Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **8**: 33–44, 1990.

Dielectric Study on Pure and KOH-doped Tetrahydrofuran Clathrate Hydrates★

O. YAMAMURO, T. MATSUO, and H. SUGA★★
Department of Chemistry and Chemical Thermodynamics Laboratory, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

(Received: 25 January 1988; in final form: 11 May 1988)

Abstract. Complex dielectric permittivities of pure and KOH-doped ($x = 1.8 \times 10^{-4}$) tetrahydrofuran clathrate hydrates were measured in the temperature range 20–260 K and in the frequency range 20 Hz–1 MHz. The relaxation time of the water reorientational motion was found to decrease drastically as a result of the doping; e.g., the relaxation time of the doped sample was 10^{-9} times shorter than that of the pure sample at 70 K. The activation enthalpy of the motion was reduced to 7.4 kJ mol^{-1}. On cooling the crystal, the value of ε' decreased suddenly at the 62 K phase transition to the $\varepsilon_{\infty 2}$ value of the pure sample and at the same time ε'' disappeared. No dispersion effect due to the guest reorientation was observed below the transition. These data indicate that both the host and guest molecules become ordered or, at least, change their mobility drastically. In the pure sample, a relaxation phenomenon of ε_{02} was found around the glass transition region. The relaxation times agreed well with those derived from the enthalpy of relaxation in a calorimetric study.

Key words. Dielectric permittivity, phase transition, doping effect, relaxation phenomenon, tetrahydrofuran clathrate hydrate.

1. Introduction

A clathrate hydrate is a rare inclusion compound in the sense that both of host and guest molecules are orientationally disordered. During the last twenty years, Davidson and his coworkers have studied various aspects of the disorder in their extensive experimental and theoretical work [1–3]. In particular, most of the dielectric and NMR data of many clathrate hydrates have been obtained by his group.

Disorder in a crystal usually disappears through a phase transition on cooling. In clathrate hydrates, however, no ordering transition except the guest ordering in trimethylene oxide (TMO) structure I hydrate [4, 5] has been observed so far. This strange feature can be considered as follows. For the guest molecules, the guest–guest interaction energy is so small, especially in structure II hydrates, that the fluctuating electric field induced by the orientationally disordered water molecules overrides it. Because the symmetry of the hydrate cages, except for the 14-hedron,

---

★ Dedicated to Dr D. W. Davidson in honor of his great contributions to the sciences of inclusion phenomena.

★★ Author for correspondence.

is quite high, guest molecules have a great deal of orientational freedom. The TMO molecules become ordered in the 14-hedral cages. The reason for the water reorientation, which is equivalent to a proton-configurational change, is not a problem associated with the interaction energy but rather one of kinetics. From a consideration of the relaxation time, the proton-configurational motion would be frozen-in at 80–100 K before the hypothetical transition temperature is reached on cooling. This is the same situation as in the case of hexagonal ice [6].

Tetrahydrofuran (THF) hydrate is the most popular structure II hydrate owing to its facile preparation. Very recently, we measured the heat capacities of pure and KOH-doped ($x = 1.8 \times 10^{-4}$) THF-hydrate crystals [7, 8]. A glass transition in the pure sample and a phase transition in the doped sample were found for the first time. They are considered to be due to freezing of the short-range order and to development of the long-range order in the proton-configuration of the host lattice, respectively. The doped KOH enhanced the proton configurational motion and enabled us to observe the equilibrium heat capacity around the phase transition, as in the case of hexagonal ice [9, 10]. The transition temperature was 61.9 K and the transition entropy was $2.36\ \mathrm{J\ K^{-1}(H_2O\text{-}mol)^{-1}}$. Another interesting finding was that the heat capacity of the doped sample was considerably smaller than that of the pure sample below the transition. Because the glass transition of the pure sample was 85 K, this heat capacity decrease should be ascribed to some modes other than the proton configuration. Entropy calculated from the heat capacity difference between 0 and 62 K was $0.82\ \mathrm{J\ K^{-1}(H_2O\text{-}mol)^{-1}}$ and so the remaining quantity $1.54\ \mathrm{J\ K^{-1}(H_2O\text{-}mol)^{-1}}$ was the entropy due to the proton ordering.

In the present study, we measured the complex dielectric permittivities of the pure and KOH-doped ($x = 1.8 \times 10^{-4}$) THF-hydrate crystals in the temperature range 20–260 K and in the frequency range 20 Hz–1 MHz. The measurements were made in order to clarify how the dopant affects the dielectric behavior of the constituent molecules and whether the transformation into the low-temperature phase is complete. In KOH-doped hexagonal ice, the transformation was not considered to be complete even with heavy doping, and dielectric dispersion due to a remaining disorder was observed [11]. The guest molecules are expected to change their motional state at the transition, as suggested from the rather large heat capacity decrease in the low-temperature phase.

2. Experimental

2.1. SAMPLES

Tetrahydrofuran was purchased from Tokyo Kasei Kogyo Co. Ltd. and was purified with a rectifier having more than 80 theoretical plates (Shibata Kagaku Kikai Co. Ltd.). Water was also purified by deionization followed by distillation. These methods of purification were the same as those used in the previous calorimetric study [7, 8].

