Additivity Rule Holds in Supercooling of Aqueous Solutions

H. Kanno,*,[‡] K. Miyata,[‡] K. Tomizawa,[‡] and H. Tanaka[†]

Department of Applied Chemistry and Department of Applied Physics, National Defense Academy, Yokosuka 239-8686, Japan

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Homogeneous ice nucleation temperatures (T_H) of aqueous solutions of methanol, ethylene glycol, glycerol, xylitol, poly(ethylene glycol)s, glucose, and fructose were measured as a function of solute concentration. It is shown that the additivity rule holds fairly well for the T_H values of the solutions of the same chemical family. Contrary to the conclusion by Koop et al. (ref 11), T_H depends strongly on the nature of a solute. It is confirmed that there is a linear relation between T_H and melting temperature (T_m) of the solution (solute: methanol, ethylene glycol or glycerol) up to high solute concentrations.

1. Introduction

Studies of aqueous solutions at low temperatures are important in various fields including the cryopreservation of living cells and organs in medical science, agriculture and biotechnology, climate physics, and food preservations at low temperatures.[1−5] In addition, mysterious properties of water may be clarified and explained from the data obtained from aqueous solutions at low temperatures.[6,7] It becomes increasingly clear that homogeneous ice nucleation temperature (T_H) is one of the important solution parameters characterizing an aqueous solution at low temperatures.[8−10]

In a recent report by Koop et al.,[11] it is asserted that the homogeneous nucleation of ice from a supercooled aqueous solution is independent of the nature of the solute but depends only on the water activity of the solution.

Here we show from experimental T_H data that the magnitude of T_H depends strongly on the nature of the solute. Furthermore, we present experimental evidence that the fractional structural unit, which may often be a functional group, in the solute molecule (or ion) plays an important role in the development of supercooling. In other words, we here show that the total supercooling is expressed by the additive contributions of supercoolings from each structural unit in a solute. These findings together with the simple relation recently found in the supercoolings of aqueous alkali halide solutions[12] provide crucial implication in clarifying the ice nucleation in supercooled aqueous solutions and in the understanding of local structures around dissolved solute molecules (ions) in aqueous solutions.

2. Experimental Section

The emulsification method initially developed by Rasmussen and MacKenzie[9] was employed to measure T_H of these aqueous solutions. The dispersant phase was a 1:1 volume mixture of methylcyclopentane and methylcyclohexane and the surfactant was Span 65 (sorbitan tristearate). The emulsions were made by using a small blender of the rotating rate of 6000/min and the mixing time was about 3 min in most cases. The volume ratio of the sample solution to the dispersant phase was 0.5 in all the measurements.

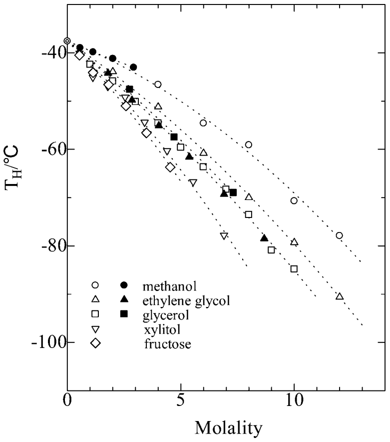

Figure 1. Homogeneous ice nucleation temperatures (T_H) for emulsified aqueous solutions of alcohols and monosaccharides. Although the T_H data for the aqueous glucose solution are not plotted in Figure 1 to avoid complexity, it must be pointed out that the T_H curve for the glucose solution is almost identical with that for the fructose solution. ◎,: T_H of pure liquid water; ○, △, □, ▽, ◇, this study; ●, Oguni and Angell;[10] ▲, ■, Rasmussen and MacKenzie.[9]

Most T_H measurements of aqueous alcohol solutions were carried out with a Mac-science 3200Stype DSC instrument with a cooling rate of 10 deg K/min. A simple DTA method was also used in the T_H measurements of the poly(ethylene glycol) solutions. The cross checking of the T_H measurements indicates that both the methods gave the concordant T_H results. The experimental uncertainty of the T_H values was estimated to be ±1.5 °C.

