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Glass Formation Study of Aqueous HX Solutions (X=F, Cl, and Br)

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Glass-forming composition regions of aqueous HX solutions (X=F, Cl, and Br) were determined. It was found that oxonium ions play an important role in glass-forming behavior of these solutions. Including the results for HI solution previously reported,[1] the general trends of glass-formation behavior of aqueous HX solutions are summarized.

As an extension of the previous work,[1] we measured the glass-transition temperatures (T_g's) of aqueous HX solutions (X=F, Cl, and Br) as a function of the HX concentration.

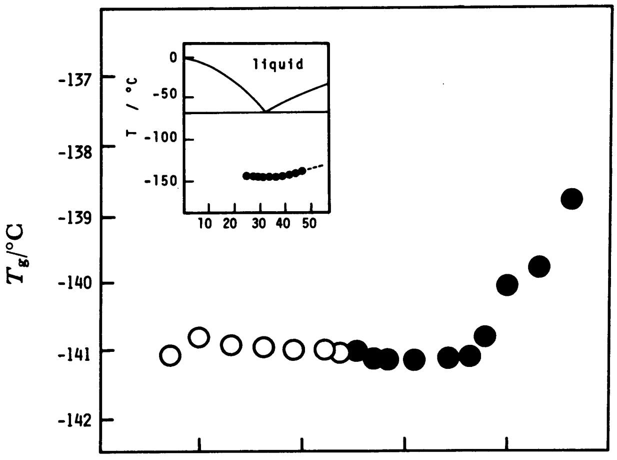
The object of this work is two-fold: (1) to see the general trends of glass-formation behavior of aqueous HX solutions, and (2) to find out the reason why the extrapolation of the T_g data of the HI–water system to pure water predicts the glass-transition temperature of glassy bulk water to be around −177 °C, far below the value (−135∼−140 °C) expected from the T_g data for other aqueous electrolyte solutions.[2,3]

Experimental

Each sample solution was prepared by simple mixing concentrated HX acid and distilled water by weight. The T_g measurements were carried out in the same way as previously described.[1] Glass formation of the quenched sample solution was visually checked. The abrupt shift of T_g is a good indicator for crystallization or partial crystallization of a quenched sample and therefore can be used for checking glass-formation (crystallization). The upper limit of the glass forming composition range was not established because of the difficulty of obtaining higher concentrated HX solutions (HF>46 wt%, HCl>35 wt%, HBr> 47 wt%).

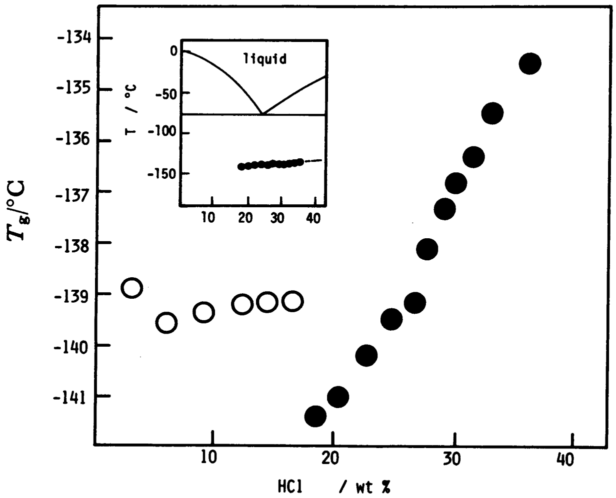
Results and Discussion

The T_g results for each HX solutions are shown in Figs. 1—3 together with the phase diagrams. Among HX solutions, glass formation of HCl solution has been well studied[4,5] and our results are in good agreement with previous reports.[4,5] Including the results for HI solution which was already reported,[1] we summarized the general trends as follows; (1) except the HF solution, T_g increases almost linearly