Pure THF-aqueous solution was prepared by mixing the desired quantities of the two liquids by a gravimetric method. The composition was $\mathrm{THF \cdot 16.61\ H_2O}$, which is slightly richer in THF than the composition at the congruent melting point determined by the calorimetric study ($\mathrm{THF \cdot 16.64\ H_2O}$). KOH-doped THF solution was prepared by mixing KOH-solution (0.1 mol dm^{-3}) (Wako Pure Chemical Ind. Ltd.) and the above purified THF and water. The composition was THF·16.59 H_2O and the mole fraction of KOH to water was 1.8×10^{-4} which is the same as that in the calorimetric study.

2.2. DIELECTRIC MEASUREMENT

The three electrode cell, newly constructed for this study, is schematically shown in Figure 1. The external shape of the cell is disc-like having a diameter of 20 mm and a height of 7 mm. The high-potential, the low-potential, and the guard electrodes are represented by B, G, and F, respectively. These are made of gold plated brass. The spaces between B and F, and between F and G are both filled with Stycast 2850-FT epoxy resin (Emerson & Cuming Japan) C, which has good electric insulating properties and adhesive strength and almost the same linear thermal expansivity (2.9×10^{-5} K^{-1}) as brass. Several temperature cycles between 20 and 300 K did not cause any trouble in the connections between the electrodes. The width between the high and low potential electrodes is 1.225 mm and the inside volume is about 0.5 cm^3. The cell constant and the floating capacitance are 0.8425 pF and 0.0132 pF, respectively. They were calibrated against vacuum and highly purified benzene.

The sample E was introduced with an injector through twin copper tubes (1 mm O.D.) attached coaxially on the top of the cell. Then the top of the copper tube was pinched off and sealed with Araldite rapid type epoxy resin (CIBA-GEIGY). The cell was set up as a solid sample (a pressed disc or a single crystal) in the cryostat previously reported [12], which is designed for solid samples. The temperature stability of the cryostat is within 0.02 K and the absolute temperature was read with a Chromel–Constantan thermocouple, the accuracy of which is within 0.1 K. Complex dielectric permittivity was measured at 15 frequencies ranging from 20 Hz to 1 MHz. Three types of apparatus were used for the measurement, depending on the frequency range: LCR Meter 4275A (Yokogawa Hewlett Packard) (1 MHz–10 kHZ), LCZ Meter 4276A (Yokogawa Hewlett Packard) (10 kHz–100 Hz), and Capacitance Bridge 1615A (General Radio) (100 Hz–20 Hz).

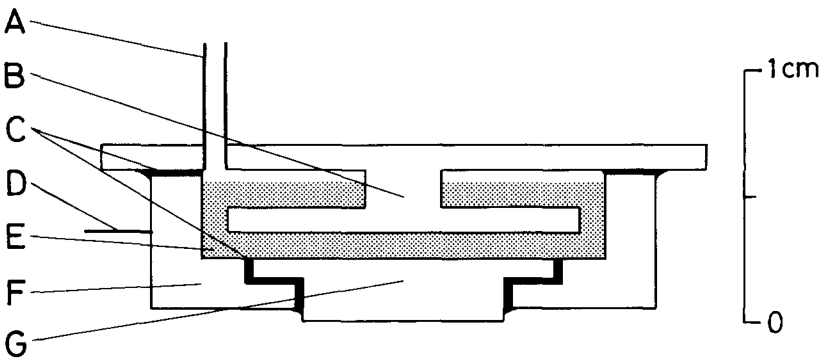

Fig. 1. Schematic drawing of the dielectric cell. A: Sample filling tube, B: high-potential electrode, C: epoxy resin, D: guard terminal, E: sample, F: guard electrode, G: low-potential electrode.

Both the pure and the KOH-doped hydrates were crystallized at about 270 K during slow cooling (0.1 K min^{-1}). They were then heated up to 275 K and annealed at that temperature for about 1 h. The temperature ranges studied were 20–260 K for the pure sample and 20–160 K for the doped sample. The appearance of jumps in ε' and ε'' due to eutectic melting limited further observation above 160 K in the doped sample. The measurement was carried out in a heating direction for the pure sample and both in heating and cooling directions for the doped sample. The temperature step of the heating and cooling experiments was normally 5 K.

Because of the simple structure of the cell, a gap between the sample crystal and the electrodes was suspected to occur during the experiment. The maximum gap was calculated to be 0.013 mm (1.1% of the total width of the sample) at 20 K on the basis of the thermal expansivity data of THF-hydrate [13] and brass. This would produce an error of 4% at 20 K, assuming the gap acts as a series condensor with the capacitance of the vacuum. However, no discontinuous change was observed over the whole temperature range and the experimental value ε' of the pure sample agreed well with the previous data, as is shown in the next section. Therefore, no correction for the gap was made when compiling the present data.

