Supercooling Behavior in Aqueous Solutions

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Using the emulsion method, we measured the homogeneous nucleation temperature depression, $\Delta T_{f,\text{hom}}$, and equilibrium melting points depression, ΔT_m, of various aqueous solutions and then calculated λ for each solute using the linear relationship $\Delta T_{f,\text{hom}} = \lambda \Delta T_m$. We defined λ as the solute-specific supercooling capacity and examined its correlation with some known hydration characteristics. The results showed that λ is correlated with D^0, the self-diffusion coefficient of solute molecules in infinite dilution.

Introduction

To meteorologists and cryobiologists, predicting and controlling the supercooling behavior of aqueous solutions is an important issue. Since the very early days of these disciplines, countless studies have been undertaken in this area. Any summary of the major achievements of such studies should include (1) confirmation of the dependence of nucleation temperature on volume in pure water and identification of the lower temperature limit;[1] (2) confirmation, using the emulsion method, of the existence of homogeneous nucleation in water and its dependence on the solute in aqueous solution;[2] and (3) theorization of homogeneous nucleation temperatures in aqueous solutions from the viewpoint of thermodynamics.[3,4]

Rasmussen and Mackenzie[2,5,6] introduced the emulsion method and used it to improve the repeatability of homogeneous nucleation temperature determination in pure water and in aqueous solutions. In this way, they proved the existence of a primary linear relationship between equilibrium melting point and homogeneous nucleation temperature in many different solutions.

$$\Delta T_{f,\text{hom}} = \lambda \Delta T_m \qquad (1)$$

Here, $\Delta T_{f,\text{hom}} = T_f^0 - T_f$ and $\Delta T_m = T_m^0 - T_m$, where T_m^0 and T_h^0 are the melting point and homogeneous nucleation temperature of pure water, respectively. In addition, in this study, T_f^0 calculated $\Delta T_{f,\text{hom}}$ as -37.6 °C.

They also showed that the tendency to undergo supercooling, λ, may be obtained by calculation from the linear equation and differs depending on the solute. These achievements were followed by further research in which the emulsion method was employed to determine homogeneous nucleation temperatures, equilibrium melting points, λ, nucleation rates, and so forth of many different aqueous solutions. For instance, Miyata and co-workers[7,8] used this method to obtain the homogeneous nucleation temperatures of aqueous solutions of alcohol, sugar, and alkali halide salts and confirmed that this value depends on the functional groups and structural units of the solute: the number of hydroxyl groups in the solute molecule, ionic radius, and so

forth. Meanwhile, Koop and co-workers[9,10] obtained homogeneous nucleation temperatures for aqueous solutions of PEG and a variety of low-molecular-weight substances and showed that these values depend on water activity. From a more theoretical point of view, Khvorostyanov and Curry[3] utilized the classical theory of nucleation to prove that homogeneous nucleation temperatures obtained using the emulsion method may be theoretically explained by certain thermodynamic parameters of equilibrium, as is the case for equilibrium melting points. Considering that, as mentioned above, some additivity holds true for homogeneous nucleation temperatures and that λ may be explained in terms of thermodynamic equilibrium, we can assume that λ, which expresses the dependence of supercooling on the solute, may be explained using hydration characteristics (interaction between the solute molecules and water). Once the relationship between λ and hydration is identified, easy prediction of supercooling behavior for aqueous solutions should be possible, which in turn can assist in control of ice nucleation temperatures in those fields of expertise in which such temperatures play an important role.

We defined λ as the supercooling capacity specific to the solute and attempted to interpret this parameter by examining its relationship with other hydration characteristics. In this study, we measured homogeneous nucleation temperatures and equilibrium melting points of different aqueous solutions, all in emulsion form, using differential scanning calorimetry (DSC), and then we obtained a value of λ for each solute. Next, we examined correlations between the λ thus obtained, the molecular weight of the solute, and some known hydration characteristics, namely, the second virial coefficient (viscosity B coefficient) of the Jones−Dole viscosity equation, the self-diffusion coefficient of the solute molecules in infinite dilution, and the rotational correlation time ratio (the ratio of the rotational correlation time of water molecules within the hydration zone to that of pure water), obtained by NMR.

