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The Anomalies of Supercooled Water

Byoung Jip Yoon* and Mu Shik Jhon¹

Department of Chemistry Korea Advanced Institute of Science and Technology P. O. Box 150 Cheongyang, Seoul 131, Korea (Received January 7, 1984)

The anomalous behaviors of supercooled water are explained by using a two-solid-like structure model in which an equilibrium is assumed between open structures and closed structures. Besides these structures, small fraction of monomer exists in liquid water. The anomalies of liquid water are classified into two groups: structural and energetic. The structural anomalies appear in enlarged fashions in a supercooled state where the free volume is small.

Introduction

Water is an unusual liquid which has the various anomalous properties, while it is representative as a liquid on earth. Up to the present, scientists have continued many experimental researches on liquid water without ceasing to add theoretical explanations and predictions but they are not satisfactory

for understanding the structure. Theoretical views for models of water group are classified into two directions. In 1957, Pople¹ suggested a bent bond model in which hydrogen bonds (H-bonds) connecting adjacent water molecules were bent to yield a continuous distribution of bond angles and energies. This model gave a little explanations for the anomalous properties of water than reproduced the Morgan and Warren's X-ray diffraction pattern.² However, continuum theories³ have been favored to scientists due, maybe, to the fact that so is the conventional concept of H-bonding

* Department of Chemistry, Kangreung National University: San -1 Jibuyngdong Kangreung, Kangwondo 200, Korea

scheme and is, in part, supported by computer simulation studies.³ The beginning of the alternative is due to Bernal and Fowler,⁴ in 1933, who suggested the simultaneous existence of two crystal forms in the liquid state. Any "mixture models" are based on the supposed existences of various crystalline-like domains in water or several species of H-bonded water molecules. Advantages of these mixture models are in explaining the properties of water, besides in their rather easy formulation of models.

The modelings for water structure are to be tested by any of new experimental measurements. The abnormal behaviors of water are found in many of its properties. Some anomalies are as follows: A maximum appears in density and the thermal expansion coefficient is negative at low temperatures (below 4°C). The compressibility is much larger than those of other simple liquids and shows a minimum. The heat capacity of water is the largest of all known simple liquids, and so on.⁵⁻⁷ It is not exaggerating, here, to say that all the properties of liquid water are abnormal compared with the other molecular liquids in its stable liquid region, and they become much more unusual at lower temperatures. Supercooled water shows the anomalous behavior in some properties. Scientific interests in the properties of supercooled water are not so recent but have been since 1820,⁸ however, a broad review article is written by Angell in 1982.⁹ The anomalies of supercooled water are observed in the values of the thermal expansion coefficient, the compressibility, and the heat capacity at constant pressure (C_p) are shown in Figure 1. Such forms have not found in any other molecular liquids, even those with otherwise water-like properties such as H_2O_2 and N_2H_4 , nor in mixtures of water with more than 20 % of these liquids.⁹

These anomalies of supercooled water exclude less reasonable models of water. When one thinks, for a little while, again the approaches to models of water, it is difficult to expect any increase in the heat capacity with cooperative changes of H-bonded network in a uniform distribution of indistinguishable H-bonds provided that the H-bonds of water are in a medium state between strong H-bonded

network of ice and its greatly disrupted one. We are only able to think that H-bonds become stronger and bond angles become similar to those of ice with supercooling in continuum H-bonded networks, and that, in this case, the results show a decrease in the heat capacity.

Results obtained from a molecular dynamic simulation of model water are used to generate a representation of liquid water which corresponds closely to "V structure" described by Eisenberg and Kauzmann.¹⁰ It is hard, at the present stage, to make any conclusion on the structure of water and to find any singularities of the thermodynamic properties of water from the simulation results because of the less perfectness of model function of H-bond energy. There are two possible approaches to quantitatively defining of H-bonds:¹⁰ "energetic" and "geometric." In the energetic approach, two molecules with interaction energy below some threshold are taken to be H-bonded. The geometric definition of H-bond is developed in terms of the internal coordinates of the dimeric species relevant to the intermolecular interactions. None of these two approaches is unimportant for precise simulations. When one uses a realistic H-bond potential that is delicate in these two respects, if possible, many of peculiar results of water will be observed by computer simulation studies.