3. Results and Discussion

3.1. PHASE TRANSITION IN THE KOH-DOPED SAMPLE

Temperature dependences of the dielectric constant ε' (upper) and loss ε'' (lower) are shown in Figure 2 for the high temperature region and in Figure 3 for the low temperature region. Open symbols (○, △, □, ▽, ◇, ✧) and closed symbols (●, ▲, ■, ▼, ◆, ✦) represent the data of the pure and KOH-doped samples, respectively. The same symbols denote the data measured at the same frequency.

The results for the pure sample were almost the same as those reported by Hawkins and Davidson [14] and Gough *et al.* [15]. Two distinct dispersions due to the host and guest molecules were observed at 130–260 K and 20–50 K, respectively. Dielectric constants at the low- and high-frequency limits were as follows: $\varepsilon_{01}(180\ \mathrm{K}) = 76$, $\varepsilon_{\infty 1}(=\varepsilon_{02})(100\ \mathrm{K}) = 5.9$, $\varepsilon_{\infty 2}(20\ \mathrm{K}) = 3.5$. These constants agreed well with the corresponding literature values observed at the same temperatures: $\varepsilon_{01} = 80$, $\varepsilon_{02} = 6.00$, $\varepsilon_{\infty 2} = 3.5 \pm 0.1$. Here the number in the suffix ‘1’ and ‘2’ refers to the host and guest, respectively.

The KOH doping dramatically changed the dielectric properties of the hydrate crystal. The dispersion of the host shifted down to the low temperature side by more than 100 K. KOH doping induced drastic acceleration of the proton-configurational motion. This is consistent with the calorimetric result that a first-order phase transition appeared in the KOH-doped sample in place of a glass transition in the pure sample [7, 8]. The constants ε'_{01} and $\varepsilon''_{\mathrm{max}}$ in the dispersion region became about 1.6 times larger than those in the pure sample and they increased steeply with temperature above that region. The rapid increase in dielectric constant was also observed in KOH-doped hexagonal ice by Ida *et al.* [16] and is considered to be due to the ionic conduction of the dopant.

The most interesting result in this study is the change in ε' and ε'' at the transition

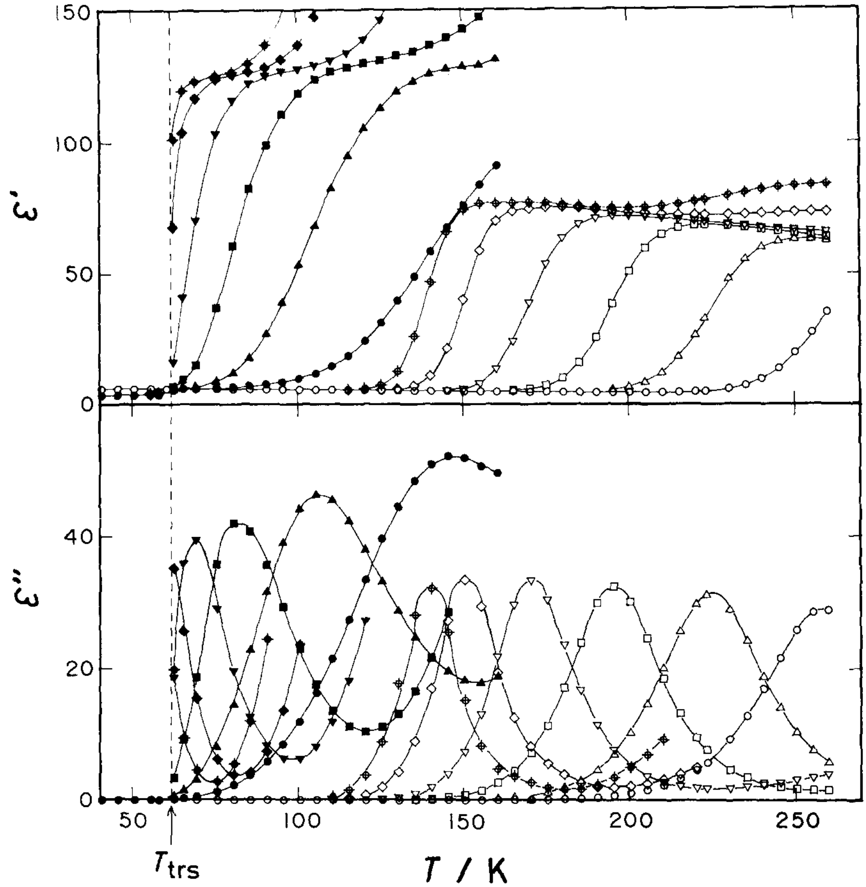

Fig. 2. Temperature dependence of ε′ (upper) and ε″ (lower) of the pure (open symbols) and KOH-doped ($x = 1.8 \times 10^{-4}$) (closed symbols) THF-hydrate crystals in the high temperature region. ○: 1 MHz, △: 100 kHz, □: 10 kHz, ▽: 1 kHz, ◇: 100 Hz, ◈: 20 Hz.

point (61.9 K) represented by a dashed line in the figures. The real part ε′ suddenly decreased down to about the value of $\varepsilon_{\infty 2}$ of the pure sample and the imaginary part ε″ disappeared at the same time. Any appreciable dispersion due to the guest molecules was no longer observed below T_{trs}. This behavior was reproduced well both in the heating and cooling through the transition. The data plotted were obtained in the heating experiment for the sample annealed at 55 K for 2 h. These results give new insight into the nature of the phase transition. The dopant catalyzed the host lattice so that it achieved the completely ordered state without any remanent disorder being apparent within a reasonable experimental time. The THF dipoles are also expected to be orientationally ordered in view of the small ε′ value below T_{trs}.