Experimental Methods

1. Preparation of Aqueous Solutions. The solutes we employed, which are all highly soluble and do not easily form precipitates at low temperatures, were NaCl, NaBr, NaI, CaCl$_2$, MgCl$_2$, urea, tetraalkylammonium bromides (Me$_4$NBr, Et$_4$NBr, Pr$_4$NBr), ethylene glycol, 1,3-propanediol, 1,4-butanediol, glycerol, glucose, fructose, xylose, sucrose, maltose, trehalose, and PEG 200, 300 and 600. Reagents of special and highest grades were obtained from Wako Pure Chemical Industries, Ltd., and

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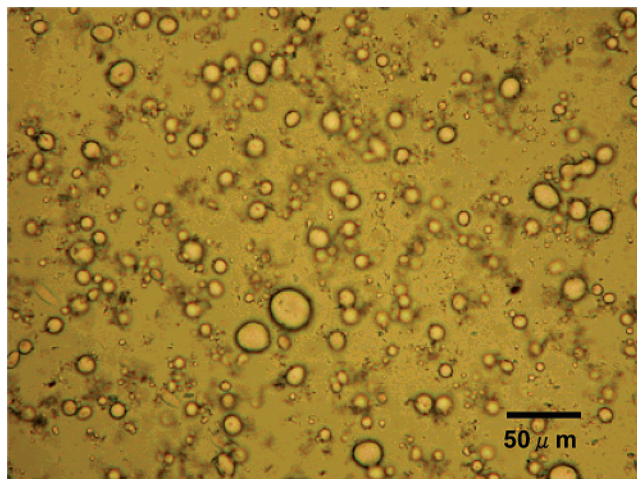† Current address: 741-29 Komejima, Shouwa-machi, Saitama, 344-0115, Japan.

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Figure 1. Span 65 (sorbitan tristearate)-stabilized emulsion of distilled water in silicon oil, used for nucleation measurements.

Figure 2. DSC curves obtained from distilled water emulsified in silicon oil. The upper curve shows cooling; the lower curve shows warming.

ordinary reagents were obtained from Sigma Chemical Corporation. Distilled water (Wako Pure Chemical Industries Ltd.) was used for preparing the solutions. The solution concentrations were 0.5, 1.0, 1.5, 2.0, 3.0, and 4.0 mol kg^{-1} for salts; 0.5, 1.0, 1.5, 2.0, 3.0, and 4.0 mol kg^{-1} for tetraalkylammonium bromides; 2.0, 3.0, 4.0, and 6.0 mol kg^{-1} for polyhydric alcohols; 1.0, 1.5, 1.75, and 2.0 mol kg^{-1} for saccharides; and 10, 20, 30, and 40 wt % for polyethyleneglycol.

2. Preparation of Emulsions. Emulsions were prepared using silicone oil (TSF451-10, GE Toshiba Silicone Co., Ltd.) and sorbitan tristearate (SPAN 65, Sigma Chemical Corporation) as the interfacial active agent. An identical quantity of each of the aqueous solutions described above was added dropwise to 5 mL of silicone oil containing 10 wt % SPAN 65, while the mixture was agitated for 10 min with a glass homogenizer (1500 rpm).

3. Measurement of Homogeneous Nucleation Temperatures and Equilibrium Melting Points by DSC. A Shimazu DSC-50 calorimeter was used to measure homogeneous nucleation temperatures and equilibrium melting points. A sample of each of the emulsions prepared as described above (2.0 ± 0.1 mg) was encapsulated in an aluminum cell. The nucleation temperature of each of the samples was measured by scanning at a cooling rate of −3.0 °C/min to −80 °C (193 K); next, the equilibrium melting point was measured by scanning at a heating rate of +3.0 °C/min to +10 °C (283 K). For correction of the measured temperatures, we used distilled water and set the temperature at the highest point of the peak for melting ice at 273 K. For this reason, we used the highest peak values for homogeneous nucleation temperatures, equilibrium melting points, and other temperature results.