3. Results and Discussion

Figure 1 shows the T_H results for emulsified aqueous solutions of methanol, ethylene glycol, glycerol, xylitol, and fructose. As evident in the T_H curves, a deeper supercooling is observed for an aqueous solution of the solute having a larger number of OH groups than that of the solute having a smaller number of OH groups. Namely, the bigger supercooling is obtained in the following order: $CH_3OH < C_2H_2(OH)_2 <$ glycerol $<$ xylitol $\leq$ fructose (=glucose). These T_H results clearly indicate that

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* Address correspondence to this author. Phone: 81-046841-3810, ext 2401. Fax: 81-0468-44-5901. E-mail: hkanno@nda.ac.jp.

[‡] Department of Applied Chemistry.

[†] Department of Applied Physics.

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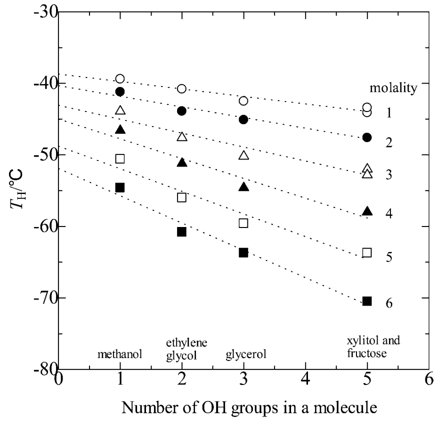

Figure 2. Linear relation between T_H and the number of OH groups in a solute molecule.

supercooling is strongly dependent on the nature of a solute. In other words, in aqueous alcohol and sugar solutions, supercooling is mainly controlled by the inhibition of ice nucleation due to the hydrogen bonds between water molecules and the OH groups of solute molecules so that T_H is strongly dependent on the number of OH groups in a solute molecule. In the early stage of the study on supercooling of aqueous alkali halide solutions,[8] it was concluded from the T_H vs pressure plots for 1 *m* solutions that the T_H depression is a colligative property. Now together with the recent T_H results[12] it is evident that this is not the case.

There have been several reported T_H values for aqueous solutions of methanol, ethylene glycol, and glycerol. The T_H values reported by Oguni and Angell[10] for methanol solutions are in good agreement with the ones obtained in this work. They obtained their T_H data using glass capillary disks with small pores (diameter ~2 μm). They avoided the emulsication method to get T_H since an alcohol with a long alkyl chain is soluble in the dispersant phase. In fact our preliminary experiment on aqueous ethanol solution gave a lower supercooling than the value reported by Oguni and Angell, indicating that the emulsion technique is not applicable to get T_H of aqueous ethanol solution. A little deeper supercooling for emulsified aqueous MeOH solution gives credence to the notion that the emulsification method is applicable to aqueous methanol solution. The T_H values for the ethylene glycol solutions by Rasmussen and MacKenzie[9] show systematic deviations from our data over the entire solute concentration range. A peculiar feature is that their T_H data of ethylene glycol solutions give almost the same supercooling behavior as our T_H data for glycerol solutions. Seeing the fact that their T_H data of other aqueous solutions (NaCl, glycerol, and glucose) give good agreement with ours, it is difficult to give adequate explanation why their T_H data for the ethylene glycol solution is lower than ours. It must be stressed that their T_H data for glycerol solutions are in good agreement with our data.