In the structure II THF hydrate, the guest molecule is enclathrated in the 16-hedral cage which is almost spherical and has tetrahedral symmetry, at least in the proton-disordered state. Davidson [17] has shown the importance of the

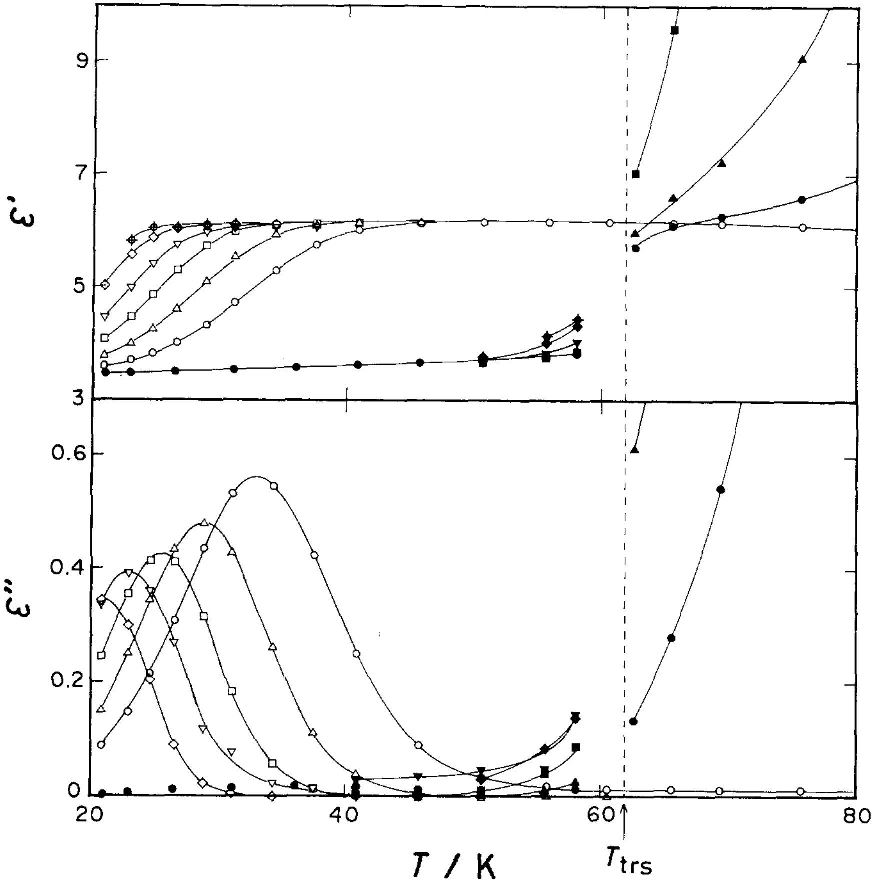

Fig. 3. Temperature dependence of ε′ (upper) and ε″ (lower) of the pure (open symbols) and KOH-doped ($x = 1.8 \times 10^{-4}$) (closed symbols) THF-hydrate crystals in the low temperature region. ○: 1 MHz, △: 100 kHz, □: 10 kHz, ▽: 1 kHz, ◇: 100 Hz, ◈: 20 Hz.

electrostatic interaction between the host and guest molecules in determining the dielectric property of the crystal. The low temperature behavior of the dielectric constant of pure THF hydrate was successfully explained by assuming that each guest molecule occupies one of four tetrahedrally disposed preferred orientations whose populations are determined by the electrostatic interactions arising from the disordered water dipoles. Ordering of the guest dipoles in the low temperature phase, if any, should be attainable by the occurrence of some non-tetrahedral electrostatic field in the 16-hedral cages produced by the proton ordering. The short-range van der Waals interaction can also restrict THF orientation but any drastic change of the cage structure is not expected to occur at temperatures as low as 62 K.