Results and Discussion

Figure 1 shows photomicrographs of emulsions of distilled water. It can be seen that each droplet is around 10 μm; this is usually considered a suitable droplet size for reproducing the homogeneous nucleation temperature of a solution, which indicates the lower limit of nucleation.[2] Although not all of the solutions used are illustrated in this figure, the droplets were of similar sizes to those seen in the distilled water solution. For this reason, we can safely assume that the influence of different solutes on emulsion droplet size was negligible. Figure 2 shows the heating and cooling DSC curves for the distilled water emulsion. It can be seen that the homogeneous nucleation temperature of distilled water by this method is −37.6 °C (235.4
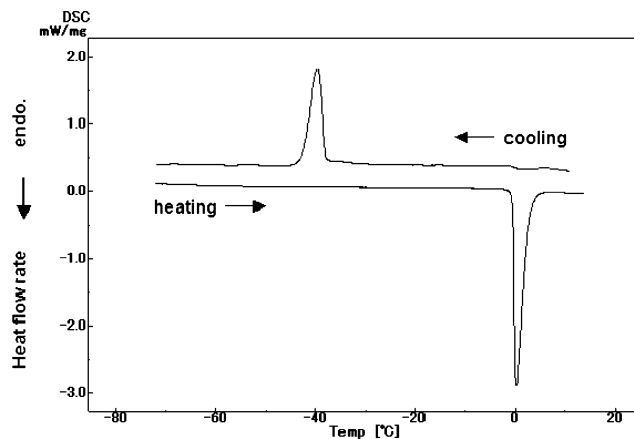
K), and the shape of the exothermic peak is close to the Gaussian distribution. This temperature and the peak shape are the standard results obtained for homogeneous nucleation temperature measurement by this method.[2,8,10] We can assume, therefore, that crystallization ascribable to unevenness (catalytic effects) was negligible in these measurements of homogeneous nucleation temperature. Figure 3a−e shows the relationships between homogeneous nucleation temperatures and equilibrium melting points for various solutes. Good linear relationships may be observed for all samples. Khvorostyanov and Curry[3] have pointed out that since λ is dependent on chemical composition and water activity, it varies in some cases depending on the solute and concentration. However, over the concentration range used in our study, we obtained a good primary linear relationship for all solutes, with correlation coefficients of $R = 0.997 - 0.999$. For this reason, λ may be treated as a supercooling capacity specific to the solute. According to past reports,[2−4,8,9] the value of λ is about 2 when the molecular weight is low. The dependence on the solute has also been investigated,[11] but no studies have discussed λ from the viewpoint of solute−water interactions or the hydration parameter. We first consider the results obtained from solutes consisting mainly of alkyl chains. It can be seen that λ becomes larger as the alkyl group grows longer (Me$_4$NBr < Et$_4$NBr < Pr$_4$NBr, PEG200 < 300 < 600, ethylene glycol < 1,3-propanediol < 1,4-butanediol). Among alkyl compounds, if we look more closely at the diols, we find that λ grows larger by around 0.3 for every methyl group added but does not increase as the number of hydroxyl groups increases (glycerol < 1,3-propanediol).

Turning to the salt solutions, we see λ is not significantly different among salts consisting of the same cation (Na$^+$) and different anions (I$^-$, Br$^-$, Cl$^-$) or the same anion (Cl$^-$) and different cations (Mg^{2+}, Ca^{2+}). However, when the counteranion is large (e.g., an organic ion), λ can vary significantly in value, as can be seen by comparing the results for tetraalkylammonium bromide and NaBr. Among the sugars, disaccharides have greater values of λ than monosaccharides. Among monosaccharides and disaccharides (in other words, among sugars with similar molecular weights and numbers of hydroxyl groups), λ was found to be different for each solute (glucose < xylose < fructose, sucrose < trehalose < maltose).

