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# Supercooling of Aqueous Solutions of Alkali Chlorides and Acetates

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Homogeneous nucleation temperatures ($T_H$'s) of aqueous alkali chloride and acetate solutions were measured as a function of salt concentration. There is a linear relation between $T_H$ and $1/r^+$ ($r^+$: ionic radius of alkali ion) for aqueous alkali chloride solutions. In the supercooling of aqueous alkali acetate solutions, the ionization constant also plays an important role in their supercooling behavior. The $T_H$ results were discussed in relation to nucleation theory.

In recent years much attention has been paid to aqueous solutions at low temperatures because of their importance for cryopreservation of living cells for agriculture and biotechnology,[1–3] atmospheric physics[4] and medical purposes.[5] The emulsification method initially developed by Rasmussen and MacKenzie[6,7] is very useful for studying supercooling behavior of aqueous solutions not only at normal pressure but also at high pressures because it can avoid heterogeneous nucleation and because emulsions made using sorbitan tristearate can survive repeated freeze–thaw cycles.

Angell and his coworkers[8–11] have made a number of investigations on emulsions of various types of aqueous solutions under several conditions. In one of their emulsion works, MacFarlane et al.,[10] using emulsified aqueous LiCl solutions, determined the TTT curves (TTT: time-temperature-transformation) and nucleation rates, and reached the conclusion that classical nucleation theory is applicable to the crystallization of aqueous LiCl solution. In another emulsion work at high pressures, Kanno and Angell[9] reported that imposition of pressure on an emulsified aqueous solution enhances supercooling of the solution and that the combination of solute concentrtation and pressure can give rise to the vitrification of an aqueous solution which is otherwise unable to be vitrified in any concentration range at atmospheric pressure with a normal cooling rate such as $10^3$ K/min. Lang and Lüdemann[12] succeeded in measuring the longitudinal deuteron relaxation times $T_1$ in heavy water in the temperature range from $T = 283$ K to 188 K and in the pressure range from atmospheric pressure to 300 MPa and obtained the results that at $P < 100$ MPa the isobaric temperature dependence of the correlation times $T_0$ can be described by an equation proposed by Speedy and Angell.[13]

In view of these successes and to extend the applicability of the emulsion methods further, it is important to examine how the property of a solute affects supercooling behavior of an aqueous solution. There seems to have been only one emulsion study by Oguni and Angell[14] devoted to investigating hydrophobic and hydrophilic solute effects on $T_H$. Therefore, as a first step toward our object, we examined the supercooling behavior of aqueous alkali chloride and acetate solutions in this study.

## Experimental

Sample solutions were prepared by dissolving vacuum dried alkali chloride (MCl, M = Li, Na, K, Rb, and Cs) or acetate ($CH_3COOM$) into distilled water by weight. Several aqueous $MgCl_2$ and $AlCl_3$ solutions were also prepared by dissolving $MgCl_2 \cdot 6H_2O$ or $AlCl_3 \cdot 6H_2O$ crystals in distilled water in order to see the effects of cation radius on supercooling behavior. The salt concentration was expressed by molality (1 $m$ = mol/kg) in most cases. The emulsification method developed by Rassmussen and MacKenzie[7] was employed to measure $T_H$ of aqueous MCl solutions. The dispersant phase used in this study was a 1 : 1 volume mixture of methylcyclopentane and methylcyclohexane, which was initially developed by Kanno et al.[8] as the dispersant liquid for high pressure works and has been widely used for various high pressure works of emulsified aqueous solutions.[9,12] Emulsions were made using a small blender at a rate of over 6000 rpm.

Most $T_H$ measurements were carried out using a Mac-Science 3200S-type DSC instrument with a cooling rate of 10 K/min. A few $T_H$ measurements were also done using a simple DTA apparatus which was used for the $T_g$ measurements ($T_g$: glass transition temperature) for various aqueous tetraalkylammonium halide solutions.[15,16] The differential electromotive force and the sample temperature were recorded on a two-pen recorder, using teflon-sheathed alumel-chromel thermocouples. The cooling rate was about 5 K/min in most measurements. It must be pointed out here that both methods gave concordant $T_H$ results. The precision of temperature reading was estimated to be ±1.5 °C.