The transition entropy determined by the previous calorimetric measurement [8] was 2.36 J $K^{-1}(H_2O\text{-mol})^{-1}$, which consisted of two parts: 1.54 J $K^{-1}(H_2O\text{-mol})^{-1}$ related to the proton ordering and 0.82 J $K^{-1}(H_2O\text{-mol})^{-1}$ related to some modes other than the proton configuration. Now one can infer that the latter is ascribed to the change in motional state of the guest dipoles, possibly by undergoing orientational ordering. The entropy of $0.82\,\mathrm{J\,K^{-1}(H_2O\text{-}mol)^{-1}}$ corresponds to $13.6\,\mathrm{J\,K^{-1}(THF\text{-}mol)^{-1}}$. The structural [17] and dielectric [15] studies indicate that the THF molecule in the 16-hedral cage effectively undergoes isotropic reorientation at a relatively high temperature. At low temperatures, however, it is natural that the energy differences between various orientations increase compared with kT and the preferred orientations become distinct, as suggested by the potential calculation [17]. If the THF dipole preferably orients one of four hexagons of the 16-hedral cage, as in the case of EO [18] and TMO [4] molecules inside the 14-hedral cages, the configurational entropy should become $R\ln 4(=11.5\,\mathrm{J\,K^{-1}\,mol^{-1}})$, which is comparable in magnitude with the experimental entropy $(13.6\,\mathrm{J\,K^{-1}\,mol^{-1}})$. Of course, it is possible that the dipole orients in other directions than the above four in the high temperature phase and the THF molecule also becomes ordered about its dipolar axis at the low temperature phase. The latter is not a dipole fluctuating motion, but this can be clarified by NMR study.

It is not so easy to explain the entropy due to the proton ordering. If the host water lattice of the hydrate follows the same 'ice rule' [20] as hexagonal ice, the entropy of ordering should be Pauling's value of $R\ln(3/2)(=3.4\,\mathrm{J\,K^{-1}\,mol^{-1}})$ [21]. The experimental value was $1.5\,\mathrm{J\,K^{-1}(H_2O\text{-}mol)^{-1}}$ which is only 44% of the theoretical value. In the case of KOH-doped hexagonal ice ($\Delta_{\mathrm{trs}}S=2.3\,\mathrm{J\,K^{-1}\,mol^{-1}}$ [9, 10]), the dielectric dispersion due to proton motion was still observed below the transition [11]; i.e. some disorder persisted below the transition. In the present case, however, no dispersion was observed in the low temperature phase. There seem to be only two ways to explain the experimental entropy. One is that the low temperature phase is partially ordered and the remaining disorder is frozen-in simultaneously with the transition. The other is that the high-temperature phase is partially ordered and the effect of ordering is buried in the so-called 'normal' heat capacity so as to reduce the apparent entropy of transition. In the host lattice, there are three crystallographically non-equivalent hydrogen-bonds and the O—O—O angles are fairly distorted. This seems to contribute to the preferential generation of six non-equivalent orientations of a water molecule in the host lattice. This circumstance will bring about a wide distribution of energy of disordered proton configurations and makes it difficult to distinguish the corresponding heat capacity contribution from those due to other lattice modes. It is not clear whether this situation can be related to the smaller Kirkwood correlation factor g of the hydrate (2.0) compared to that of ice I_h (3.7) [15]. The possibility of the partially-ordered high-temperature phase will be examined quantitatively by a direct measurement of the absolute entropies of both the pure and KOH-doped THF-hydrates. The precise heat capacity and $p-T-x$ phase diagram of the gas-liquid equilibrium of the THF–water system is required for this.

3.2. RELAXATION TIME OF THE PROTON-CONFIGURATIONAL MOTION

The relaxation time τ governing the proton-configurational motion (water reorientational motion) determined in the previous dielectric and calorimetric studies (open symbols) can be compared with the present dielectric study (closed symbols), and the results are summarized in Figure 4. In the present study, the dielectric relaxation time of the pure (■) and doped (◆) samples were determined by finding a temperature at which the dielectric loss at each frequency had a maximum. The data represented by ● and ▲ will be described later. The present data of the pure sample (■) agreed well with those reported by Hawkins and Davidson (□) [14]. These were drastically shortened by the KOH-doping. Not only the absolute values but also the slope of the relaxation data decreased. The value around 70 K is 10^{-9} times shorter than that obtained from the enthalpy relaxation phenomenon (○). This is the reason why the proton ordering takes place at 62 K in the KOH-doped sample within a reasonable time. From the slope of the curve, the effective activation enthalpy of the proton-configurational motion in the KOH-doped sample was found to be 7.4 kJ mol^{-1}. This value was about 1/4 of that for the pure sample (31 kJ mol^{-1}) and about half of that for the KOH-doped hexagonal ice (14.6 kJ mol^{-1}) [11] and cubic ice (14.9 kJ mol^{-1}) [22].