As described so far, our experimental results show that the values of λ, homogeneous nucleation temperature, and equilibrium melting point vary depending on the functional groups and structural units of the solute. Therefore, we examined correlations between the λ values obtained and various hydration
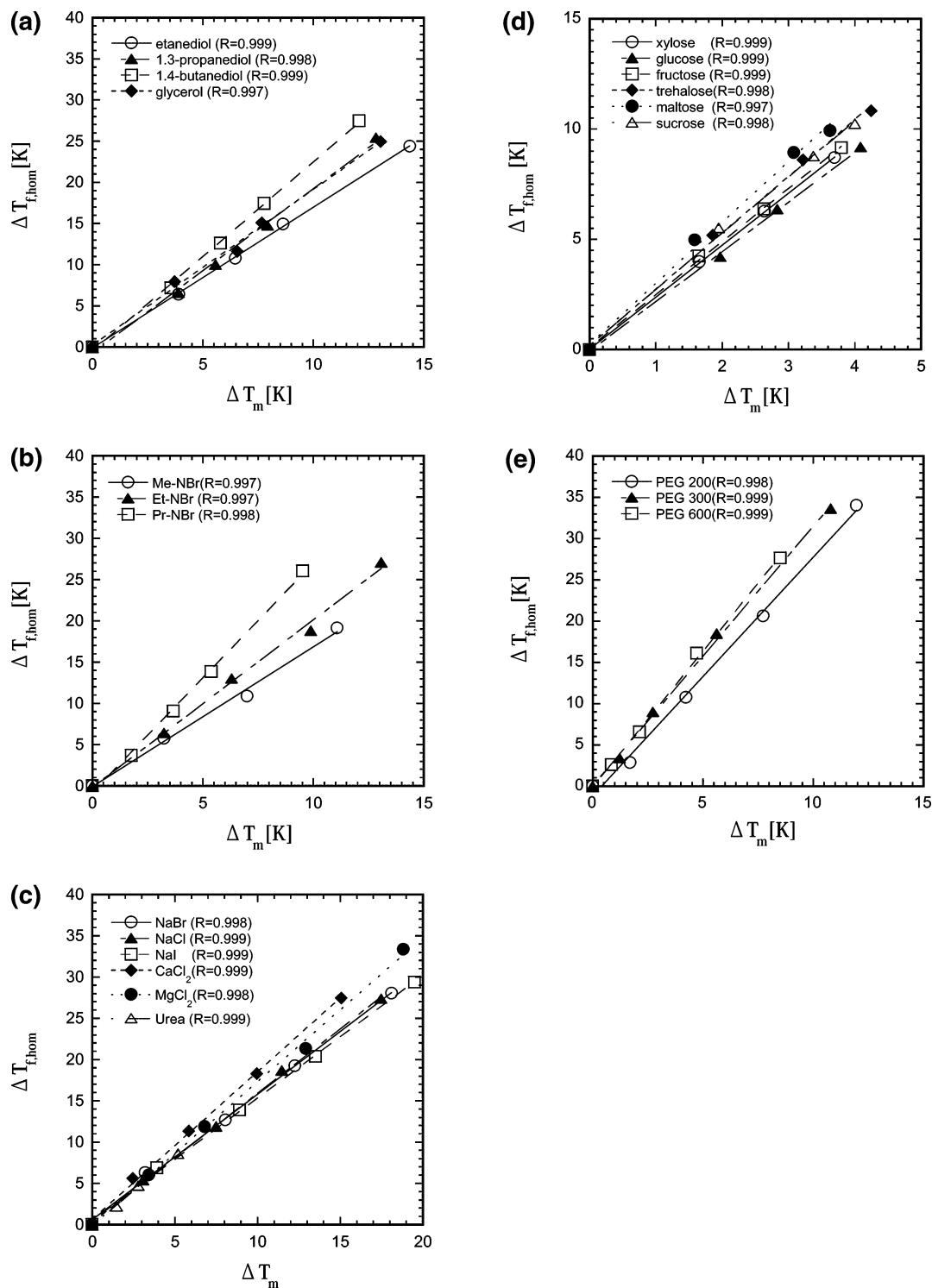
Figure 3. Homogeneous nucleation temperature depression ($\Delta T_{f,\text{hom}}$) as a function of equilibrium melting point depression (ΔT_m) in aqueous solutions. (a) Polyhydric alcohol solutions, (b) tetraalkylammonium bromide solutions, (c) salt solutions, (d) monosaccharide and disaccharide solutions, and (e) polyethylene glycol solutions.