## Results and Discussion

Before we examine the experimental $T_H$ values, it is important to see what parameters in the nucleation equation mainly affect $T_H$. According to the nucleation theory developed by Dufour and Defay,[17] which is based on a combination of the classical treatment by Turnbull and Fisher[18] and the theory of absolute reaction rate,[19] the free energy of formation, $\Delta G$, of a cluster of radius $r$ is given by

$$\Delta G = (4/3)\,\pi r^3 \Delta G_v + 4\pi r^2 \sigma, \tag{1}$$

where $\sigma$ is the interfacial tension between water and ice, and $\Delta G_v$ is the volume free energy reduction in transferring water to ice. $\Delta G_v$ is expressed by

$$\Delta G_v = -\Delta H_f (T/T_m)(\Delta T/T_m), \tag{2}$$

where $\Delta H_f$ is the heat of fusion at $T$, $T_m$ is the melting point, $\Delta T$ is the degree of supercooling ($= T_m - T$). Maximizing $\Delta G$ with respect to $r$ we obtain the following relation for the critical size ($r^*$) of the cluster with $\sigma$ and $\Delta G_v$

$$r^* = -2\sigma/\Delta G_v \tag{3}$$

and the maximum value ($\Delta G^*$) of $\Delta G$ is

$$\Delta G^* = 16\pi\sigma^3/3\Delta G_v^2. \tag{4}$$

The rate at which nuclei appear per unit volume per unit time is assumed to be given by

$$J(T) = A^* f N_i^*, \tag{5}$$

where $A^*$ is the surface area of the critical cluster, $f$ is the frequency per unit area with which water molecules jump into the surface of the cluster, and $N_i^*$ is the number of clusters of critical size per unit volume. $f$ can be approximated by the expression:

$$f = X_1 (kT/A^* \mathrm{h}) \exp(-\Delta G_d/kT) \tag{6}$$

where $X_1$ is the mole fraction of the crystallizing component and $\Delta G_d$ is the activation energy for a diffusion jump across the liquid cluster interface. $\Delta G_d$ is assumed numerically equal to the activation energy for viscous flow ($\Delta G_m$) at $T$. $N_i^*$ is expressed by Boltzmann statistics as follows

$$N_i^* = N_0 \exp(-\Delta G^*/kT), \tag{7}$$

where $N_0$ is the number of monomers per unit volume present in the solution. Using these equations, Rasmussen and MacKenzie[7] evaluated $\Delta G_m/kT_H$ and $\sigma$ values from the $T_H$ values for aqueous ethylene glycol and PVP solutions under several assumptions and estimates for parameters in the nucleation equations. They reported that $\Delta G_m/kT_H$ increases rapidly while $\sigma$ decreases with increasing solute concentration. Franks et al.[20] examined the ice nucleation in supercooled aqueous polymer solutions and reported that $J(T)$ is reduced by a solute in the following three ways: (1) the radius of the critical cluster size ($r^*$) is increased due to the change of $\sigma$, (2) the activation energy for viscous flow ($\Delta G_m$) is affected, and (3) as a cluster grows, its surface becomes surrounded by a region impoverished in water molecules which retards the growth of the ice clusters.

First we examined the supercooling behavior of emusified aqueous alkali chloride solutions. Figure 1 shows the $T_H$ results for aqueous alkali chloride solutions as a function of salt concentration. As expected, every solution exhibits deeper supercooling with increase in salt concentration. First of all, it must be pointed out that supercooling is deeper in the order: LiCl > NaCl > KCl > RbCl > CsCl at a given salt concentration. When $T_H$ values are plotted against reciprocal of ionic radius, an almost linear relation holds for all members of alkali ions between $1/r^+$ ($r^+$: ionic radius) and $T_H$ (Fig. 2). As most thermodynamic and transport properties of aqueous alkali halide solutions are well correlated with ionic radii of alkali halides,[21–23] this linear relation is a clear indication that Coulomb interaction is the main factor affecting $\Delta G_m$ and $\sigma$. Without more theoretical works, it is difficult, at present, to determine which term is more dominant in determining the magnitude of $T_H$ in the case of aqueous alkali chloride solutions.