In a previous study by Oguni and Angell,[10] it is reported that supercooling of an aqueous solution of a normal monohydric-alcohol becomes larger with an increase in alkyl chain. In addition, they concluded by analyzing the T_H data for aqueous hydrophobic and hydrophilic solute solutions that the additivity rule holds for the supercooling of aqueous alcohol solutions: addition of each additional $-CH_2$ bead produces an additional depression of T_H at a constant mole fraction of solute. To test the additivity rule, the T_H results are plotted against the number of OH groups in an alcohol molecule (Figure 2). An interesting point is that there is an almost linear relation between T_H and *n* (the number of OH groups in an alcohol molecule) at a constant molality (*m*) up to very high alcohol concentrations. As the chemical formulas of alcohols used in this study are generally represented by $H_2\{CH(OH)\}_n$, it can be said that these linear relations add another strong support for the validity of the additivity rule in the supercooling of aqueous solutions. Furthermore, the important implication derived from the linear relations is that local liquid structures of water in the immediate vicinity of a solute molecule (ion) are strongly affected by the local structures of the solute.

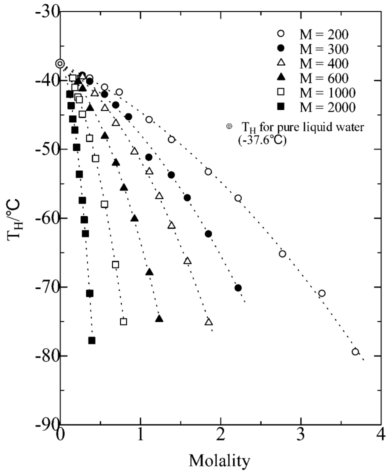

Figure 3. Homogeneous ice nucleation temperatures (T_H) for emulsified aqueous PEG solutions. All the T_H data were obtained by using a simple DTA method described previously.[12]

A remarkable point is that despite the large structural differences between xylitol (chain alcohol) and fructose, which has a ring structure, both solutions give almost the same T_H value although it appears that the latter solution gives a little deeper supercooling than the former one at higher solute concentrations. Therefore, it is evident that in these solutions the number of the structural unit {CH(OH)} is the key parameter for the magnitude of T_H. It is to be noted here that T_H of the glucose solution is almost identical with that of the fructose solution within experimental uncertainty. This means that the small configurational difference such as the difference between equatorial OH and axial OH gives rise to negligible T_H difference.

To strengthen our conclusion and to find out the limit of the additivity rule, we here add the T_H data of aqueous poly(ethylene glycol) (PEG) solutions of various average molecular weights. As there is a wide range of molecular weights in water-soluble poly(ethylene glycol)s, we can test the additivity rule in a much wider molecular weight difference. Figure 3 shows the T_H results for various aqueous poly(ethylene glycol) solutions as a function of solute concentration. Since the general chemical formula of poly(ethylene glycol)s is given by $H(OCH_2CH_2)_nOH$, we can regard (OCH_2CH_2) as the structural unit and can use the average molecular weight (denoted as *M*) as abscissa in plotting the T_H data. An immediate observance from the T_H curves shown in Figure 3 is that a higher molecular weight solution gives a deeper supercooling. Applying the least-squares curve fitting method to each set of T_H data, we obtain a quadratic curve for each solution. From the obtained quadratic curves, we calculated the T_H values at the solute concentrations of 0.3, 0.5, 1.0, and 1.5 mol/kg, respectively, for all the solutions. The calculated T_H values are plotted against the average molecular weight (Figure 4). It is now evident that T_H at a constant solute concentration varies in a quadratic way with increasing molecular weight. This feature is expected and is only natural because T_H falls in a quadratic way with increasing solute concentration

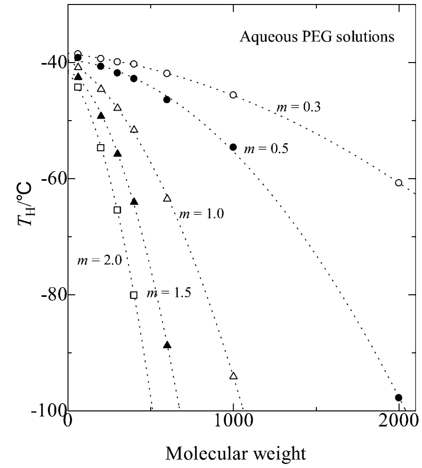

Figure 4. Relationship between T_H and M (average molecular weight) at a constant molality. The T_H values at $m = 0.3$, 0.5, 1.0, 1.5, and 2.0 mol/kg were calculated by using the best-fit quadratic curves obtained for each set of T_H data. There is some uncertainty in the nominal molecular weights for the commercially obtained poly(ethylene glycol)s, in particular, for the molecular weights of $M = 200$, 300, and 400.

