83	237.8	192.51	341.0
21.31	23.03	75.55	129.9	132.74	239.0	134.02	242.0	192.96	340.6
22.44	25.29	77.20	133.2	134.96	243.8	136.18	246.1	193.50	341.5
23.51	27.61	78.96	136.5	137.23	247.3	138.31	249.8	194.74	342.8
24.65	29.70	80.67	139.7	139.46	251.8	140.41	253.6	196.39	345.6
25.93	32.29	82.34	143.0	141.63	255.9	142.48	257.3	198.43	348.4
27.35	35.22	83.98	146.3	143.81	259.6	144.50	261.2	200.72	352.2
28.77	38.01	85.64	149.4	146.00	264.0	146.78	265.3	203.24	355.8
30.15	40.88	87.32	152.6	148.16	267.5	148.93	269.5	205.73	359.8
31.56	43.81	88.97	155.8	150.30	271.6	151.05	273.9	208.23	363.2
33.03	46.78	90.64	158.9	152.42	275.5	153.22	279.3	210.74	367.4
34.52	49.86	92.44	162.3	154.50	279.7	155.44	284.7	213.23	371.2
36.00	52.91	94.25	165.8	156.16	281.8	157.71	289.5	215.69	374.6
37.45	55.81	95.97	169.0	157.28	284.3	159.87	294.1	218.14	378.8
38.84	58.53	97.75	172.3	158.80	289.1	162.01	297.8	220.57	382.2
40.21	61.29	99.58	175.9	160.79	294.9	164.12	301.4	222.99	385.7
41.58	64.01	101.38	179.2	162.79	299.2	166.20	304.8	225.39	389.1
43.08	66.96	103.21	182.7	164.80	301.8	168.27	308.8	227.77	392.6
44.69	70.15			166.80	306.3	170.31	312.8	230.13	396.0
46.25	73.16	(quenched)		168.78	309.5	172.67	318.2	232.47	400.0
47.87	76.40			170.73	313.4	174.58	320.8	235.15	404.0
49.51	79.60	96.54	169.7			176.48	325.2	237.47	407.0
51.12	82.70	98.19	173.3	(annealed)		178.36	329.4	239.78	411.0
52.69	85.72	99.94	176.6			180.22	333.5	242.07	413.9
54.23	88.84	101.83	180.1	105.29	186.6	182.06	338.3	244.34	417.6
55.77	91.80	103.78	183.8	106.79	189.5	183.87	342.5	246.76	421.1
57.27	94.73	105.76	187.4	108.51	192.9	185.76	347.3	249.34	424.9
58.82	97.72	107.80	191.4	110.63	196.6	187.45	353.6	251.89	429.0
60.42	100.83	109.93	195.0	112.70	200.6	188.77	358.6	254.42	432.5
62.09	104.01	112.13	199.7	114.73	204.6	189.55	362.8	256.98	436.1
63.83	107.53	114.42	204.5	116.77	208.6	190.16	367.7	259.58	440.6
65.55	110.85	116.75	208.3	118.85	212.6	190.67	372.1	262.16	444.0
67.24	114.08	119.09	212.6	120.97	217.1	191.07	604.8	264.72	447.6

respectively. The heat capacity contribution from the excess water was corrected for below 260 K by using the heat capacity data of the ice and heavy ice.[7,8] The heat capacity data are collected in Tables 1 and 2. Figure 2 gives the plots of the data together with those for the deuterate in an enlarged scale on the left side (110 K—145 K).

Both the hydrate and deuterate underwent a phase transition around 190 K as expected from the DTA result. Since the transitions are of the first order, all the measurements below the transition temperatures were made on the samples precooled slowly to 100 K in order to avoid incomplete conversion of the crystal into the low temperature phase. The temperature equilibration in the sample proceeded very slowly near the transition points, requiring a few days in the worst case. The temperature drift was followed for 12 h in most of the measurements in this region. The equilibrium temperature for the heat capacity calculation was determined by extrapolation of the temperature *vs.* time curve to the infinity of time assuming the exponential relation between them.

