

Isotope Effect of the Glass Transition Temperature of Aqueous Solution. LiCl and ZnCl₂ Solutions in Water and D₂O

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Synopsis. Glass transition temperatures of the LiCl and ZnCl₂ solutions in both water and D₂O were measured as a function of the concentration of the salt. The composition dependence of isotope effect is briefly discussed for these solutions.

In recent years, the glass formation of binary solution systems have been extensively studied.^{1–5)} It is clear from these studies that glass transition temperature (T_g) is a good parameter such as melting and boiling points to represent the thermodynamic properties of liquid systems, though it is not a fixed point and varies a little with experimental conditions (*e.g.*, cooling and heating rates) and the method by which T_g is determined. To maximize the glass transition temperature as a diagnostic tool for clarifying thermodynamic properties of supercooled liquid systems and their glassy states, it is of importance to investigate the effects of various factors affecting the magnitude of T_g .

In this note, we report the study of the T_g measurements of aqueous LiCl and ZnCl₂ solutions in both water and D₂O. Aqueous solutions of LiCl and ZnCl₂ were prepared by dissolving anhydrous LiCl and ZnCl₂ in either water or D₂O (E. Darmstadt, 99.8% atom D). A conventional, simple DTA system was used for the T_g measurements. The experimental arrangements were essentially the same as used by Angell and Sare²⁾ in their T_g measurements. Overall cooling rate during quenching a sample solution was about 2×10^3 K/min. The T_g value was obtained

at a heating rate of about 5 K/min in the warmup DTA trace from liquid nitrogen temperature with using benzene as a reference material. A Teflon-covered chromel-alumel thermocouple system was used for the differential emf and temperature measurements. The accuracy of the T_g values was estimated to be $\pm 1^\circ\text{C}$ by determinations of the melting points of ethylether, acetone and other low melting organic compounds. However, the reproducibility of T_g is better than $\pm 0.2^\circ\text{C}$.

The results are shown in Figs. 1 and 2. From these figures, we see that $\Delta T_g (=T_g \text{ in D}_2\text{O} - T_g \text{ in H}_2\text{O})$ increases almost linearly with the increase in R ($=\text{mol of water/mol of salt}$) in the concentration region where the T_g measurements were carried out. As there is, to authors' knowledge, no reported T_g value for glassy bulk water and D₂O, it is difficult to estimate how much ΔT_g will be in more diluted concentration region where no glass-forming is observed. However, we expect that homogeneous nucleation temperatures (T_H) of water and D₂O can be a guide for this purpose. The T_H values of water and D₂O are reported to be -38 and -33°C at normal pressure, respectively.⁶⁾ Another possible candidate for estimating ΔT_g between glassy bulk water and D₂O is the glass transition temperatures of glassy crystals SnCl₂·2H₂O and SnCl₂·2D₂O (150 and 155 K, respectively).⁷⁾ From these results, the maximum of ΔT_g is estimated to be 5°C

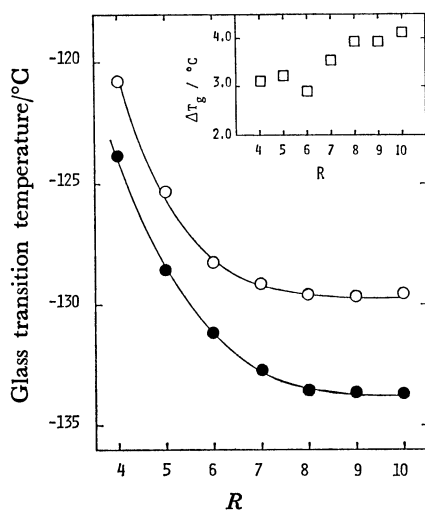


Fig. 1. Glass transition temperatures of the LiCl solutions in H₂O and D₂O.

