3308 © *1982 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **55**, *3308—3311 (1982)* [Vol. 55, No. 10

Glass Formation in the HI + Water System

Yoshifumi Akama and Hitoshi Kanno*
Department of Chemistry, Meisei University, Hino, Tokyo 191

(Received February 12, 1982)

Glass transition temperature (T_g) of aqueous HI solution was measured as a function of HI concentration. The T_g data of aqueous HI solution suggest an anomalously low T_g value for glassy bulk pure water. Double-glass-transition phenomenon is observed at the water-rich edge of glass-forming composition range.

Recent papers of Angell *et al.*[1,2] and of Lesikar[3–5] have shown that the glass transition temperature (T_g) can be a useful diagnostic tool for clarifying various thermodynamic properties of solutions. In addition, there is gathering evidence[6–8] that spectroscopic and structural studies of aqueous solutions in the glassy state can give unique information unobtainable from investigations at ordinary temperatures, *e.g.*, Kanno and Hiraishi[8] have recently showed that unambiguous detection of low frequency Raman bands, which are hidden or obscured by the strong Rayleigh scattering wing in a Raman spectrum for the liquid state, becomes possible in a Raman spectrum for the glassy state. Therefore, accumulation of glass formation data for various aqueous solutions should be worthwhile as the first step for adding aqueous solutions in the glassy state to our objectives of solution chemistry.

In this study, the glass formation of the HI+water system was investigated as a function of HI concentration. As iodide ion is a typical structure breaker and HI is a structurally simple acid, glass formation data of this system will be useful to see effects of various factors (*e.g.*, ionic radius, structure making or breaking properties of ions) on the glass-forming ability of aqueous solutions.

Experimental

Sample of hydriodic acid with various concentrations were prepared from an encapsulated 57 wt% HI aqueous solution and distilled water by simple mixing of the required amounts of them. Sample solutions got colored with pale yellow due to slight decomposition of HI soon after the mixing. T_g measurements were usually made within an hour after sample preparation. As the sample solution left standing for 2 d gave the same T_g value as the one obtained immediately after the preparation, we concluded that the trace of HI decomposition has a negligible effect on the glass formation and T_g value to the sample.

A sample solution (*ca.* 0.05 ml) in a 2 mm diameter Pyrex glass tube, in which an alumel-chromel thermocouple junction was inserted, was vitrified in liquid nitrogen. The overall cooling rate was about 1000 K/min. A simple differential thermal analysis technique was used to measure T_g.[1] Benzene was used as the reference material, and the temperature difference between the vitrified sample and the reference was recorded together with the temperature of the quenched sample. T_g and T_c (crystallization temperature) values were taken to represent the onset of transition as shown in Fig. 2. DTA measurements were carried out at a heating rate of about 5 K/min in the glass transition temperature region. T_g values were found to be reproducible in this study to within 0.5 K and the accuracy of temperature reading is estimated to be ±1 K from a determination of melting points of several guaranteed grade reagents (absolute ethanol, acetone, and chloroform). Quenched samples were checked for crystallinity by visual inspection. Any incompletely vitrified samples were associated with loss of transparency. Visual inspection showed that the glass-forming composition region of HI+water system ranges from *ca.* 40 to 57% (wt% HI). The upper limit of the glass-forming composition range was not well established because of the non-availability of higher HI concentrations (>57%) in this study. The glass transition was also observed for incompletely vitrified samples, and this arises from the fact that the residual portion which remains uncrystallized in the quenching process becomes a glassy state.

Results and Discussion

The results of T_g and T_c are shown in Fig. 1 together with the phase diagram of the $HI+H_2O$ system as an inset. It is clearly seen that the solution near the first eutectic composition is prone to supercooling to a vitreous state. This tendency is in accordance with many other binary systems.[1,9–11] In fact, most liquid mixtures which have glass-forming composition regions are usually glass-forming at the first eutectic composition.

In the glass-forming composition region of aqueous HI solution, T_g increases almost linearly with increase in HI concentration, ranging from -140 ± 1 °C at 40 wt% HI to -124 ± 1 °C at 57 wt% HI. Simple linear composition dependence of T_g is usually observed for a nearly ideal solution.[6] With this system, we may regard the solution as an ideal or quasi-ideal solution of water and $HI\cdot4H_2O$. A simple least-square curve fitting yields the following formula for the concentration dependence of T_g:

$$T_g = 0.91X - 177, \tag{1}$$

where X is concentration of HI in wt% and T_g in °C.