The heat capacity curves have additional small anomalies around 150 K for the hydrate and around 130 K and 160 K for the deuterate, respectively. The data in the anomalous regions are shown in Fig. 3 as the encraty (C_p/T) *vs.* the temperature. The equilibration time became extremely long in these regions, and either an exothermic or endothermic effect was observed depending on the thermal history of the sample. The following series of measurements was performed in order to study the hysteretic behavior in more detail. The hydrate sample was first equilibrated at 180 K and cooled with two different rates, $\simeq$8 mK min^{-1} and $\simeq$1.7 K min.$^{-1}$) The heat capacity measurement of the slowly cooled crystal was started at 125 K and continued up to 170 K by the step-by-step heating method in which the temperature increment was kept

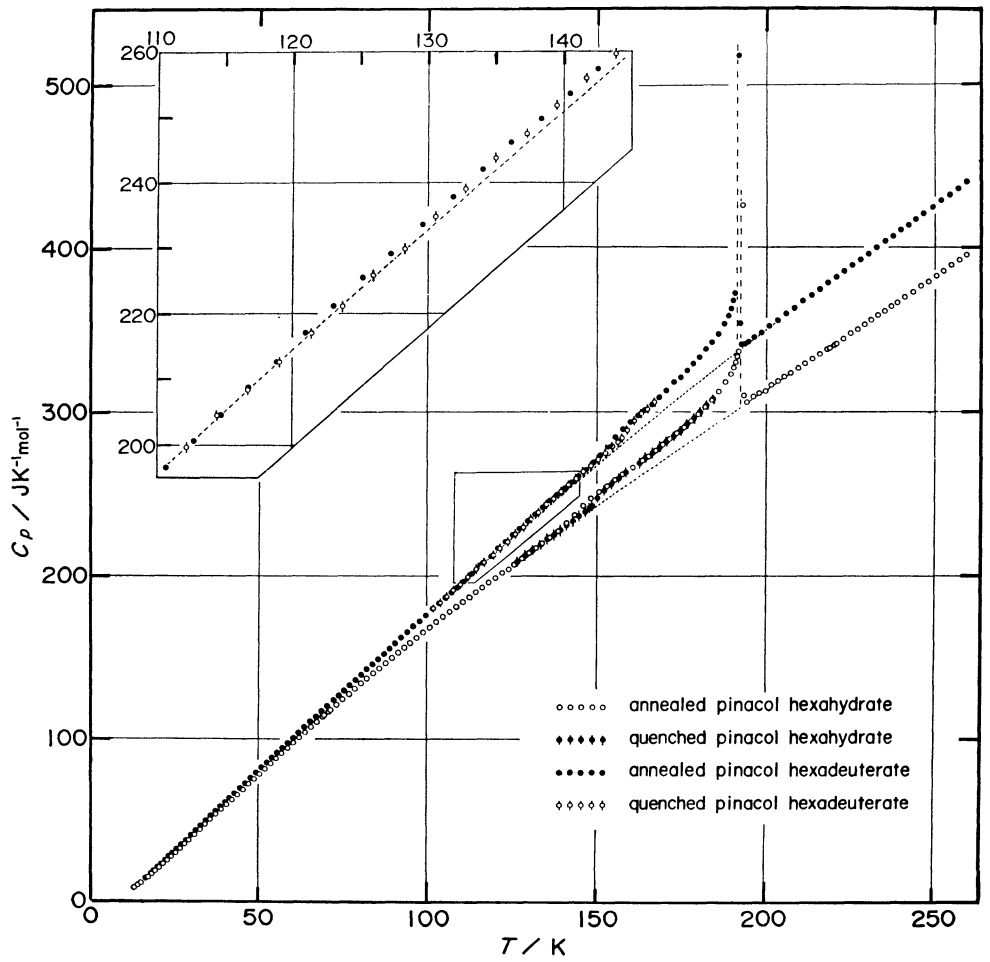

Fig. 2. Heat capacity of pinacol hexahydrate and pinacol hexadeuterate crystals.

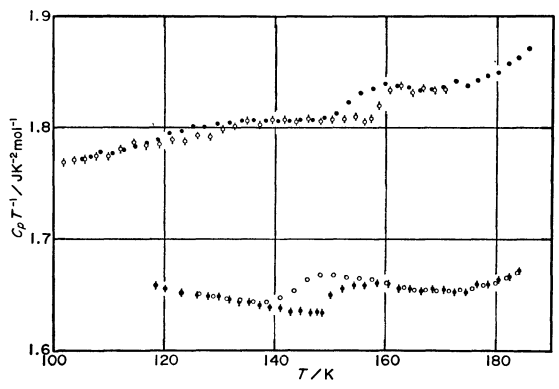

Fig. 3. Encraty (C_p/T) of pinacol hexahydrate (lower curve) and pinacol hexadeuterate (upper curve). The barred circles (⊖ and ⊜) represent the quenched crystal and the plain circles (○ and ●) the slowly cooled crystal.