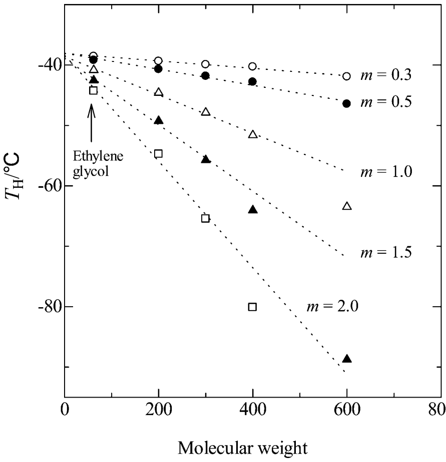

Figure 5. Test of the additivity rule on the T_H values of emulsified aqueous PEG solutions of low average molecular weights at low solute concentrations. The T_H data of aqueous ethylene glycol solutions were included in the graph.

for all the solutions we have examined.[13,14] Therefore, the additivity rule does not hold in a stringent sense in a very wide solute (structural or functional group) concentration range. The fact that T_H falls in a quadratic way with increasing solute concentration suggests that overlap of the hydration spheres enhances the inhibition of the formation of ice nuclei viable to grow to ice crystals. Structural changes associated with increasing solute concentration must contribute to some extent to accelerate the supercooling.

To examine the T_H vs M relation more closely, the expanded view of Figure 4 in the low molecular weight region was shown in Figure 5. It is clear that the linear relation between T_H and M holds fairly well at least in the low solute concentration region of the low molecular weight solutions. Therefore, we can conclude that the additivity rule holds fairly well as long as the difference of the molecular weights is not so large. This is well confirmed further between the T_H curves for the $M = 1000$ and 2000 solutions. Figure 6 shows the T_H curves of the $M = 1000$ and 2000 solutions and the hypothetical T_H curve for the $M = 2000$ solution by doubling the solute concentration of the $M = 2000$ solution without changing the T_H value. Complete overlapping of the hypothetical T_H curve of the $M = 2000$ solution with the T_H curve for the $M = 1000$ solution clearly demonstrates that the additivity rule holds quite well for the PEG solutions of $M = 1000$ and 2000. In other words, the supercooling given by one PEG molecule of $M = 2000$ is exactly twice as large as that of one PEG molecule of $M = 1000$.

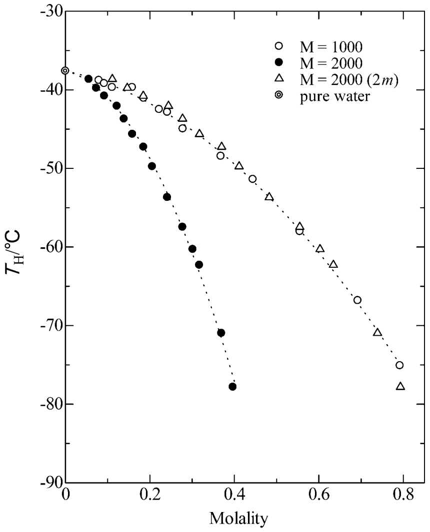

Figure 6. Test of the additivity rule on the T_H data for the PEG solutions of $M = 1000$ and 2000. ○, ●, observed T_H values; △, hypothetical T_H values by doubling the molality of the $M = 2000$ solution.