●: T_g of the solutions in H₂O, ○: T_g of the solutions in D₂O, □: $\Delta T_g (=T_g \text{ in D}_2\text{O} - T_g \text{ in H}_2\text{O})$. The inset shows the variation of ΔT_g as a function of R .

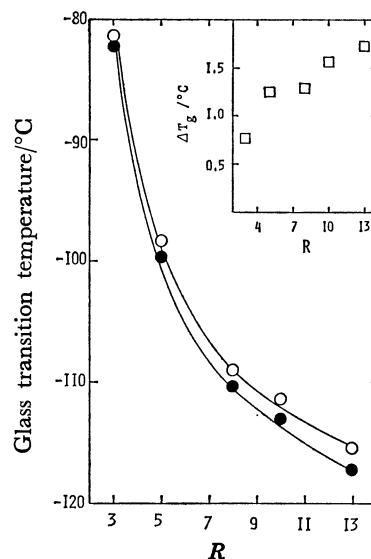


Fig. 2. Glass transition temperatures of the ZnCl₂ solutions in H₂O and D₂O.

●: T_g of the solutions in H₂O, ○: T_g of the solutions in D₂O, □: ΔT_g . The inset shows the variation of ΔT_g as a function of R .

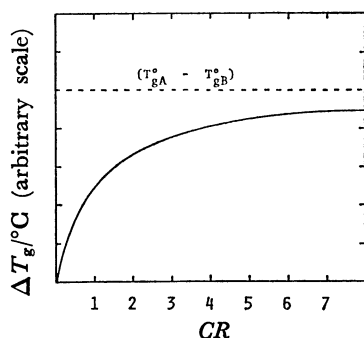


Fig. 3. Variation of ΔT_g as a function of CR .

for these aqueous solutions.

Aqueous solution is a typical non-ideal solution for which no applicable theory exists to interpret isotope effect. However, it is of interest to consider what relation exists between ΔT_g and R in a simple binary solution. An empirical equation which has proven successful in the fitting of experimental T_g data of a binary mixture is⁹⁾

$$T_{gA}(x) = \frac{xT_{g1}^0 + C(1-x)T_{gA}^0}{x + C(1-x)} \quad (1)$$

where T_{g1}^0 and T_{gA}^0 are the glass transition temperatures of pure components 1 and A, respectively, C is the adjustable parameter and x is the mole fraction of the component 1. If component A is replaced by the isotopic species B, we get the following relation under the assumption that C would not change for the isotopic substitution;

$$T_{gB}(x) = \frac{xT_{g1}^0 + C(1-x)T_{gB}^0}{x + C(1-x)} \quad (2)$$

From these two equations, the difference of the glass transition temperatures of the two solutions will be

$$\begin{aligned} \Delta T_g(x) &= T_{gA}(x) - T_{gB}(x) = \frac{(1-x)C(T_{gA}^0 - T_{gB}^0)}{x + (1-x)C} \\ &= \frac{CR(T_{gA}^0 - T_{gB}^0)}{1 + CR} \end{aligned} \quad (3)$$

When $CR \ll 1$, Eq. 3 can be approximated to be

$$\Delta T_g(R) \simeq CR(T_{gA}^0 - T_{gB}^0) \quad (4)$$

and when $CR \gg 1$, we get

$$\Delta T_g(R) \simeq (T_{gA}^0 - T_{gB}^0). \quad (5)$$

The variation of $\Delta T_g(R)$ is shown in Fig. 3 as a function of the variable CR . It is interesting to apply Eq. 3 to the LiCl and $ZnCl_2$ solutions, though there is some ambiguity about the applicability of Eq. 3 to aqueous solutions. Assuming that $(T_{gA}^0 - T_{gB}^0)$ is 5 °C, the calculations give $C=0.4 \pm 0.1$ for the LiCl solution and $C=0.05 \pm 0.01$ for the $ZnCl_2$ solution. The C value should be 1 in an ideal solution. From these values, it may be said that the non-ideality of the solution is larger for the $ZnCl_2$ solution than for the LiCl solution.

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