characteristics. Table 1 shows these values for each solute.[12−24] Our study employed the molecular weights (Mw) of the respective solutes as well as some values characteristic of aqueous solutions, namely, the second virial coefficient (viscosity B coefficient) based on the Jones−Dole experimental formula of viscosity and the self-diffusion coefficient (D^0), and the ratio of rotational correlation time (τ_c^h/τ_c^0) between water molecules in a hydration zone and those in pure water, which can be obtained from the T_1 relaxation time in NMR in aqueous solution and the number of molecules in the vicinity of the solute.[20]

Figure 4a shows the relationship between λ and molecular weight for various solutes. Some previous studies have shown that high-molecular-weight solutes show larger values of λ than low-molecular-weight solutes.[2,10,25] Our study results show a similar increase, which suggests that λ is a function of the solute's molecular weight.

Figure 4b shows the relationship between λ and the viscosity B coefficient. Although the number of points plotted is rather small, a linear proportional relationship between the coefficient and λ may be observed. Thus, solutes which have viscosities

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TABLE 1: Supercooling Ability and Hydration Characteristics in Aqueous Solution at 25 °C

no.	compound	supercooling capacity $(\Delta T_{f,\text{hom}}/\Delta T_m)\ \lambda$	molecular weight Mw	viscosity B coefficients $(\text{cm}^3\ \text{mol}^{-1})$ B	self-diffusion coefficient $(\times 10^{10}\ \text{m}^2\ \text{s}^{-1})\ D_o$	rotational correlation time T_c^h/T_c^0
1	NaI	1.48	149.93	0.0178 (ref 19)	16.16 (ref 23)	0.92 (ref 19)
2	NaCl	1.56	58.44	0.0793 (ref 19)	16.12 (ref 23)	1.19 (ref 19)
3	NaBr	1.51	102.84	0.0443 (ref 19)	16.27 (ref 23)	1.05 (ref 19)
4	MgCl$_2$	1.74	95.21	0.3712 (ref 19)	12.51 (ref 23)	2.32 (ref 19)
5	CaCl$_2$	1.78	110.98	0.2710 (ref 19)	13.35 (ref 23)	1.77 (ref 19)
6	ethylene glycol	1.70	62.07	0.169 (ref 22)	11.4 (ref 21)	1.36 (ref 18)
7	1.3-propanediol	1.99	76.09	0.236 (ref 22)		1.56 (ref 18)
8	1.4-butanediol	2.29	90.12	0.303 (ref 22)		1.68 (ref 18)
9	glycerol	1.89	92.07	0.225 (ref 14)	9.21 (ref 21)	1.52 (ref 20)
10	urea	1.66	60.06	0.035 (ref 14)	13.82 (ref 23)	0.98 (ref 17)
11	Me$_4$NBr	1.69	154.05	0.083 (ref 13)		1.23 (ref 19)
12	Et$_4$NBr	2.02	266.26	0.340 (ref 13)		1.68 (ref 19)
13	Pr$_4$NBr	2.77	322.37	0.820 (ref 13)		2.53 (ref 19)
14	glucose	2.25	180.16		6.75 (ref 15)	4.10 (ref 15)
15	fructose	2.40	180.16		7.002 (ref 15)	3.75 (ref 15)
16	xylose	2.35	150.13		7.495 (ref 15)	3.58 (ref 15)
17	maltose	2.76	342.30		5.201 (ref 15)	3.72 (ref 15)
18	sucrose	2.55	342.30	0.8786 (ref 14)	5.223 (ref 15)	3.52 (ref 15)
19	trehalose	2.56	342.30		5.08 (ref 16)	3.54 (ref 16)
20	PEG200	2.89	200		4.86 (ref 12)	1.75 (ref 24)
21	PEG300	3.14	300		3.77 (ref 12)	1.94 (ref 24)
22	PEG600	3.29	600		2.44 (ref 12)	2.25 (ref 24)
22	PEG9000	4.95 (ref 2)	9000		0.45 (ref 12)	

that are heavily dependent on concentration allow easy supercooling, while less-dependent solutes allow less supercooling. Considering that, generally speaking, the B coefficient is a value physically determined by the hydrodynamic sizes and shapes of the solute molecules, we can assume that some correlation exists between the coefficient and λ, since both are dependent on the size or molecular weight of the solute molecules. Our results suggest that the viscosity of the aqueous solution plays an important role in determining the value of λ for different solutes.