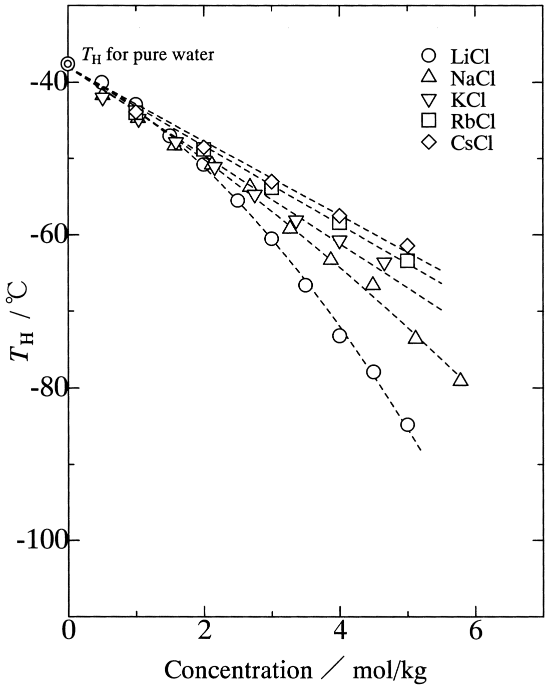

Fig. 1. $T_H$ variations with salt concentration for aqueous alkali chloride solutions. ◎: the $T_H$ value for pure water (−38 °C).

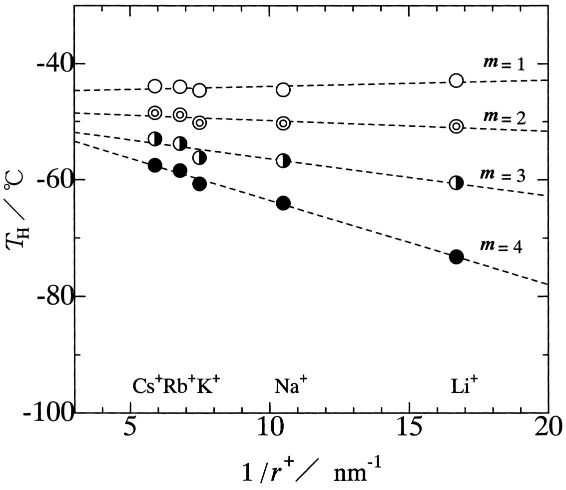

Fig. 2. Relationship between $T_H$ and $1/r^+$ for aqueous alkali chloride solutions.

Close examination reveals that there is a slight break at $K^+$. This is coincident with the point where separates alkali ions between structure breakers ($K^+$, $Rb^+$, $Cs^+$) and structure mak-

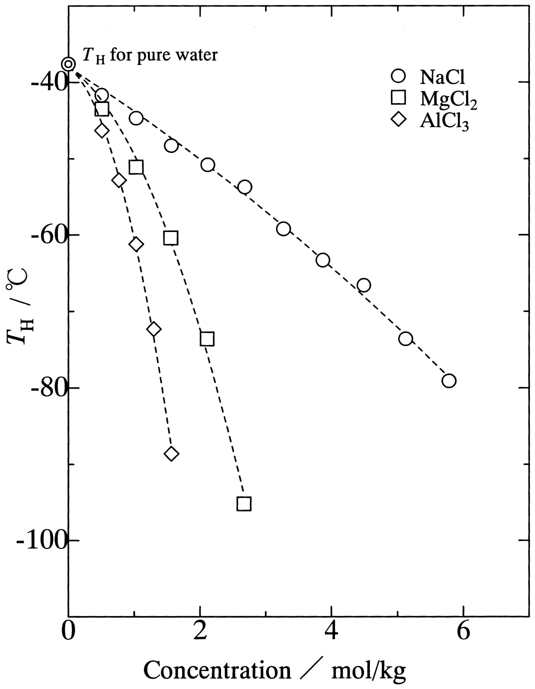

Fig. 3. $T_\mathrm{H}$ variations with salt concentration for aqueous NaCl, $MgCl_2$ and $AlCl_3$ solutions.