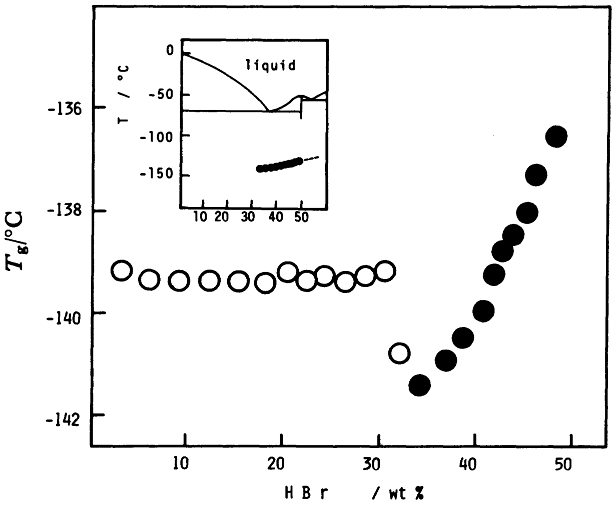
Glass forming region of the HF-H_2O system

Fig. 1. Variation of T_g with solution composition. The inset shows the phase diagram of the HF–Water system [from J. Timmermans, "Physico Chemical Constants of Binary Systems," Interscience Publishers, New York (1960) vol. 4, p. 439.]
●: T_g in the glass-forming composition region. ○: T_g of the portion remained uncrystallized in the non-glass-forming composition region.



Glass forming region of the HCl-H_2O system

Fig. 2. Variation of T_g with solution composition. The inset shows the phase diagram of the HCl–Water system [from the same reference as the HF–Water system, p. 446].
●: T_g in the glass-forimng composition region. ○: T_g of the portion remained uncrystallized in the non-glass-forming composition region.



Glass forming region of the HBr-H_2O system

Fig. 3. Variation of T_g with solution composition. The inset shows the phase diagram of the HBr–Water system [from the same reference as the HF–Water system, p. 461].

●: T_g in the glass-forming composition region. ○: T_g of the portion remained uncrystallized in the non-glass-forming composition region.

with HX (in wt%) concentration, (2) the lowest T_g value for each glassy HX solution is about −141 °C, and (3) the first eutectic composition is glass-forming for all HX solutions (X=F, Cl, Br, and I).

Among these trends, the last one is generally observed for most glass forming aqueous solutions.[3] In fact, a binary solution of the eutectic composition is most prone to be glass forming if it has any glass forming composition range.[6]

Glass formation of the HF solution begins from the concentration of about 25 wt% up to ≈46 wt%HF (above which experiment was not made in this study). An interesting point is that T_g is nearly invariant in the concentration range from ≈25 wt% to ≈40 wt% HF and then rises up at higher HF concentrations. Similar behavior has been observed for aqueous LiCl and $MnCl_2$ solutions.[2,7] In these solutions, T_g decreases with water content, then tends to level off at a certain salt concentration and becomes concentration independent of further increase in water content.[2,7,8] There are two possible causes: One is a precursor phenomenon of a phase-separation (liquid–liquid immiscibility)[9,10] and the other the partial crystallization of the solution in the quenching process. In the former case, a homogeneous solution splits into two phases (one is a water-rich phase and the other is a salt-rich one) as the temperature of the solution is lowered.[10] Due to the large thermal instability of the water-rich phase in a high-degree supercooled state, the water-rich liquid phase (possibly dispersed as fine micro-droplets in the solution) crystallizes in the quenching process and only the salt-rich phase is quenched to a vitreous state. In the latter case, the partial crystallization of the solution occurs in the quenching process. As water content increases in the solution, the energy barrier for ice nucleation becomes very low due to the very low stability of bulk supercooled water against ice crystallization.[11] At present it is difficult to determine which is the cause for the observed T_g behavior of the HF solution.

Comparing the solution compositions at which the HX solution becomes glass-forming with the cooling rate of about 600 K min^{-1}, we immediately know that the order of the HX concentration is HF>HBr>HCl>HI, indicating that the HX solution tends to be glass forming with a lower concentration of HX when X^- is a stronger structure breaker: A HI solution is glass-forming at $R \approx 10.2$ or less but a HF solution can be vitrified only at $R \approx 3.3$ or less (R=moles of water/moles of HX). This glass-forming feature is opposite to the trend for other aqueous electrolyte solutions, which are tend to be glass forming when containing small structure-making ions as a component (or components) of an electrolyte in the solutions.[2] Therefore, we consider that the glass forming ability of aqueous HX solutions should be relevant to oxonium ions in the solutions.

