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Pressure Dependence and Cationic Radius Effect of the Glass Transition Temperature in Aqueous Alkali Acetate Solutions

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The glass transition temperature (T_g) is measured as a function of pressure up to 200 MPa for the aqueous Li, Na, K, Rb, and Cs acetate solutions. The effects of cation radius on the glass transition of these solutions are discussed and some attempts are made to correlate T_g (and associated properties) with r (cation radius).

Glass transition is characterized by a heat absorbing inflection in a DTA trace and affected by many factors.1) In recent glass formation studies,2,3) it is shown that glass transition temperature (T_g) is a good diagnostic parameter to represent thermodynamic and transport properties of a supercooled liquid and glass system. In contrast to silicate and borate systems,4) glass formation studies of aqueous solutions have been still scarce.

As aqueous electrolyte solutions in high concentrations are a very complicated system, defying any simple theoretical treatment, it is of importance, as a first step, to investigate the effects of various factors affecting the magnitude of T_g. Ionic radius of ions (r) is of course an important factor in transport and thermodynamic properties of aqueous solutions.5) Alkali ions are simple in structure and essentially ionic so that aqueous solutions of alkali salts are a suitable target if only they are glass-forming. It is expected that the effect of pressure on T_g can be an auxilliary diagnostic tool to clarify the structure and thermodynamic properties of concentrated aqueous solutions.

In this work, we have measured the glass transition temperatures of aqueous alkali acetate solutions as a function of pressure and discussed the effects of pressure and cation radius on the glass transition of the solutions.

Experimental

Aqueous solutions of alkali acetates were prepared by dissolving guaranteed grade alkali acetates in distilled water. The concentration was all set to be $R=10$ ($R=$mol of water/mol of salt). The high pressure DTA cell is essentially the same one as used in the measurements of homogeneous nucleation temperature of emulsified aqueous solutions and water.6) The sample container used for the high pressure experiment was a 1 mm inner-diameter capillary glass cell, in which an aliquot of sample solution was filled and an alumel-cromel thermocouple junction (Omega-clad 0.02 inch o.d. thermocouples) was inserted. As a pressure transmitting fluid and the reference material, a 1:1 mixture of methylcyclopentane and methylcyclohexane was used because of its low vitrification temperature (below -150 °C at atmospheric pressure).

Vitrification of the sample solution was made at pressure of about 30 MPa by plunging the high pressure cell directly into liquid nitrogen. The overall cooling rate was about 200 K/min. Then the differential and temperature emf's were recorded at a heating rate of about 5 K/min in the temperature range where the glass transition took place Immediately after observing the glass transition, pressure was increased by 20—30 MPa and then the high pressure cell was cooled to liquid nitrogen temperature. This process was repeated up to pressure about 200 MPa.

T_g at atmospheric pressure was also measured with a simple DTA method. The reference material in this case was benzene. Vitrification of the sample solution in a 2 mm diameter Pyrex glass cell was carried out by immersing the cell in liquid nitrogen. The overall cooling rate in this case was about 10^3 K/min. The DTA trace was recorded at a heating rate of about 5 K/min.

Results and Discussion

The T_g values obtained at normal pressure are shown in Fig. 1 together with two insets in which a typical DTA trace and the (T_c/T_g) *vs.* $1/r$ plot are presented (T_c: crystallization temperature). As is already pointed out,6) T_g for the sodium acetate solution is the maximum among all alkali acetate solutions.

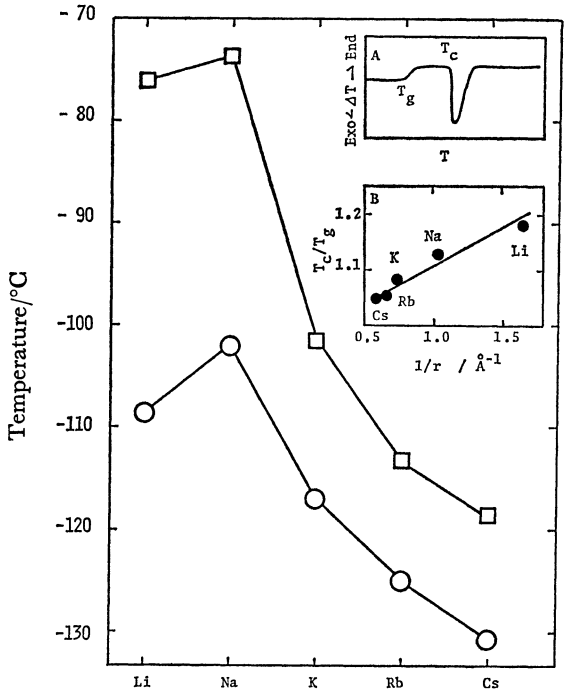

Fig. 1. Glass transition temperature (T_g) and crystallization temperature (T_c) of aqueous alkali acetate solution.