In the form of extended version of the early paper¹², Jhon and Yoon¹³ have explained the various properties of water and heavy water in the normal liquid region above the melting point by using a three-structure model (a more precise description is a two-solid-like structure model) which also considered the differences between solid-like structure of water and infinite network of ice structure from the viewpoint of broken H-bonded molecules. They have presented that, in the two-solid-like structure model, an equilibrium is established between open structures and closed structures, probably, of which a basic form is a five-membered ring connection. The open structures are not suspected as six-membered ice-I-like clusters. Besides these structures, the small fraction of monomers exists in liquid water.

Rasmussen and Mackenzie¹⁴ suggested that water molecules tends to, during supercooling, form ice-like clusters incorporating six or more monomers. To verify further the model proposed, we extended to examine to reproduce the anomalous properties of water in its supercooled state in this paper.

Model

In addition to the early model concept,¹² Jhon and Yoon have considered that the large heat capacity of water is due to the breaking of H-bonds with temperature increase, that gives large fluctuation in H-bond energy incorporating with H-bonded molecules, *i.e.*, the increase in the internal energy of liquid water comes out not only from excitations of intermolecular vibrations but also from H-bond breaking. From the spectroscopic data of intermolecular vibrations, the heat capacity is approximately half the actual heat capacity of water and is close to the value for ice. The additional quantity other than the vibrational heat capacity described

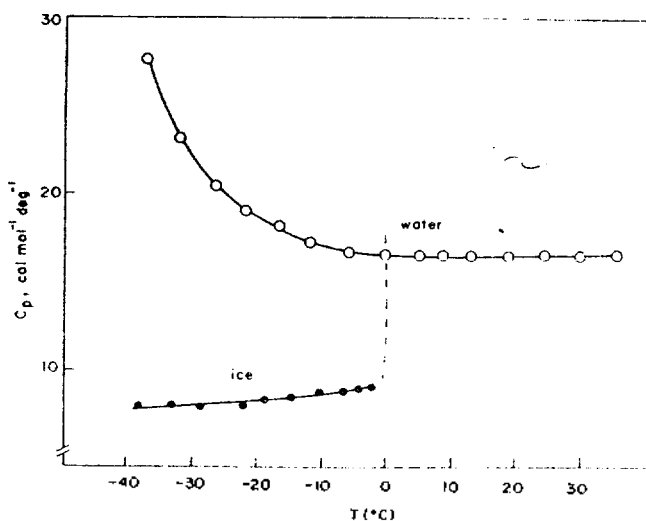


Figure 1. The anomalous behavior of heat capacity at constant pressure of supercooled water (from ref. 9).

by Eisenberg and Kauzmann,⁷ has been given by assuming the following simple relations.

$$\chi = 1 - \exp(E_V/E_H) \quad (1)$$

where χ is the fraction of molecules with broken H-bonds, E_V is the total intermolecular vibrational energy and E_H is the H-bond energy. E_V is calculated from the vibrational energy and E_H is the H-bond energy. E_V is calculated from the vibrational partition function using the spectroscopic data of intermolecular vibrational frequencies. One finds that the distribution of molecules with broken H-bonds is far from the Boltzmann distribution in their excitation which is a cooperative phenomenon. If $E_V \ll E_H$, Eq. 1 becomes $\chi = E_V/E_H$, that is a similar form to the cooperative thermal excitation of Fermi electrons.