The estimation of T_g for a pure non-glass-forming liquid from T_g data of binary mixtures by extrapolation is now well established and the T_g values estimated give concordant results.[2,4] Rasmussen and MacKenzie[12] measured glass transition temperatures of several binary aqueous solutions: water+methanol, water+glycerol, and water+ethylene glycol. The extrapolation of the obtained T_g data to pure water gives -137 ± 2 °C as the T_g of glassy bulk water. Angell and Sare[1] also gave a similar value from studies of a large number of aqueous electrolyte solutions. This value is almost identical with the glass transition temperature (-139 °C) obtained[13] for an amorphous solid water made by the vapor deposition method. All these data, therefore, suggest that T_g of bulk pure water will be very close to -138 °C if a glassy bulk water is successfully formed

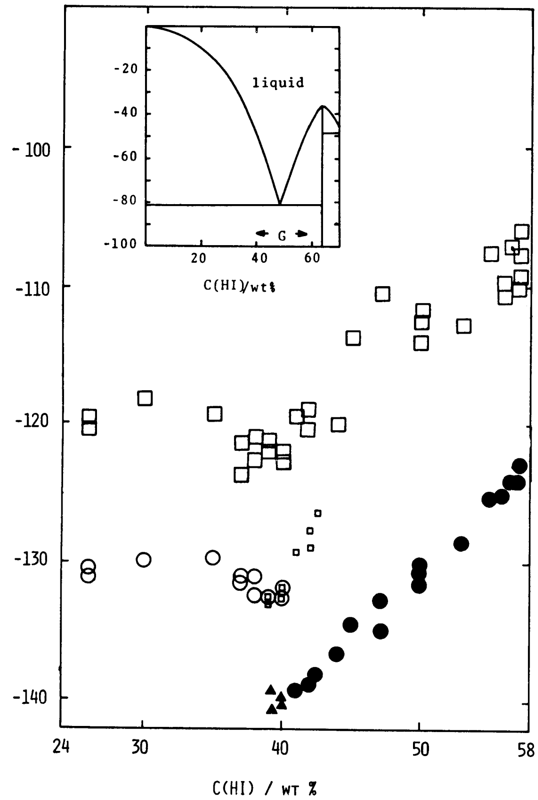

Fig. 1. Variation of T_g and T_c as a function of HI concentration (C). The inset shows the phase diagram of the $HI+H_2O$ system [from: J. Timmermans, "Physico Chemical Constants of Binary Systems," Interscience Publishers, Inc., New York (1960), Vol. 4, p. 466].
●: T_g in the glass-forming composition region, ○: T_g of the portion remained uncrystallized in the non-glass-forming composition region, or the second glass transition temperature (T_{g_2}) in the double glass transition region, ▲: the first glass transition temperature (T_{g_1}) in the double glass transition region, □ : the first crystallization temperature (T_{c_1}), □: crystallization temperature (T_c) or the second crystallization temperature (T_{c_2}).
The -G- mark in the inset shows the glass forming composition range.

and subjected to T_g measurement. However, it is interesting to note that Eq. 1 predicts T_g of glassy bulk pure water to be -177 °C, far below the T_g value (-138 °C) expected from other data.[1,12,13)]

There have been a few interesting observations[14,15)] which might offer a clue to clarifying this anomalously low T_g value. In a recent positron annihilation study of a γ-irradiated ice, Eldrup[14)] reported that monovacancies produced by γ-irradiation become mobile at -175 ± 5 °C. Another suggestive coincidence, though it might be merely accidental, is that the glass transition in a glassy crystal ice, which is claimed to be associated with proton disorder in the ice crystal,[15)] occurs at -173 °C. In addition, the T_g values so far reported for the vapor deposited amorphous ice and glassy bulk water scatter from -170 to -120 °C,[15)] although recent data are clustering around -138 ± 2 °C. We cannot, at present, give any clear-cut explanation to this low T_g (-177 °C) expected from a simple extrapolation based on Eq. 1 for the glassy bulk water. However, we conjecture, though rather intuitively, that hydronium ions stabilized in the glassy HI solution may be responsible for this low T_g. In fact, the T_g data of HX solutions (X=F, Cl, and Br)[16)] also predict that the glass transition of a glassy bulk water should be lower than -139 °C. Furthermore, a recent finding of polymorphism of amorphous ice[17)] adds a new possibility and complication to a clear-cut explanation. The T_g measurement on a high density amorphous ice will be very valuable in clarifying this situation.