○: Glass transition temperature, □: crystallization temperature. The inset A shows a schematic DTA trace of a glassy sample. The inset B shows the correlation of T_c/T_g with $1/r$.

As acetate anions in these aqueous solutions are common, variation of T_g with a solute can be ascribed to cationic effect. A general trend is the decrease of T_g with the increase in cation radius and is in parallel with the observations for aqueous solutions of lanthanoid chlorides and perchlorates.⁷⁾ Kanno and Akama⁷⁾ have recently shown that T_g of aqueous rare earth chloride and perchlorate solutions is sensitive to an inner-sphere hydration number of cations. This clearly indicates that the inner-sphere hydration number of cations is one of the key parameters for the magnitude of T_g in aqueous solution. While a smaller ion is expected to have a small number of near neighbor water molecules on account of its small size, it has a greater polarizing power than a larger one, thus accomodating a larger total hydration sphere.⁸⁾ As the glass transition takes place at a temperature above which there are relatively rapid translational motions of ions (molecules),⁹⁾ a higher T_g is expected for a solution in which ions have a larger hydration sphere. Therefore, the trend of the T_g increase with decreasing ionic radius in these solutions is very reasonable.

The apparent deviation of T_g for the lithium acetate solution from the above-mentioned general trend deserves a special attention because the total hydration sphere of lithium ion should be the largest among all alkali ions. From X-ray diffraction studies of aqueous LiCl and NaCl solutions, the inner-sphere hydration numbers of Li^+ and Na^+ ions are determined to be four although there remains some uncertainty in the case of Na^+ ion.¹⁰⁾ Consequently it is difficult to ascribe the anomalous T_g behavior of the lithium acetate solution to the difference of the inner-sphere hydration number between Li^+ and Na^+.

A plausible explanation, though tentative at the moment, may be resorted to the fact that the electropositivity of lithium ion is rather weak among alkali ions.¹¹⁾ The lithium ion-water interaction is claimed to be partially covalent.¹²⁾ This is simply exemplified by Samoilov's positive and negative hydration concept¹³: the hydration of K^+, Rb^+, and Cs^+ is classified as negative (structure breaker), Na^+ is almost on the borderline between positive and negative hydration and Li^+ is strongly positive (structure marker) in hydration. From T_g's of a vapor-deposited amorphous ice^{14,15)} and binary mixtures of water and organic compounds,¹⁶⁾ the glass transition temperature of a bulk glassy water is expected to be very near −139 °C. Accordingly, the structure making effect of Li^+ ions should act T_g of a lithium salt solution to become nearer to T_g of a bulk water.

In contrast to the above irregularity, the linear relation between T_c/T_g and $1/r$, shown in the inset of Fig. 1, is interesting. The transport properties of supercooled liquids are well described by the Vogel-Tammann type equation¹⁷⁾

$$\rho = \rho_0 \exp\left\{\frac{B}{(T-T_0)}\right\}, \tag{1}$$

where ρ is the transport property such as viscosity, electrical conductivity of supercooled liquid, T_0 is the temperature below which the liquid contains no free volume and is considered to be near T_g, and ρ_0 and B are constants. Replacing T_0 with T_g and rearranging Eq. 1, we obtain

$$T_c - T_g \simeq B/\ln(\rho_c/\rho_0), \tag{2}$$

where ρ_c is ρ at T_c. Therefore, knowing that T_c is one of the corresponding states, the linear relation between T_c/T_g and $1/r$ demonstrates that the transport properties such as viscosity and conductivity of supercooled aqueous alkali acetate solutions are well correlated with ionic radius of alkali ions.