The equilibrium constant, K , between open structures and closed structures is given by,

$$K = [\exp(-\Delta H + T\Delta S - p\Delta V)/RT]^q \quad (2)$$

where ΔH , ΔS , and ΔV are the respective changes of enthalpy, entropy, and molar volume between the two structures. R is the gas constant, and T is a absolute temperature. Eq. 2 has been used in early paper.¹² The average number of molecules, q , which change their structures cooperatively is assumed to decrease with temperature rise as the increase of the fraction of broken H-bonded molecules and is given by

$$q = q^*(1 - \chi) \quad (3)$$

The solid-like volume, V_s , is expressed in terms of V_{s1} and V_{s2} , which are the respective molar volumes of open structures and closed structures as follows,

$$V_s = \frac{K}{1+K} V_{s1} + \frac{1}{1+K} V_{s2} \quad (4)$$

The open structures are considered to have small fractions of six-membered structure of ice-I.

The thermal expansion coefficient, α , and the compressibility, β , of a liquid are commonly explained by the effect of introducing free volume of fluidized vacancies. However, in the case of liquid water, the contributions due to the change of solid-like volume are added to the values contributed by fluidized vacancies in the following way

$$\alpha = \alpha_f + \frac{V_s}{V} \alpha_s \quad (5)$$

and

$$\beta = \beta_f + \frac{V_s}{V} \beta_s \quad (6)$$

where V is the molar volume of water, and the subscript, f , denotes the contribution of fluidized vacancies. α_f and β_f have been calculated from the partition function while α_s and β_s are calculated from Eq. 4. Here, α_s has a negative value as the equilibrium is shifted, with increasing temperature, to closed structures which have the smaller molar volume than open structures. The calculated results of α , and β , gave good agreements with those estimated by

Eucken¹⁵ and by Smith and Lawson,¹⁶ respectively.

Rasmussen and Mackenzie¹⁴ suggested that the increase in the heat capacity at constant pressure, C_p , in a supercooled state, is an additional or structural specific heat. We also think that this anomaly is a structural one rather than an energetic anomaly found in a normal liquid range. C_p is expressed in two terms as follows

$$C_p = C_v + \frac{TV\alpha^2}{\beta} \quad (7)$$

Although the heat capacity at constant volume, C_v , follows a behavior in the extrapolated fashion from above the melting point, the second term in Eq. 7, in our model, gives the exponential increase with temperature decrease according to the change of equilibrium from closed structures to open structures.

Calculation and Discussion

The changes observed in the density of water supercooles indicate a tendency toward the more open packing of molecules possibly increased ice-likeness.¹⁴ The thermal expansion coefficient and the compressibility of V_s , due to the change in equilibrium are expressed by the following equations

$$\alpha_s = \frac{1}{V_s} \frac{qK}{(1+K)^2} \frac{\Delta H + p\Delta V}{RT^2} \Delta V \quad (8)$$

and

$$\beta_s = \frac{1}{V} \frac{qK}{(1+K)^2} \frac{(\Delta V)^2}{RT} \quad (9)$$

where $\Delta V = V_{s1} - V_{s2}$ and $p = 1$ atm. The increases in magnitudes of α_s and β_s , with temperature decrease are easily shown in a two-solid-like structure model. The extended calculation is shown in Figure 2 for the thermal expansion coefficient with the parametric values¹³ that are used to calculate the thermodynamic properties in a normal liquid range and are shown in Table 1. According to the results¹³ the remarkable decreasing tendency of free volume has been obtained near the melting point (about 1%) with cooling

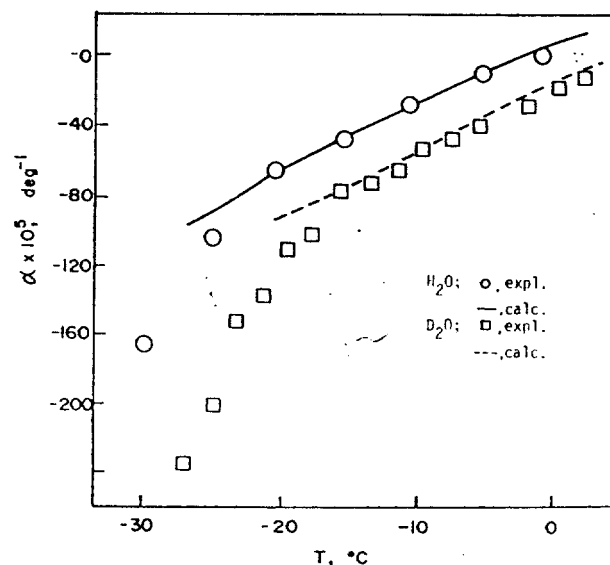


Figure 2. The thermal expansion coefficient of supercooled water.