Furthermore, to clarify the relationship between λ, the hydrodynamic size and shape of the solute molecule, and the effect of electrostatic interactions, we examined the relationship with the self-diffusion coefficient (D^0) of the solute in infinite dilution. It is known that D^0 shows a correlation with a parameter denoting the 3D conformation of the solute molecule. For example, for a monosaccharide in water, D^0 varies depending on the average number of hydroxyl groups at the molecule's equatorial position.[26] Figure 4c shows the relationship between D^0 and λ. The results show that a better linear relationship exists between λ and the logarithm of the self-diffusion coefficient than between λ and the viscosity B coefficient.

$$\lambda = 4.31 - 2.33 \log D^0 \quad R = 0.982 \quad (2)$$

To our great interest, extrapolation to around $D^0 = 1 \times 10^9 \sim 10^{10}\ \text{m}^2\ \text{s}^{-1}$, which is equivalent to that of an aqueous solution of a solute with a molecular weight of $1 \times 10^3 \sim 10^4$, gives us $\lambda = 4 \sim 5$, which is close to the value ($\lambda = 4 \sim 5$) given for high-molecular-weight aqueous solutions by Mackenzie[25] and Koop.[10] For reference, if we plot the λ values of PEG9000 as obtained by Rasmussen and Mackenzie[2] (Figure 4c), we see that their values also exhibit a linear relationship as in this study. If the linear relationship is extrapolated to $22.9 \times 10^{10}\ \text{m}^2\ \text{s}^{-1}$ or to the self-diffusion coefficient value[27] of water at 235 K, the λ value will be about 1. Because $\lambda = \Delta T_{f,\text{hom}}/\Delta T_m$, the λ of water cannot be defined but can be considered as the λ of an aqueous solution containing a solute with a diffusion coefficient as close to that of water as possible. On the basis of these observations, we consider that the relationship between λ and

D^0 is valid. Thus, it is now evident that the parameter λ is correlated by D^0. The D^0 used in this study is at 298 K and differs from the value observed at around 230 K, where nucleation occurs. Considering that the temperature dependence of the self-diffusion coefficient conforms to the linear Arrhenius relationship in the low-temperature area,[28,29] we can assume the linear relationship between aqueous solutions in the homogeneous nucleation temperature area will be in parallel to that at 298 K and that D^0 will not differ greatly between solutes.[21]

Generally, for a spherical solute, D^0 is obtained using the Stokes−Einstein equation.[30]