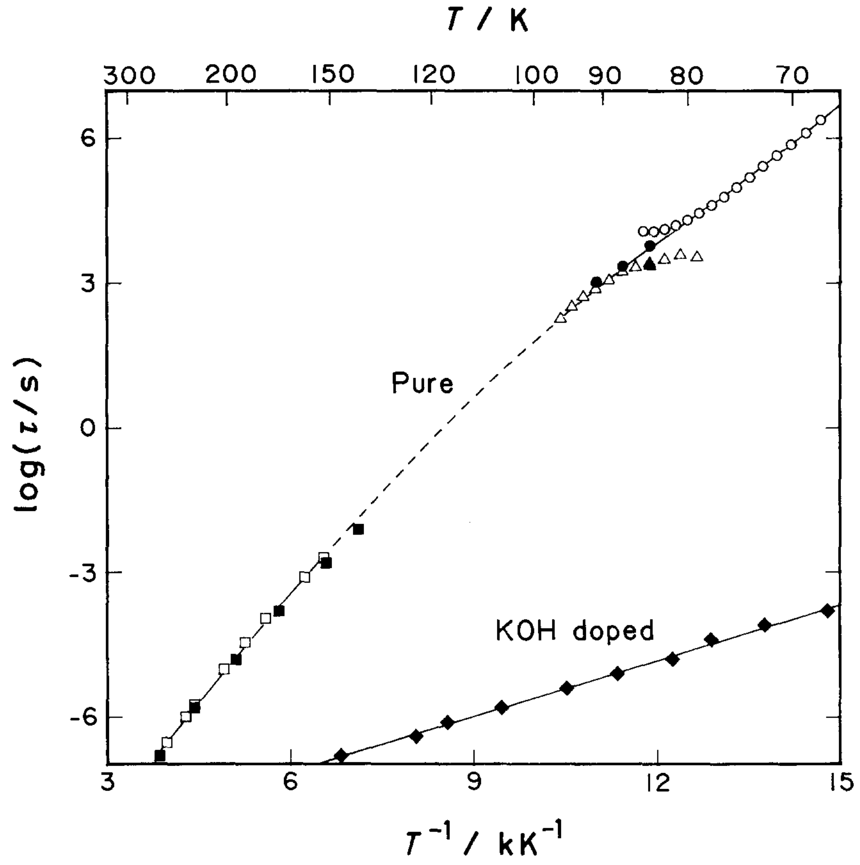

Fig. 4. Temperature dependence of the various relaxation times related to the water reorientational motion of the pure and KOH-doped ($x = 1.8 \times 10^{-4}$) THF-hydrates.

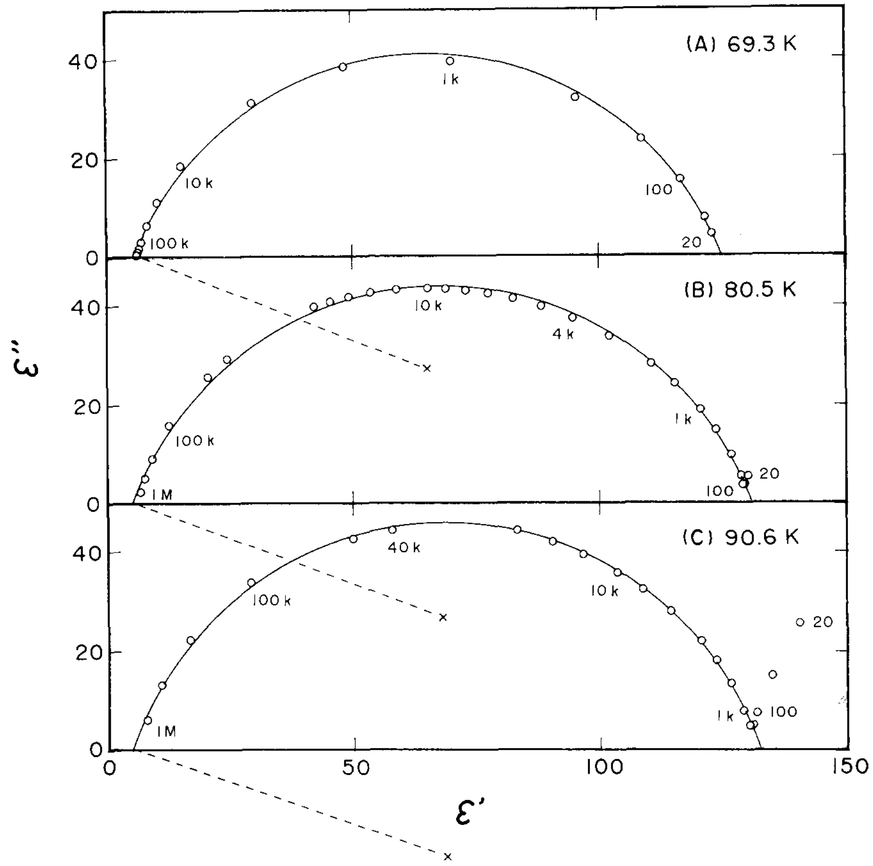

Fig. 5. Complex permittivity loci of the KOH-doped ($x = 1.8 \times 10^{-4}$) THF-hydrate. Frequencies are in Hz.

Figure 5 shows the Cole–Cole arcs obtained for the KOH-doped sample at three different temperatures above the transition. The parameter α representing the width of the distribution of relaxation time was as follows:

T/K	69.3	80.5	90.6
α	0.23	0.22	0.21

Comparing these data with those for the pure sample (0.02–0.06 at 150–270 K) [14], it is clear that the KOH-doping induced a large distribution of relaxation times. The same parameter obtained for the KOH-doped hexagonal ice was also around 0.2 [11]. This agreement suggests that the wider distribution is a common property of the KOH-doped hydrogen-bonded systems.