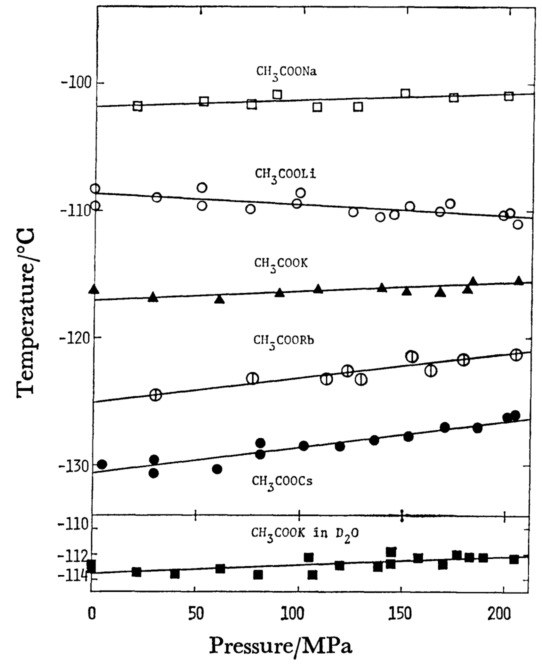

Fig. 2. Pressure dependence of T_g for aqueous alkali acetate solutions (R=10).
The (dT_g/dP) values are, CH_3COOLi: −0.85; CH_3COONa: 0.55; CH_3COOK: 0.70; CH_3COORb: 1.91; CH_3COOCs: 2.07; CH_3COOK in D_2O: 0.66 K/kbar (or $\times 10^{-2}$ K/MPa). The estimated error for each (dT_g/dP) is about ±0.30 K/kbar.

The T_g data at high pressures are presented in Fig. 2. The results for the CH_3COOK solution in D_2O are shown in the bottom inset of Fig. 2. A remarkable point is that the (dT_g/dP) value increases in the order $Li^+<Na^+<K^+<Rb^+<Cs^+$. Another is the negative pressure dependence of T_g for the lithium acetate solution. The latter point is already pointed out by William and Angell.¹⁸⁾ They interpreted this negative pressure dependence as evidence for the failure of the free volume theory for transport properties of liquid. The (dT_g/dP) value obtained in this work is $-0.8_5\pm0.3$ K/kbar (1 kbar=100 MPa), in fair agreement with the value ($-0.6_4\pm0.3$) by William and Angell.¹⁸⁾

The (dT_g/dP) *vs.* $1/r$ plot is shown in Fig. 3. We again obtain an approximately linear relation between (dT_g/dP) and $1/r$. Although the glass transition is not an equilibrium phase transition and is still controversial whether it is a kind of second order transition or a kinetic phenomenon due to slow relaxation,^{19–21)} the applicability of the following thermodynamic relations is often noted at the glass transition^{9,22)}

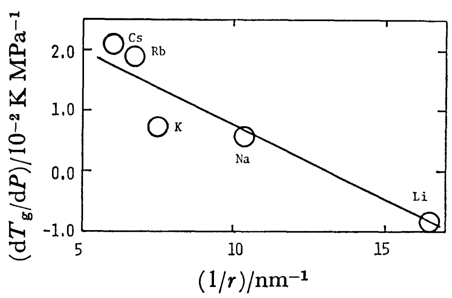

Fig. 3. Correlation of (dT_g/dP) with ionic radius of alkali ion.

$$\frac{dT_g}{dP} \simeq V_g T_g \frac{\Delta\alpha}{\Delta C_p}$$

$$\frac{dT_g}{dP} \simeq \frac{\Delta\kappa}{\Delta\alpha},$$

where $\Delta\alpha$, ΔC_p, and $\Delta\kappa$ are the changes in volume expansion coefficient, constant pressure heat capacity and isothermal compressibility at T_g, and V_g is molar volume of glass. Without experimental data for $\Delta\alpha$, ΔC_p, $\Delta\kappa$, and V_g, it is difficult to single out the factor responsible for the order of the (dT_g/dP) values in alkali acetate solutions. However, knowing that T_g is in the order $Na^+ > Li^+ > K^+ > Rb^+ > Cs^+$ and $\Delta\alpha$ can not be a major cause, we infer that V_g and $\Delta\kappa$(or one of them) should be the major factors for the magnitude order of (dT_g/dP) in alkali acetate solutions. This is partially supported by the fact that the partial molal volume of alkali metal ion in an aqueous solution increases in the order $Na^+ < Li^+ < K^+ < Rb^+ < Cs^+$ [5] (Note: $T_g(\mathrm{Li})V_{\mathrm{Li}} < T_g(\mathrm{Na})V_{\mathrm{Na}}$, $V_{\mathbf{a}}$: partial molal volume for ion **a**) and that it is closely connected with ionic radius of ion. Clearly more data are needed before we can give a more clear-cut interpretation about the sequence of the (dT_g/dP) values.

Finally it is worth mentioning about the isotope effect on T_g at high pressures. The pressure dependence of T_g for the potassium acetate solution in D_2O ($R=10$) is shown in the inset of Fig. 2. The least-square best fit yields $0.6_6 \pm 0.3$ K/kbar for the slope (dT_g/dP) of the D_2O solution, which is almost identical to the value for the H_2O solution ($dT_g/dP = 0.7_0 \pm 0.3$ K/kbar). This feature is very similar to the isotope effect of melting temperature of water along the melting curve. The difference of melting temperature between H_2O and D_2O is 3.82 °C at normal pressure and changes little with pressure up to 200 MPa.[23]

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