$$D^0 = kT/6\pi\eta^0 a \quad (3)$$

Here, k is the Boltzmann constant, T is the absolute temperature, η^0 is the viscosity of the quasi-solvent, and a is the Stokes radius, which is an expression of the molecule's size. However, since the viscosity of the water molecules around the solute molecules is different from that of bulk water molecules, η^0 depends on the interaction between solute and water molecules in the vicinity of the solute molecules (rotational relaxation time).[31,32] On the basis of this, the electrostatic interaction at D^0 is equivalent to the rotational relaxation time, and λ is expected to be dependent on these terms. Therefore, we examined the relationship of λ with the rotational correlation time ratio (the ratio of the rotational correlation time of water molecules within the hydration zone to that of pure water molecules) obtained by the NMR method. Figure 4d shows the results of this examination: no obvious relationships were observed between λ and the rotational correlation time ratios of the solutes. However, by categorizing the solutes into groups (alcohols, sugars, tetraalkylammonium salts, etc.), a relationship may be recognized between the rotational correlation time ratio and λ. In this way, we find that λ is larger for a solute with a greater rotational correlation time ratio, which means it is easier to constrain the movements of water molecules within the hydration zone than to constrain the rotational movement of pure water molecules. In contrast, a solute with a smaller correlation time ratio (in which the movement of water molecules is constrained with more difficulty) tends to have a smaller value of λ.
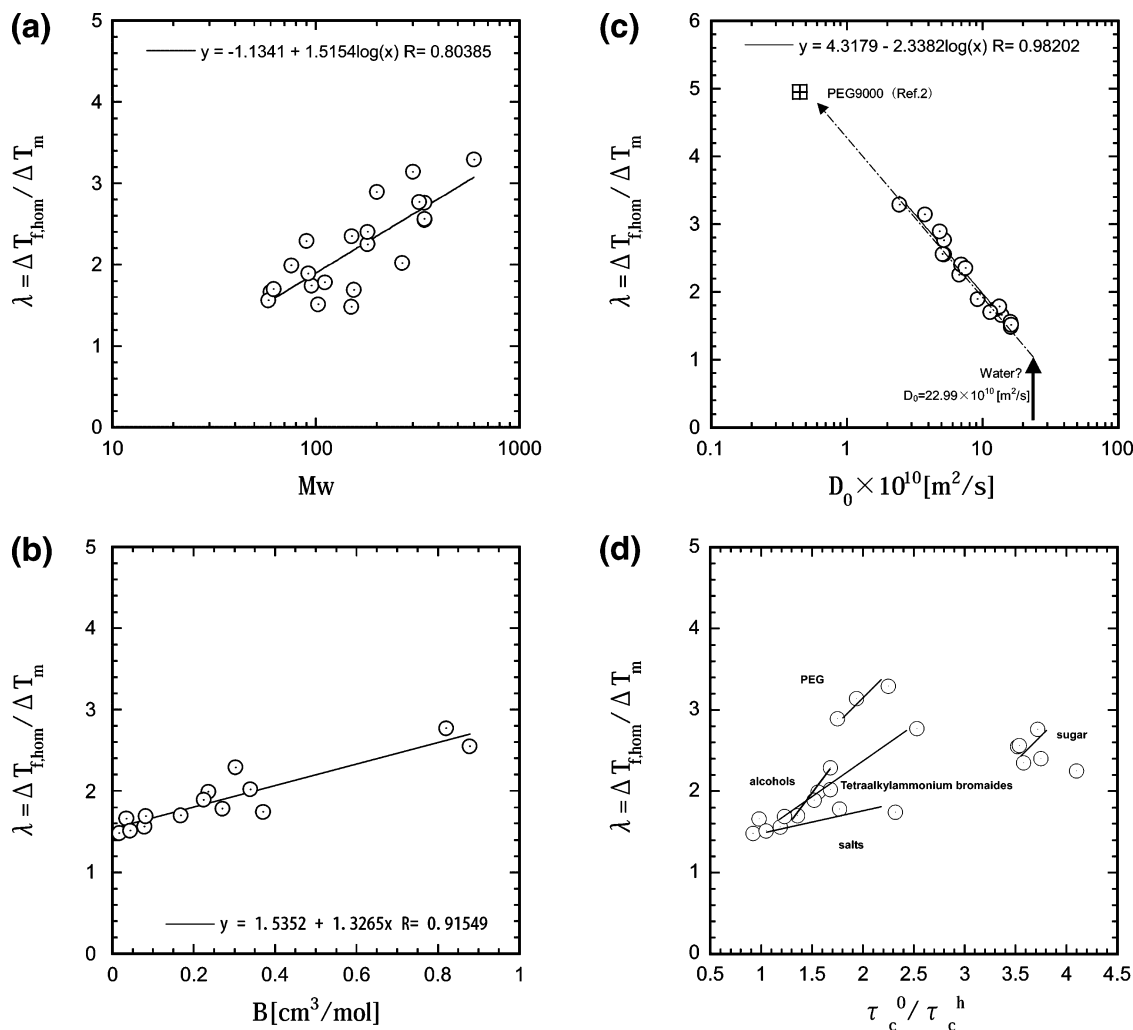
Figure 4. Relationship between hydration ability of solutes and supercooling ability λ for solutions listed in Table 1. (a) Molecular weight, (b) viscosity B coefficient, (c) self-diffusion coefficient, and (d) rotational relaxation time.