3.3. TIME DEPENDENCE OF ε_{02} AROUND THE GLASS TRANSITION OF THE HOST

Since the enthalpy of relaxation associated with the water reorientation was observed in the pure specimen around the glass transition region, the corresponding dielectric phenomenon would be expected to occur in the same temperature range. This was observed in the experiment. Figure 6 shows the time dependence of ε' measured at 100 kHz of the pure sample during the course of 7 h. The sample was cooled rapidly down to 84.2 K (A), 87.5 K (B), 90.9 K (C), and warmed rapidly to 84.2 K (D) after annealing at 78 K for 48 h. The dielectric constants observed correspond to ε_{02}, and they tend to relax towards the equilibrium values at the respective temperatures with characteristic times τ. The relaxation seems to proceed

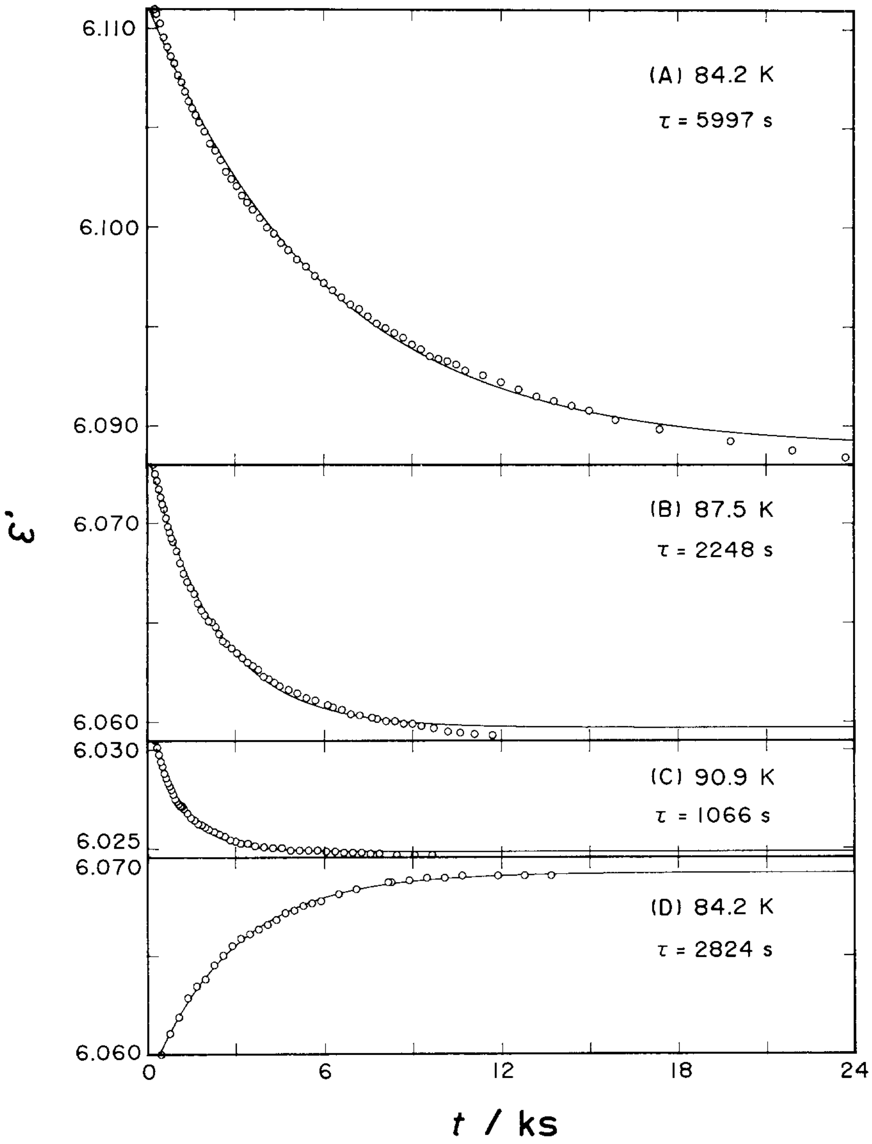

Fig. 6. Relaxation of ε' measured at 100 kHz around the glass transition region of the pure THF-hydrate. (A), (B), (C): after rapidly cooling, (D): after rapidly warming for the sample annealed at 78 K for 48 h.

with exponential behavior. The time constant τ and the amount of relaxation decreases with increasing temperature. Solid lines in Figure 6 were determined by fitting the data with the function

$$\varepsilon_{02}(t) = A \exp(-t/\tau) + B,$$

where A and B are constants and t the time. Each relaxation time is shown in Figure 6 and plotted in Figure 4 with symbols ● for (A), (B), (C) and ▲ for (D). Interestingly, both plots lie on the curve of the relaxation time derived from the enthalpy of relaxation at the glass transition [8]. Moreover, each set of dielectric data corresponds to the calorimetric data of the sample having the same thermal history: the data ● lie on the curve extrapolated from the exothermic enthalpy of relaxation of the rapidly cooled sample (○), and ▲ on the curve from the endothermic relaxation of the annealed sample (△). Thus the time dependent behavior of ε_{02} can be correlated with the proton-configurational change in the host lattice. The low frequency permittivity limit of the guest dispersion, ε_{02}, decreases as the proton short-range order progresses (exothermic relaxation) and increases as the disorder progresses (endothermic relaxation). The coupling between the guest and host is clearly observed in the short-range ordered state of the host lattice.