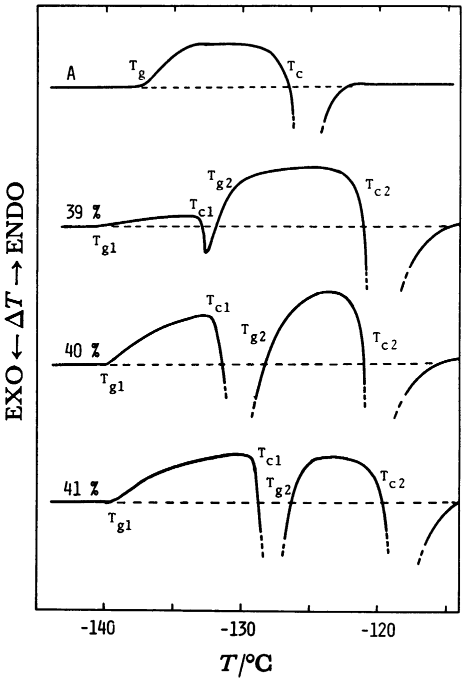

Fig. 2. DTA traces of glassy aqueous HI solutions. The A trace shows a typical DTA trace of a glassy sample.

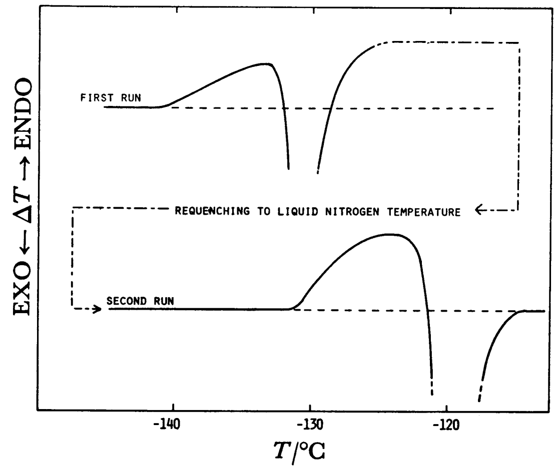

Fig. 3. Confirmation of the second glass transition in the glassy HI solution (HI=40 wt%).

Another interesting feature in the glass formation of the HI+water system is the observation of the double glass transition phenomenon at both boundaries of the glass-forming composition range. In the water-rich side of the glass-forming boundary, thermal effect of the first glass transition grows with increase in HI concentration and the two glass transitions gradually merge into a single large glass transition around 42 wt% HI (see (b), (c), and (d) DTA curves in Fig. 2).

As it is difficult to see clearly the second glass transition in the DTA traces shown in Fig. 2, we carried out the following additional experiment to confirm that there are really two glass transitions in these DTA traces: just after recording the first T_g and T_c curves as usual in the first run, the sample was requenched to the liquid nitrogen temperature and then a DTA trace was recorded again. The schematic DTA traces thus obtained are shown in Fig. 3, where we clearly see the second glass transition in the second warm-up DTA trace. This phenomenon reflects the phase separation in the supercooled solution. However, it is difficult at present to determine whether the observed double glass transition is a reflection of a "real" liquid-liquid immiscibility or of a simple pseudo-phase separation produced in the process of vitrification.

The first phase-separated portion, which is very unstable in the liquid state as evidenced by its immediate crystallization after the first glass transition in the warm-up DTA trace, is considered to be a water-rich phase because the T_g and T_c values of the other phase-separated portion are very close to those of the solution with the eutectic composition. Therefore, the phase separation must be described as: the solution → a water-rich phase+a phase of eutectic composition. The closeness of T_g of the water-rich phase to that of a vapor-deposited amorphous ice indicates that the composition of the water-rich phase should be very close to pure water.

The fact that the double glass transition phenomenon in aqueous solution has been observed only at the edge of the glass-forming composition region, seems to suggest that the phenomenon is associated with a metastable immiscibility. Two mechanisms have been postulated for the phase separation in supercooled solutions and glasses.[18,19] The invariance of the concentration of one phase (the phase of eutectic composition) in the phase-separated glasses in this study indicates that the observed phase separation in the $HI+H_2O$ system is due to the nucleation and growth mechanism.

It is to be noted here that there have been several attempts to detect a possible liquid-liquid immiscibility in the $LiCl+H_2O$ system at low temperatures and normal pressure.[20–22] Despite of two positive reports,[20,21] recent works have given rather a negative view for phase separation in the $LiCl+H_2O$ system.[22]

In contrast to the good reproducibility of the two-glass-transition phenomenon in the water-rich side of the glass-forming composition range, the double glass transition phenomenon in the vicinity of *ca.* 57 wt% HI solution is not good in reproducibility; even the sample which has shown two glass transitions in the first run does not necessarily give two glass transitions in the second run. Therefore, this "seemingly two" glass transition may not be due to phase separation. As the quenched sample is translucent, we come to conclude that it is in an incomplete glassy state and is not a phase-separated glass. It may be considered that the rearrangement motion of micro-crystals in the quenched sample is the cause for the second T_g-like heat anomaly in the DTA trace though no detailed mechanism is known.