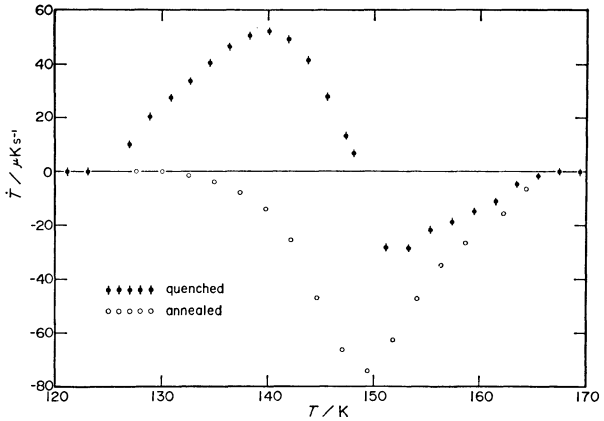

Fig. 4. Temperature drift *versus* temperature curves of pinacol hexahydrate.

approximately equal to 2 K and the drift followed for 35 min. Only endothermic drift was found in this series of measurement.

The measurement on the quenched sample was initiated at 120 K and followed the similar procedure up to 180 K. In this case the exothermic temperature drift occurred first and then an endothermic one as the temperature was raised. The former drift was followed for 40 min, and the latter for 60 min. The exothermic effect started around 125 K, reached the maximum rate at 140 K, decreased rapidly and disappeared around 149 K. The endothermic effect appeared above 149 K and remained appreciable up to 168 K, above which temperature the equilibration time

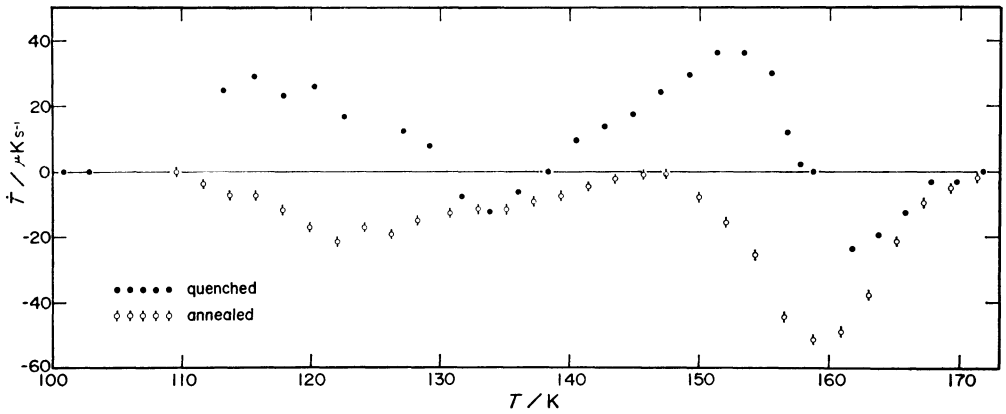

Fig. 5. Temperature drift *versus* temperature curves of pinacol hexadeuterate.

returned to its normal value. Figure 4 shows the rate of the temperature drift of the calorimeter cell determined at 30 min after turning off the heater.

For the deuterate, the temperature of the sample was equilibrated at 175 K where the equilibrium was reached rapidly, and decreased to the liquid nitrogen temperature at two different cooling rates. Measurement of the temperature drift was started at 110 K for the slowly cooled sample and at 100 K for the quenched one. The observed change of the drift rate with the temperature is shown in Fig. 5. In the case of the slowly cooled sample, only an endothermic effect was observed with two minima in the drift rate around 125 K and 160 K. In the quenched sample, positive and negative temperature drifts appeared alternately twice on heating. The drift approached the normal behavior above 170 K.