It is now established that oxonium ions in aqueous HX solutions (except X=F) are mostly preserved from a liquid state at room temperatures to a glassy state.[12] On the other hand, ionic dissociations of HNO_3, H_2SO_4, and H_3PO_4 in concentrated aqueous solutions are greatly reduced at low temperatures.[13] In these solutions, Raman bands arising from neutral acid molecules increase in their intensities at low temperatures.[13] Glass formation of aqueous HNO_3 solution begins from 35 wt% HNO_3 (R=6.5) to higher HNO_3 concentrations.[14] The need of higher acid concentration for glass forming of the HNO_3 solution as compared with HX solutions (X=Cl, Br, and I) should be partly due to the decrease of ionization of HNO_3 at low temperatures.

From X-ray and neutron diffraction studies,[15,16] it is concluded that the structure of hydrated oxonium ions in aqueous HCl solutions is trigonal pyramid $OH_3^+(OH_2)_3 \cdots (HOH)$, in which three water molecules combine with a H_3O^+ ion through rather strong hydrogen bonds and one water molecule lies at the apex of the $OH_3^+(OH_2)_3$ pyramid. The existence of strong hydrogen bonds between oxonium ions and water molecules is considered to be a good inhibitor to ice nucleation.

The formation of oxonium ions should also be a major cause of the anomalous low T_g prediction for pure bulk water in the T_g data of aqueous HI solution. When a pure liquid is not glass -forming, estimation of its T_g is made successfully by the extrapolation of the T_g data of binary solution.[2,3,17] Though there have recently been a few reports[18,19] claiming that bulk water can be vitrified, at least partially, by ejecting highly compressed water into cryogenic solvents held at very low temperatures, there has been no reliable T_g datum for bulk glassy water. The estimated T_g for bulk water from the T_g data for binary aqueous solutions is around −138 °C.[2,3] In the cases of HCl and HBr solutions, least-square-curve-fitting calculations give the following formulae:

$$T_g = 0.43Y - 150(°\mathrm{C}) \text{ for aqueous HCl solution, and}$$
$$T_g = 0.37Y - 158(°\mathrm{C}) \text{ for aqueous HBr solution,}$$

where Y is wt% of HX. As previously reported,[1] the HI solution predicts T_g for a bulk glassy water to be around −177 °C. Acid strength increases in the order HF>HCl>HBr>HI,[20] and the strength of hydrogen bonds between X^- ions and water molecules is in the order HI>HBr>HCl>HF.[21] In acid solutions, protons move about between water molecules very rapidly.[22] It is well known that the ionic mobility of protons in aqueous solution is about nine times larger than that of lithium ions at 18 °C though the data are at infinite dilution.[23] Thus, knowing that glass transition occurs when diffusion is almost suppressed in a liquid[24] and that ionization of HX in aqueous HX solution is very high even at low temperatures,[12] we expect that the predicted T_g for pure water should reflect the high mobility of protons in the HX solutions. If the expectation is the case, the low T_g for bulk water predicted from the T_g data of aqueous HX solutions is reasonable. The fact that the stronger the HX acid is the lower the predicted T_g for pure water becomes can be taken as a validity of the above explanation. One supporting experimental evidence comes from the observation that the glass transition in a glassy ice crystal, which is claimed to be related to proton movements, occurs at −173 °C.[25] Another, though indirect, evidence is that the T_g data of HNO_3 solution predicts the T_g of pure water to be −144 °C,[14] in parallel with the observation that ionization of concentrated HNO_3 solution is much reduced at low temperatures.[13] However, these data are not so conclusive to warrant our conclusion definitely. Therefore, further experiments are needed before the anomalously low T_g prediction from aqueous HX solutions is fully clarified.

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