TABLE 1: The Parametric Values used in the Calculation

H ₂ O	D ₂ O
ΔH ; -223 cal/mol	ΔH ; -256 cal/mol
ΔS ; -0.9304 eu	ΔS ; -1.016 eu
V_{l1} ; 19.58 cm ³ /mol	V_{l1} ; 19.58 cm ³ /mol
V_{l2} ; 17.36 cm ³ /mol	V_{l2} ; 17.37 cm ³ /mol
q^* ; 22.4	q^* ; 22.4

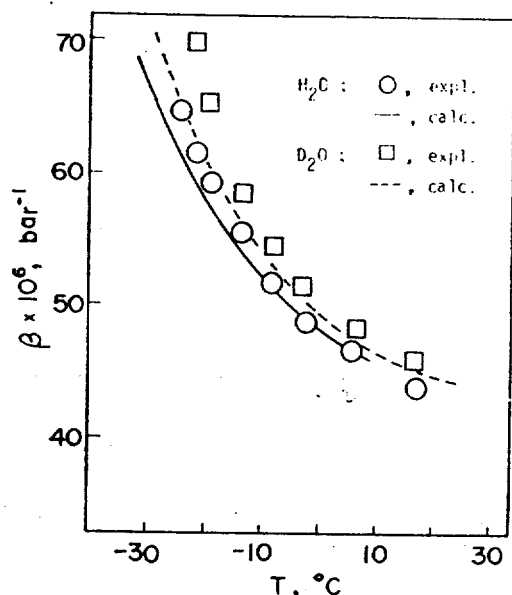


Figure 3. The compressibility vs. temperature. Experimental points were selected from ref. 9, and the experiments were performed at 1 bar, while the calculations at 1 atm.

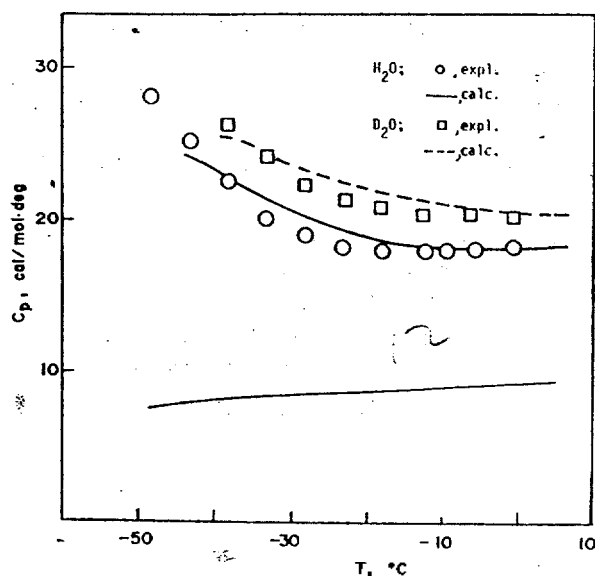


Figure 4. Calculated heat capacities at constant pressure are compared with experiments. The thin line is the vibrational heat capacity.

temperature, and thus the contribution of fluidized vacancies is expected very small in a supercooled state. Therefore, α_f is neglected in this calculation. The calculated values give good results to -20°C where the experiment was performed in bulk water¹⁸ and show discrepancies far below -20°C where the experiment was in capillaries¹⁹ or with emulsion of water.²⁰ The experiment of D₂O in Figure 2 was done in

capillaries.¹⁹

The compressibility of supercooled water is calculated from Eq. 9 adding the extrapolated ones of β_f from the values of normal liquid range. β_f is small but not so much as α_f at the melting point. The results are in Figure 3 which gives a good agreement to -20°C compared with experiment.²⁰ The lower-temperature experiments in capillaries would be estimated with a boundary effect or small-volume effect.