On the basis of our results, we may conclude that λ, the supercooling capacity of a solute, shows a strong correlation with the self-diffusion coefficient of the solute in infinite dilution.

$$\lambda = K \cdot \log D^0 \tag{4.1}$$

$$D^0 = f(\text{size, int}) \tag{4.2}$$

Equation 4.2 shows that D^0 is dependent on the solute's molecule size and the electrostatic interaction (int) between the solute and the solvent. However, although there was some tendency toward dependence of λ on the rotational correlation time ratio, we were not able to identify any obvious relationship for all values of λ.

$$\lambda \neq g(\text{int}) \tag{4.3}$$

Therefore, while D^0 is dependent on both molecule size and electrostatic interaction, we consider that molecule size, by which we mean the hydrodynamic size and shape of the solute molecule, is the more important of the two factors.

$$\lambda = h(\text{size}) \tag{4.4}$$

In other words, our results suggest that λ is affected to a greater extent by the macroscopic viscosity of the solution than

by the microscopic interaction between solute and water. Let us now explain this relationship between λ and D^0 on the basis of the viscosity of the solution, utilizing known theories of nucleation. For example, the nucleation rate within supercooled liquids, that is, the number of nuclei formed in 1 s within a unit meter cubed of the liquid, is given by the following equation:[33,34]

$$J = N_A v_0 \Gamma_z \exp\left(-\frac{\Delta G^\#}{kT}\right) \exp\left(-\frac{\Delta G^*}{kT}\right) \tag{5}$$

where v_0 ($2\pi kT/h$, h: Planck's constant) is the atomic frequency, Γ_z is the Zeldovich constant, ΔG^* is the free energy of nucleation, and $\Delta G^\#$ is the free activation energy of water diffusion. Since the self-diffusion velocity depends on fluidity, however, $\Delta G^\#$ can ultimately be used as an activation energy for viscous flow.[33] From eq 5, we see that the homogeneous nucleation temperature can be calculated as the temperature where the number of nuclei per unit volume becomes 1, by using the following equation with a cooling velocity of V_t.

$$\int_{T_m}^{T_{f,\text{hom}}} \frac{J}{V_t} dT = 1 \tag{6}$$

If the Stokes−Einstein formula relating the diffusion coefficient and viscosity coefficient is assumed to be applicable to

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supercooled liquids, eq 5 can be converted as a function of the viscosity $[\eta]$ of the supercooled liquid as[35]

$$J = \frac{k\Gamma_z}{\eta(T)} \exp\left(\frac{-\Delta G^*}{kT}\right) \quad (7)$$

From eq 7, we can see that J changes sharply with viscosity. The viscosity of a solution has been reported to have correlation with the self-diffusion coefficient of its solute.[36]

From the above relations, D^0 can be considered as affecting the nucleation velocity or nucleation temperature through the activation energy for viscous flow $\Delta G\#$ or through $\eta(T)$. D^0 has correlation with λ because although D^0 is a kinetic coefficient which indicates the solute−water interaction at infinite dilution, it could be considered a thermodynamic solution parameter which is not concentration dependent and, therefore, like λ is a constant independent of composition.

Conclusions

As described indirectly above, existing theories of nucleation suggest that the supercooling capacity of an aqueous solution, λ, is correlated by the self-diffusion coefficient of the solute in infinite dilution, that is, the viscosity of the solution. To date, no study on the supercooling of aqueous solutions has drawn clear comparisons with hydration characteristics. Our study has shown that λ is dependent on parameters that are based on molecular structure, such as the self-diffusion coefficient of the solute. This dependence on the solute should enable us to predict supercooling of emulsions of aqueous. In addition, although more detailed examination is required, our study results suggest that λ is related to D^0 in aqueous solutions not only of low-molecular-weight solutes but also of many high-molecular-weight compounds.We hope that our study results will be of some help in situations which require prediction and control of supercooling in aqueous solutions.

Supporting Information Available: Table showing the $\Delta T_{f,\text{hom}}$ and ΔT_m values for various solutes. This material is available free of charge via the Internet at http://pubs.acs.org.

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