Appearance of different thermal drifts depending on the cooling rate is characteristic of a glass transition in the extended sense[5] as we have shown with tin chloride dihydrate,[6] hexagonal ice,[7,8] and orthoboric acid.[9] We interpret the relaxational anomalies in the present substances in the similar way. The main consequence of this interpretation is that a relaxational reorientation of the molecules is associated with the glass transition and that its relaxation time at the glass transition temperature is comparable with the time required for a single heat capacity measurement. The two relaxational anomalies in the deuterate crystal suggest that two different molecular processes are involved. The problem is then to assign molecular motions to the anomalies in the hydrate and deuterate and will be discussed later in this section. It should be added that there is an ambiguity in the determination of the heat capacity in the glass transition region due to irreversible changes occurring in the crystal. The values given in Tables 1 and 2 were calculated as elsewhere.[6,9]

Determination of Enthalpy and Entropy of the Transition. The anomalous part of the heat capacity was separated from the total by drawing a base-line which joins smoothly the heat capacity curves above 220 K and

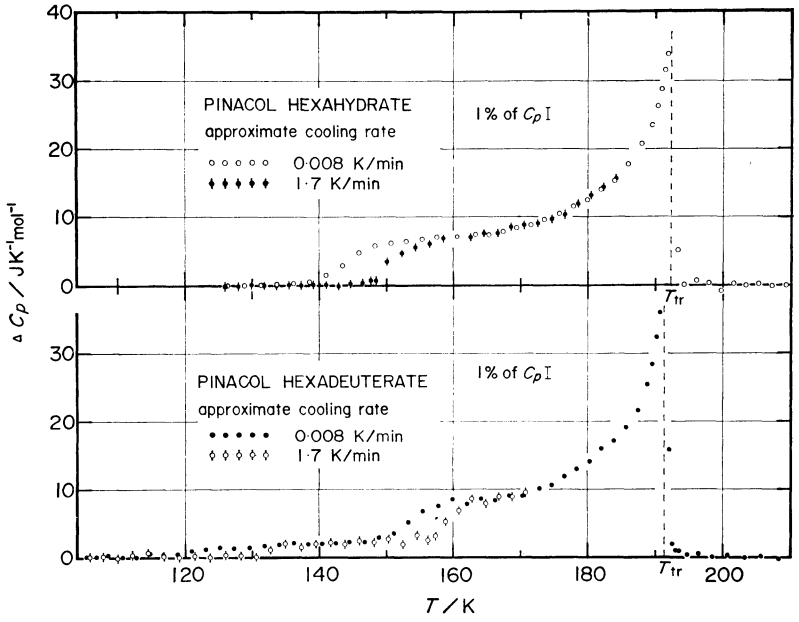

Fig. 6. Anomalous part of the heat capacity of pinacol hexahydrate and pinacol hexadeuterate.

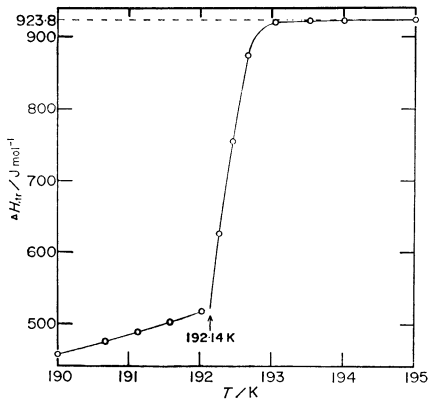

Fig. 7. Excess enthalpy *versus* temperature curve of pinacol hexahydrate.

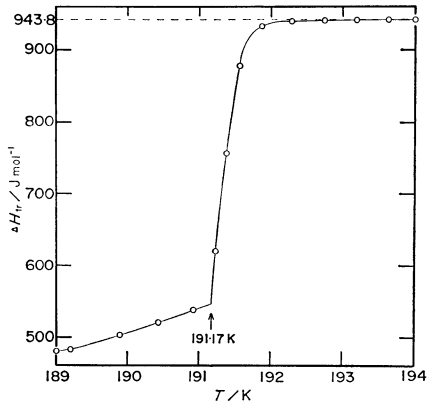

Fig. 8. Excess enthalpy *versus* temperature curve of pinacol hexadeuterate.

below the glass transition, as shown in Fig. 2. The anomalous part thus obtained is plotted in Fig. 6 where the upper half of the figure represents the hydrate and the lower the deuterate. The enthalpy and entropy of the transition were calculated by a numerical integration of the anomalous heat capacity for the slowly cooled sample and found to be 924 J mol^{-1} and 5.10 J K^{-1} mol^{-1} for the hydrate and 944 J mol^{-1} and 5.28 J K^{-1} mol^{-1} for the deuterate, respectively. The transition temperature was determined as the temperature at which the abrupt increase of the enthalpy occurred. Figures 7 and 8 show the excess enthalpy against the temperature around the transition point for the hydrate and the deuterate. The broken lines in the figures represent the total transition enthalpy. The transition temperature is 192.14 K for the hydrate and 191.17 K for the deuterate.