The larger magnitudes in case of D₂O than of H₂O is due to the larger value of K . The interaction energy of D₂O is larger than that of H₂O and gives greater value in an equilibrium constant.

The overall values of C_p are in Figure 4. Our two-solid-like structure model predicts the supercooled anomalies well. The sharper increase in C_p at lower temperature seems to form the more larger clusters than this calculation. However, recent improved data²¹ show that the low-temperature increases are a little less sharp than shown in Figure 1. The structural effect of heat capacity, C_{st} , is given by

$$C_{st} = \frac{qK}{(1+K)^2} \frac{(\Delta H + p\Delta V)^2}{RT^2} \quad (10)$$

Eq. 10 gives similar values measured by Rasmussen and MacKenzie¹⁴ who suggested the structural specific heat of supercooled water. The contribution of C_{st} is negligible in a normal liquid range with very small values of K . Such increase in C_p appears in several experiments which change their structures at melting. The greater value of D₂O is natural from the fact that D₂O has larger values in q , K , and ΔH than H₂O. It is not inconsistent that, although the clustering takes place to form stable H-bonds, the specific heat increases, *i.e.*, the system changes to higher energy levels, because clusters of closed structures are more stable than ice-like open structures. Thus the structures of closed clusters which exist mainly above the melting point in the calculation¹³ must be energetically stable at high temperatures and at atmospheric pressure and be unstable when the clusters grow to a certain size at low temperature.

Conclusion

It has been difficult to find any theories and models which account for all the properties of water including supercooled anomalies. The supercooled state is a very good test for models of water because the unusual behaviors above the melting point appear in their distinguished forms. This is probably due to the fact that, in a supercooled state, the occupancy of free volume of liquid water is very small compared with in other temperature range, while most properties of common liquids are determined by the effects of free volume. Considering the little free volume and the great H-bond energy, it is interesting that water supercooles even to a relatively low temperature range.

In this sense of small free volume, the phase transition of ice to water is different from those of other solids which introduce fluidized vacancies about 20 % at melting. Therefore, the fluidity of water is due to small clusters with short

life times showing cooperative phenomenon.

For a general conclusion of liquid water, the anomalous behaviors in any of its states depend, of course, on the fact that water molecules themselves are able to form various H-bonded structures whether they are distinguishable or not in a sufficient relaxation time. The authors classify the anomalies of water into two groups: "structural" and "energetic" anomalies. This is a similar idea to the two methods of defining H-bond¹¹ in the introduction. The concept of cooperative H-bond breaking with temperature rise has been introduced for the anomalies concerning the energetic properties such as the internal energy, the entropy, and the heat capacities, which are larger values than are calculated from the intermolecular vibrational energy. The more rigorous description for the distribution of broken H-bonded molecules is of interest. And the idea of two solid-like structure model enables to provide the qualitative and more or less quantitative calculations for, what we call here, the structural anomalies concerning the volumetric properties such as the molar volume, the thermal expansion coefficient, and the compressibility. The structural anomalies appear in their enlarged fashions in a supercooled state where the free volume is small. It was not unfortunate that in the previous paper,¹³ the calculation of free volume was very small near the melting point.

The characteristic properties of the two kinds of anomalies are the heat capacity and the compressibility which are in relation to the fluctuations in energy and in volume, respectively. Both values are large. Therefore, water is an interesting substance which shows the cooperative phenomena in a normal liquid region, while the phenomena are easily seen near at the critical point in common liquids. Thus the mixture model, here we have, is in two respects: heterogeneous distributions of H-bond energy by H-bond breaking and also heterogeneous distributions of local structures in equilibrium between closed structures and open structures. The closed structures which are stable in high temperature seem to have five-membered ring connections. Five membered ring connections are stable in energetically²² when the sizes are small but are hard to make infinite networks.

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