ers ($Na^+$, $Li^+$).[23] Water molecules are strongly attracted to cations with smaller cationic radius so that smaller cations exert stronger effect on breaking intrinsic water structure. According to the x-ray diffraction studies[24] on the hydration of alkali ions, the inner-sphere hydration number is reported to be 4 for $Li^+$ and $Na^+$, and 6 for $K^+$, $Rb^+$ and $Cs^+$. Another interesting coincidence is the Samoilov's positive and negative hydration[25] in which $K^+$, $Rb^+$ and $Cs^+$ are classified as a negative hydration group while $Li^+$ and $Na^+$ are classified as a positive hydration group. It is already reported that solution properties of an aqueous ionic salt solution are greatly dependent on the inner-sphere hydration number of cations.[26] In fact, the glass transition temperature ($T_\mathrm{g}$) of aqueous rare earth perchlorate solution exhibits a break at $Gd^{3+}$ due to the hydration number change taking place at the region in the rare earth series. Therefore, a small irregular variation around $K^+$ in the $T_\mathrm{H}$ vs $1/r^+$ plot can be most appropriately ascribed to the difference of the inner-sphere hydration number change between $Na^+$ and $K^+$. To confirm that the electrostatic force is the main factor for controlling the supercooling ability of an aqueous electrolyte solution, we also measured $T_\mathrm{H}$ of aqueous $MgCl_2$ and $AlCl_3$ solutions as a function of salt concentration. The $T_\mathrm{H}$ results are shown in Fig. 3. As expected, aqueous $AlCl_3$ solution gives the deepest supercooling in molar salt concentration scale. The hydration sphere around an $Al^{3+}$ ion becomes very big and water molecules around the $Al^{3+}$ ion are strongly attracted to it so that ice nucleation is severely hampered by these large hydrated cations. Combining the $T_\mathrm{H}$ results for aqueous alkali chloride solutions with those for aqueous $MgCl_2$, and $AlCl_3$ solutions, we get an almost linear relation again when the $T_\mathrm{H}$ values compared in the $n$ scale ($n = z\,m$, $z$ is the charge of cation) are plotted against $1/r^+$ (Fig. 4).

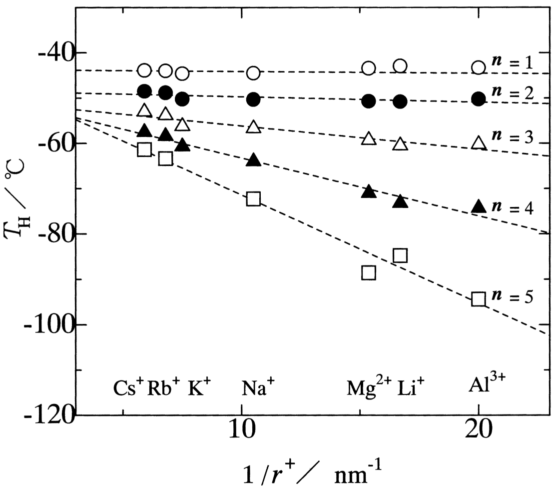

Fig. 4. Variations of $T_\mathrm{H}$ with the reciprocal of ionic radius of cation for aqueous alkali chloride, $MgCl_2$ and $AlCl_3$ solutions. Here to express the salt concentration in these solutions the $n$ value ($n = z\,m$, $z$ is the charge of cation) is used.

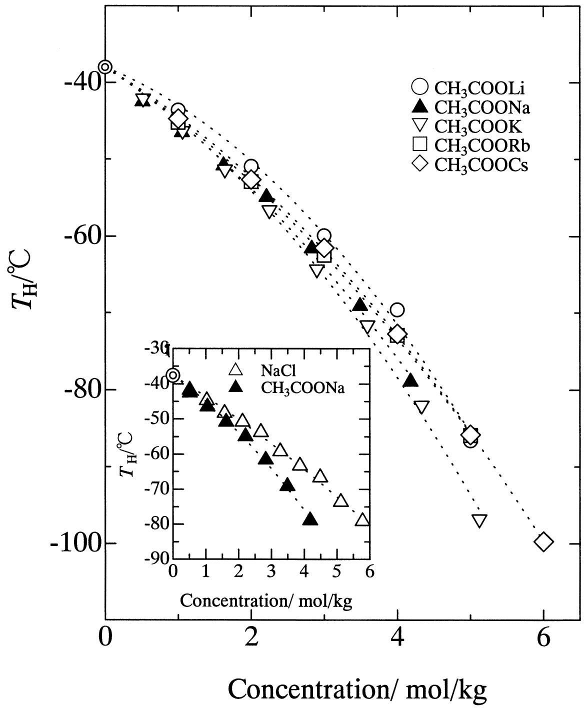

Fig. 5. $T_\mathrm{H}$ variations with salt concentration for aqueous alkali acetate solutions. The inset shows the comparison of the $T_\mathrm{H}$ values for aqueous NaCl and $CH_3COONa$ solutions.