Mechanism of the Phase Transition and the Deuterium Isotope Effect on the Transition Temperature. In an NMR study published separately, we measured the proton spin-lattice relaxation times T_1 and $T_{1\rho}$ of the present substances.[13] The both substances showed almost the same magnitude of discontinuity in $T_{1\rho}$ at the transition temperature. This indicates that the phase transitions are closely related to the motion of the pinacol molecules rather than the water molecules.

It has been shown by the X-ray study[2] at the room temperature that the pinacol molecules are in a disordered state. If the phase transitions are due to ordering of the orientational disorder of the molecules the transition entropy is expected to be $R\ln 2$ ($=5.76$ J K^{-1} mol^{-1}). The entropy change experimentally determined is approximately equal to this value. The phase transition can thus be interpreted in terms of the order-disorder change in the orientation of the pinacol molecules.

The transition temperature may be taken as a certain measure of the strength of the interaction among the pinacol molecules. The deuteration causes a slight decrease ($\simeq 1$ K) in the transition temperature, indicating the corresponding decrease in the interaction. If we assume the inverse sixth power dependence of the interaction energy on the pinacol–pinacol distance, the isotope effect in the transition temperature is reproduced by 0.09% increase of the intermolecular separation on deuteration. The lattice constants of the deuterate have not been determined, but in the relatively short ($\simeq 0.26$ nm) hydrogen bonds, the O–O distance in the deuterium bond is longer than in the corresponding hydrogen bond by up to 0.0022 nm or 0.8% of the bond length.[14] If a similar elongation of the hydrogen bonding occurs in the pinacol hexadeuterate, the negative isotope effect in the transition temperatures will be understood by the above argument based on the simple geometrical consideration.

The Relaxation Time and Activation Enthalpy. The exothermic and endothermic drift in the high temperature glass transition region of the deuterate were analysed by fitting an exponential function of time in which linear change of the temperature with the time was also taken into account to allow for the residual heat leak between the calorimeter cell and its surrounding. The relaxation times thus calculated are plotted in Fig. 9. The activation enthalpy determined from the plot was (33 ± 4) kJ mol^{-1}. The relaxation time becomes 1 ks at 167.2 K.

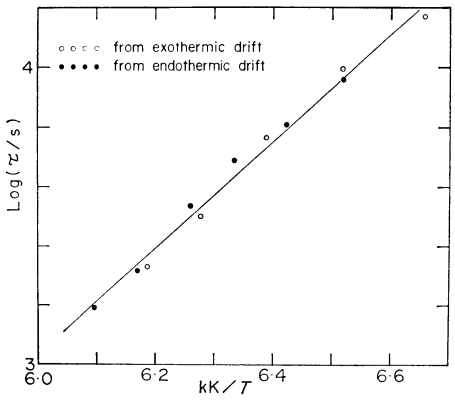

Fig. 9. Arrhenius plot of the enthalpy relaxation time derived from the calorimetric temperature drift at the upper glass transition of pinacol hexadeuterate. The open circles from the exothermic drift of the quenched crystal and the closed circles from the endothermic drift of the slowly cooled crystal.

Origin of the Glass Transitions. A glass transition takes place in principle whenever a molecular process involving passage by the molecule over a potential barrier occurs with the rate constant comparable with the inverse of the time scale of the experiment. There are two possibilities for such molecular motions in the pinacol hexahydrate. Kim and Jeffrey[2] suggested from the crystal symmetry that the hydrogen atoms in the hydrogen bonds are disordered. Cook and Meakins[3] pointed out a close similarity in the dielectric property between the pinacol hexahydrate and the ice I_h crystal. Namely, ε'_0 was found to be 77 along the water layer and 16 perpendicular to the layer, and the maximum absorption frequency at -5 °C is 6 kHz, comparable with 5 kHz in the ice. The large value of ε'_0 can be explained in terms of the reorientation of the water molecules. From the structural and dielectric evidences we can suppose that the hydrogen bonds are in dynamic disorder at the room temperature. At lower temperatures the dynamic disorder will change either to the order through a phase transition or to a static disorder by falling out of thermal equilibrium with other degrees of freedom of the substance. The dielectric study by Cook and Meakins shows that the latter is more likely. If we take 1 ks as the demarcation between the dynamic and static disorder and the Arrhenius parameters given by Cook and Meakins, the glass transition will occur at 170 K.