Due to scarcity of the water activity data on aqueous solutions, in particular, at low temperatures (<0 °C), it is difficult to test one of the assertions by Koop et al.[11] that T_H depends only on the water activity of aqueous solution. In the derivation of their conclusion, they assumed that for a fixed solution composition water activity (a_w) is independent of temperature between melting temperature (T_m) and T_H and used the a_w value at T_m to reach the water activity criterion for the homogeneous ice nucleation. However, large structural and compositional changes are observed in most aqueous solutions from room temperature to low temperatures.[15−18] It is reported that ionization of aqueous sulfuric acid is enhanced at low temperatures.[16] In the 1 m sulfuric acid, the main ionic species at room temperature are H^+ and HSO_4^- ions while H^+ and SO_4^{2-} ions are dominant at low temperatures.[18] In the case of the aqueous gallium chloride solution of medium salt concentrations (∼2 m), $GaCl_4^-$ ions are dominant at room temperature but $[Ga(OH_2)_6]^{3+}$ ions become major gallium species at low temperatures.[15] In view of these reports, the validity of their assumption is questionable. In addition, the water activity criterion is based on the additional assumption that all salts (electrolytes) are fully dissociated. As already pointed out,[16−18] sulfuric acid, which is a typical strong acid, is not fully dissociated even at 1 m aqueous H_2SO_4 solution. Fleissner et al.[19]showed that contact ion pairing increases with decreasing temperature in dilute aqueous magnesium, calcium, and strontium nitrate solutions. A similar trend was observed in dilute aqueous solutions of alkali metal thiocyanates when going from ambient temperature to supercooled temperatures.[20] Therefore, it seems that the validity of the assumption that a_w is independent of temperature between T_m and T_H is rather implausible.

In the connection with water activity in supercooled aqueous solution, it is interesting to point out that Rasmussen and MacKenzie[9] found a very interesting linear relation between T_H and T_m as early as 1972. As the melting point depression is ascribed to reduction in water activity with increasing solute concentration, it is evident that there is an apparent direct relation

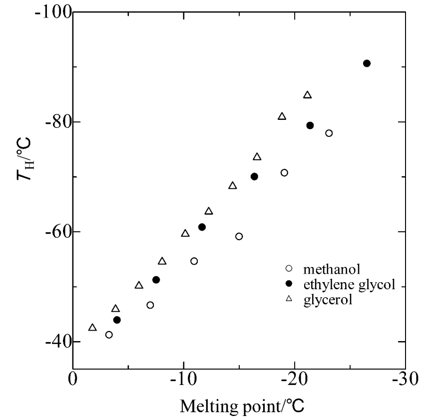

Figure 7. Linear relations between T_H and T_m for aqueous solutions of methanol, ethylene glycol, and glycerol. The T_m data are from ref 23.

between T_H and the water activity in the solution. In an attempt to rationalize the linear relation between T_H and T_m, Franks,[21] using thermodynamic relations and several approximations, derived the following relation as a first approximation,

$$\Delta T_H = A\Delta T_m \qquad \text{(A is a constant)} \qquad (1)$$

Here $\Delta T_H = T_H(0) - T_H(m)$, $\Delta T_m = T_m(0) - T_m(m)$, and $T_H(x)$ and $T_m(x)$ are the homogeneous ice nucleation temperature and the melting point of the solution at molality $x = 0$ and m, respectively. In the early treatment,[21] the value of 1.5 was assigned to A but in the later discussion[22] it was amended to be 1.98, using newly added T_H data. Although homogeneous ice nucleation is a dynamic process, relation 1 tells us that it takes place at the temperature at which the ratio $\Delta T_H/\Delta T_m$ becomes a certain common value. Furthermore, seeing that the additivity rule holds fairly well in the supercooling of aqueous solution, we can expect that the additivity rule might also hold in the melting depression of aqueous solution. Using the melting data reported in the literature,[23] we checked whether A is constant enough for aqueous methanol, ethylene glycol, and glycerol solutions (Figure 7). Although the linear relation between T_H and T_m holds very well up to high solute concentrations, A varies a little from one system to another as already reported by Rasmussen and MacKenzie.[9] Thus with presently available T_H and T_m data, it is difficult to say that the additivity rule holds in the melting depression of aqueous alcohol solutions (alcohols = methanol, ethylene glycol, and glycerol).

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