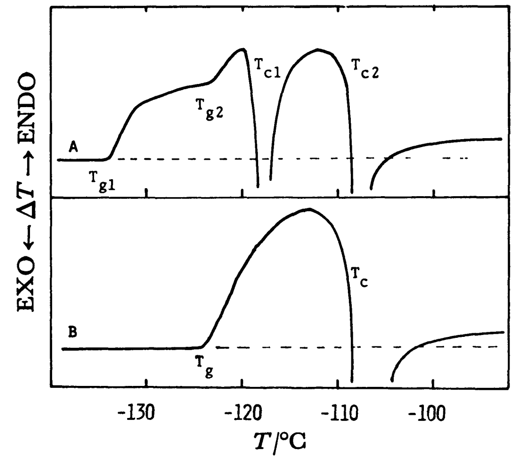

Fig. 4. DTA traces of the glassy aqueous HI solution (HI≈57 wt%).
(A): There are two glass transitions, (B): there is only one glass transition.

Lastly we point out the importance of crystallization temperature, to which little attention has been paid, as an auxiliary diagnostic parameter in the study of glass-forming properties of aqueous solutions. In fact, two crystallization peaks are observed in the concentration range where two glass transitions are observed. It can be seen in Fig. 1 that the solution at HI concentrations less than 40 wt% will divide into two phases (one is ice and the other the solution of eutectic composition) in the crystallization process, the latter phase being glass-forming in the rapid cooling. This is supported by the observation that the T_g value of the portion uncrystallized is very close to the T_g of the solution at HI=48 wt% (the eutectic composition). The invariance of T_c in this non-glass-forming composition range is also an additional support for the conclusion.

We are thankful to Professor C. A. Angell at Purdue University for his criticism on the first draft. This work was in part assisted by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

References

1) C. A. Angell and E. J. Sare, *J. Chem. Phys.*, **52**, 1058 (1970).

2) C. A. Angell, J. M. Sare, and E. J. Sare, *J. Phys. Chem.*, **82**, 2622 (1978); C. A. Angell and J. C. Tucker, *ibid.*, **84**, 268 (1980).

3) A. V. Lesikar, *Phys. Chem. Glasses*, **16**, 83 (1975).

4) A. V. Lasikar, *J. Chem. Phys.*, **63**, 2297 (1975); **66**, 4263 (1977); **68**, 3323 (1978).

5) A. V. Lesikar, *J. Solution Chem.*, **6**, 81, 839 (1977).

6) M. H. Herzog-Cance, J. Potier, A. Potier, P. Dhamelincourt, B. Sombret, and F. Wallart, *J. Raman Spec-*

trosc., **7**, 303 (1978).

7) H. Kanno and Y. Akama, *Chem. Phys. Lett.*, **72**, 181 (1980).

8) H. Kanno and J. Hiraishi, *Chem. Phys. Lett.*, **62**, 82 (1979); **72**, 541 (1980); *J. Raman Spectrosc.*, **9**, 85 (1980).

9) E. Thillo, C. Wiecker, and W. Wiecker, *Silikattechnik*, **15**, 109 (1964).

10) M. Imaoka, "Advances in Glass Technology," Plenum Press, New York (1962), Part 1, p. 149.

11) L. C. Shepley and A. B. Bestul, *J. Chem. Phys.*, **39**, 680 (1963).

12) D. H. Rasmussen and A. P. MacKenzie, *J. Phys. Chem.*, **75**, 967 (1971).

13) M. Sugisaki, H. Suga, and S. Seki, *Bull. Chem. Soc. Jpn.*, **41**, 2591 (1968).

14) M. Eldrup, *J. Chem. Phys.*, **64**, 5283 (1976).

15) H. Suga and S. Seki, *J. Non-Cryst. Solids*, **16**, 171 (1974).

16) H. Kanno and K. Satoh, to be published.

17) S. A. Rice, *Topics Current Chem.*, **60**, 109 (1975); A. H. Narten, C. G. Venkatesh, and S. A. Rice, *J. Chem. Phys.*, **64**, 1106 (1976).

18) J. W. Cahn, *J. Chem. Phys.*, **42**, 93 (1965); J. W. Cahn and R. J. Charles, *Phys. Chem. Glasses*, **6**, 181 (1965).

19) H. Rawson, "Inorganic Glass Forming System," Academic Press, London (1967), Chaps. 7 and 8.

20) C. A. Angell and E. J. Sare, *J. Chem. Phys.*, **49**, 4713 (1968).

21) S. Y. Hsich, R. W. Gammon, P. B. Macedo, and C. J. Montrose, *J. Chem. Phys.*, **56**, 1663 (1972).

22) J. Dupuy, J. F. Jal, C. Fierador, P. Chieux, A. Wright, R. Caleczuk, and C. A. Angell, *Nature*, **296**, 138 (1982).