Another possibility for the molecular origin of the glass transition is the reorientational motion of the pinacol molecule. It was shown already that the orientation of the pinacol molecules orders at the phase transition. Thus, one may at first think that this degree of freedom need not be considered in the discussion of the origin of the glass transition because the orientation of the pinacol molecule is already ordered when the crystal is cooled to the glass transition temperature. However, the ordering can be incomplete at some temperature in the low temperature phase as is often the case in order-disorder transitions. The residual disorder would then cause a glass transition when it freezes into a static disorder. The glassy state so formed has a peculiar property that the frozen-in degree of freedom possesses a long range order. The magnitude of the heat capacity increment at the glass transition is determined by the temperature dependence of the transitional heat capacity and the relaxation time. The glass transitions in tin chloride dihydrate and orthoboric acid are of this kind. The phase transitions in the present substances are of the first order but there are excess heat capacities below the transition temperatures. Therefore the partial disorder in the low temperature phases can be responsible for the glass transitions.

As described in the experimental section, there are two glass transitions in the deuterate around 130 K and 160 K, whereas there is one in the hydrate around 150 K. Our previous experience on the hydrogen bonded systems show that if there is a glass transition in a hydrate crystal then there is a glass transition in the deuterate analogue and *vice versa*. Generalizing this observation to the present case, we assume that two different mechanisms are involved in the glass transition of the hydrate corresponding to the two glass transitions in the deuterate. This assumption is supported by the following evidence. First, the glass transition in the hydrate occurs at an intermediate temperature between the two glass transitions of the deuterate and none occurs above or below. Second, the glass transition region of the hydrate is broader than either of the glass transition regions of the deuterate (Figs. 3 and 4).

If one accepts that both the hydrate and deuterate undergo two glass transitions, the next step is to assign them to the two possible molecular motions discussed above. It was shown by the nuclear magnetic relaxation method that the reorientational motion of the water molecules occurs at higher temperature than the pinacol molecule.[13] The upper glass transition of the deuterate is attributed to the reorientation of the water molecule and the lower to the pinacol molecule. The activation enthalpy derived from the temperature drift data of the deuterate (33 ± 4) kJ mol^{-1} is equal to the activation enthalpy (33 kJ mol^{-1}) of the water reorientation in the hydrate obtained by NMR. In tin chloride dihydrate and ice I_h where reorientation of the water molecules is responsible to the glass transition, the glass transitions shift to higher temperature on deuteration.[6-8] The shifts (5—10 K) of the glass transitions in these compounds are comparable with the difference in temperature of the glass transition of the hydrate and the upper glass transition of the deuterate.

The lower glass transition in the deuterate is assigned to the second of the molecular motion discussed above, the reorientation of the pinacol molecule in the void of the clathrate-like structure. This motion is directly related to the phase transition. In the above, possibility of the lattice expansion on deuteration was discussed in relation to the negative isotope effect in the phase transition temperature. The same lattice expansion will enlarge the void in which the pinacol molecule reorients and thus decrease the height of the potential barrier hindering the molecular motion. This will result in faster reorientation of the pinacol molecule when compared at the same temperature and hence in the lower glass transition temperature in the deuterate than in the hydrate in agreement with above assignment of the molecular motion.

So far as has been known, the glass transition temperature increases invariably on deuteration. The present case is an exception in this respect. This will not be surprising if we consider that only the water and the hydroxyl part of the pinacol molecule were deuterated in the present crystal. The main part of the molecule responsible for the phase transition and the lower glass transition has not been deuterated. In contrast to this, motion of the deuterium itself is responsible for the glass transitions in those substances which undergo positive isotope effect on deuteration in the glass transition temperatures. Properties of the methyl-deuterated pinacol compounds will be interesting in this respect.

Conclusion

We have shown that pinacol hexahydrate and hexadeuterate undergo phase transitions and glass

transitions and discussed their molecular mechanisms from the calorimetric data. The molecular motions emerging from the discussion are generally consistent with the structural, dielectric, and NMR information available. However, a fundamental question of why the water molecules are disordered down to the lowest temperature has not been answered yet. This is closely related to the residual entropy of the ice I_h crystal and is in sharp contrast to the behavior of the layer hydrogen bonded crystals containing metal ions.[15] Low temperature study of other clathrate and clathrate-like hydrates formed by organic molecules will be interesting with regard to their transitional and relaxational properties.

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