It is well known that ε_{02} rises as $1/T$ on cooling at relatively high temperature but begins to deviate from $1/T$ around 120 K and becomes almost flat around 50 K [15]. This phenomenon has been explained by the existence of an energy difference between preferred orientations of dipoles in the perfect disordered cage in the proton configuration [15, 17]. The present result indicates that the development of the short-range ordering also give an important effect on the phenomenon. The calorimetric result [8] showed that the short-range ordering began to develop at about 120 K and stopped around 80 K.

4. Conclusion

The present dielectric study combined with the calorimetric one [7, 8] showed the existence of coupling between the guest and host molecules both in the short- and long-range ordered states of the proton configuration. Our previous calorimetric studies always showed the guest dependence of the ordering properties of proton systems. The glass transition was observed in dipolar THF [8] and EO [23] hydrate but not in nonpolar Ar [24] and Xe, Kr [25] hydrates. The phase transition was induced in KOH-doped THF-hydrate [7, 8] but only a glass transition in KOH-doped Ar-hydrate. These phenomena are all consistent with the present results. To investigate further the mechanism of the guest–host coupling, it would be interesting to study the thermal properties of hydrates of nonpolar, nonspherical guest molecules such as cyclopentane. One more interesting problem remaining is the possible ordered configurations of both the host and guest molecules in the low-temperature phase of the doped sample. This will be determined by using neutron diffraction.

Acknowledgements

We express our thanks to Associate Professor Kei-ichiro Adachi for his useful advice on the dielectric measurement. We are deeply indebted to Miss Noriko Onoda for her help in the measurement, creating the figures, and typing the manuscript.

References

1. D. W. Davidson: in *Water – A Comprehensive Treatise*, Vol. 2, Ed. F. Franks, Plenum Press, New York-London, 1972, Ch. 3.
2. D. W. Davidson and J. A. Ripmeester: *J. Glaciology* **21**, 33 (1978).
3. D. W. Davidson and J. A. Ripmeester: in *Inclusion Compounds*, Vol. 3, Eds. J. L. Atwood, J. E. D. Davies, and D. D. MacNicol, Academic Press, London, 1984, Ch. 3.
4. S. R. Gough, S. K. Garg, and D. W. Davidson: *Chem. Phys.* **3**, 239 (1974).
5. Y. P. Handa: *Can. J. Chem.* **63**, 68 (1985).
6. O. Haida, T. Matsuo, H. Suga, and S. Seki: *J. Chem. Thermodyn.* **6**, 815 (1974).
7. O. Yamamuro, M. Oguni, T. Matsuo, and H. Suga: *Solid State Commun.* **62**, 289 (1987).
8. O. Yamamuro, M. Oguni, T. Matsuo, and H. Suga: *J. Phys. Chem. Solids.* **49**, 425 (1988).
9. Y. Tajima, T. Matsuo, and H. Suga: *Nature* **299**, 810 (1982).
10. Y. Tajima, T. Matsuo, and H. Suga; *J. Phys. Chem. Solids* **45**, 1135 (1984).
11. S. Kawada and H. Dohata: *J. Phys. Soc. Jpn.* **54**, 477 (1985).
12. T. Matsuo and H. Suga: *Solid State Commun.* **21**, 923 (1977).
13. J. S. Tse: *J. de Physique (Paris), Colloq. C1*, **48**, 543 (1987).
14. R. E. Hawkins and D. W. Davidson: *J. Phys. Chem.* **70**, 1889 (1966).
15. S. R. Gough, R. E. Hawkins, B. Morris, and D. W. Davidson: *J. Phys. Chem.* **77**, 2969 (1973).
16. M. Ida, N. Nakatani, K. Imai, and S. Kawada: *Sci. Rep. Kanazawa Univ.* **11**, 13 (1966).
17. D. W. Davidson: *Can. J. Chem.* **49**, 1224 (1971).
18. T. C. W. Mak and R. K. McMullan: *J. Chem. Phys.* **42**, 2732 (1965).
19. R. K. McMullan and G. A. Jeffrey: *J. Chem. Phys.* **42**, 2725 (1965).
20. J. D. Bernal and R. H. Fowler: *J. Chem. Phys.* **1**, 525 (1933).
21. L. Pauling: *J. Am. Chem. Soc.* **57**, 2680 (1935).
22. O. Yamamuro, M. Oguni, T. Matsuo, and H. Suga: *J. Phys. Chem. Solids* **48**, 935 (1987).
23. O. Yamamuro, Y. P. Handa, M. Oguni, and H. Suga: *J. Incl. Phenom.*, **8**, 45 (1990) (this issue).
24. O. Yamamuro, M. Oguni, T. Matsuo, and H. Suga: *J. Inc. Phenom.*, **6**, 307 (1988).
25. Y. P. Handa, O. Yamamuro, M. Oguni, and H. Suga: submitted to *J. Chem. Thermodyn.*