The $T_\mathrm{H}$ results for aqueous alkali acetate solutions are interesting and worthwhile for comparison with those for aqueous alkali chloride solutions. Figure 5 gives the $T_\mathrm{H}$ results by taking molar concentration as abscissa. At a first glance of the graph, $T_\mathrm{H}$ curves of all acetate solutions behave the same way and the $T_\mathrm{H}$ difference between any two members is apparently small. This is not the case as will be shown soon. When the $T_\mathrm{H}$ values for the acetate solutions are plotted against the reciprocal of ionic radius of alkali ion (Fig. 6), a V-type $T_\mathrm{H}$ variation is observed with $1/r^+$ in contrast with the linear relation for the

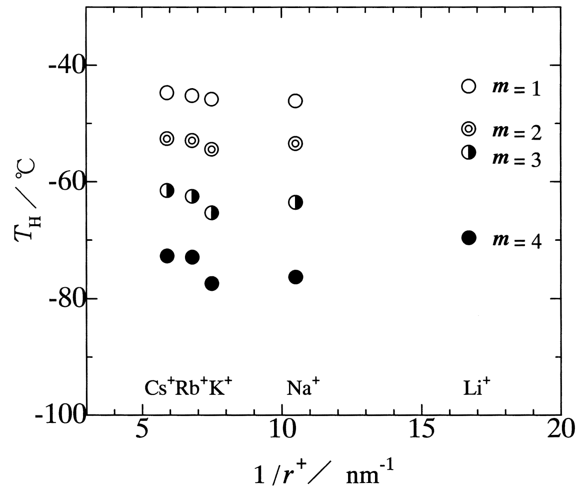

Fig. 6. Relationship between $T_H$ and $1/r^+$ for aqueous alkali acetate solutions.

alkali chloride solutions. Comparison of the $T_H$ results for aqueous NaCl and $CH_3COONa$ solutions clearly indicates that the acetate solution exhibits deeper supercooling, demonstrating that promotion of supercooling by acetate ions is larger than that of chloride ions. In the DSC study of solute effects on the $T_H$ values, Oguni and Angell[14] analyzed the $T_H$ values of various aqueous solutions in terms of the additive contributions from each functional group in a solute molecule. They assigned a very small value for $\Delta T_H$ of methyl group ($-CH_3$). Therefore, the rather large depression of $T_H$ for alkali acetate solution may be largely due to the effects of $COO^-$ group. In fact, large $\Delta T_H$ values (−4.0 °C for –OH, −6.1 °C for $-NH_2$, as compared to −0.8 °C for $-CH_3$) are assigned to hydrophilic functional groups. A remarkable point is that the lithium acetate solution shows the smallest supercooling among all the alkali acetate solutions. It is important to point out that both the LiCl and $CH_3COOLi$ solutions give almost identical $T_H$ values up to high salt concentrations. These are surely ascribed to the small ionization constant of $CH_3COOLi$ as compared with those of other alkali acetate salts. It is well known that $Li^+$ ion is the least electropositive among alkali ions and the $Li^+$-water interaction is partially covalent. As every aqueous solution gives a deeper supercooling with increasing solute concentration, it is only natural that aqueous solution of an electrolyte with a smaller ionization constant shows a shallower supercooling than the one with a larger ionization constant when compared at a given solute concentration and when other effects of the solutes are not large.

According to the time-of-flight neutron diffraction study[27] of a 20 mol% aqueous $CD_3COOLi$ solution, it is shown that three oxygen atoms of water molecules and two oxygen atoms of an acetate ion consist of the inner-coordination sphere. This clearly indicates that a large amount of $Li^+$ ions exists in the contact ion pair state in aqueous lithium acetate solution.

In the glass-forming study[28] of aqueous $CH_3COOM$ solutions (M = Li, Na, K, Rb, and Cs), $T_g$ at a given salt concentration (e. g., R = 10, R = moles of water/moles of salt) is in the order $Na^+ > Li^+ > K^+ > Rb^+ > Cs^+$. A peculiar feature is that except lithium salt solution the order of $T_g$ values is just the reverse of the $T_H$ values for the Na, K, Rb, and Cs salt solutions. Angell and Sare[29] reported that there is a strong correlation between the magnitude of $T_g$ and the viscosity B coefficient of the anions. From the tabulated viscosity B coefficients for cations, we confirmed that a similar correlation between $T_g$ values and the viscosity B coefficient exists for cations.

Recently Koop et al.[30] have asserted that the homogeneous nucleation of ice from a supercooled aqueous solution is independent of the nature of a solute but dependent only on the water activity of the solution. They derived the conclusion from the reported $T_H$ data for 18 different aqueous solutions under two important assumptions: (1) the melting point depression is dependent only on a solute concentration but is independent of its nature, and (2) all salts are fully dissociated. However, it is clear that their two assumptions are not valid in a strict sense. Our experimental data clearly indicate that their conclusion is valid only in a primitive base but not in quantitative one.

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