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Anomalous Crystallization Behavior in the Glass Forming Composition Region of the H_2O-HNO_3 System

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Synopsis. Glass formation composition region of aqueous HNO_3 solution is determined. Anomalous crystallization behavior was observed for the solution having the composition near $HNO_3 \cdot 3H_2O$. From T_g data, T_g for a bulk glassy water is estimated to be -144 ± 2 °C.

Glass forming composition regions in aqueous solution systems have recently been determined for a relatively large number of both inorganic salt–water and binary organic compound mixture systems.[1–3] From these studies, it has become evident that glass transition temperature (T_g) can be a useful parameter for characterizing thermodynamic and transport properties of a liquid at low temperatures.[1–4]

In this note, we report an anomalous crystallization behavior of an aqueous HNO_3 solution in the composition near $HNO_3 \cdot 3H_2O$, which is very suggestive for clarifying both glass formation mechanism and structure changes of the solution with composition.

All solutions were made by weighing out and mixing required amounts of a commercially available guaranteed-grade ≈62 wt% nitric acid and distilled water. The glass transition temperature of each solution was measured by a conventional, simple DTA method. The details of the experiment were essentially the same as previously reported.[3] Overall cooling rate of the sample solution contained in a 2 mm i.d. Pyrex glass cell was about 10^3 K/min. The T_g value was obtained at a heating rate of about 5 K/min in the warm-up DTA trace using chromel-alumel thermocouples.

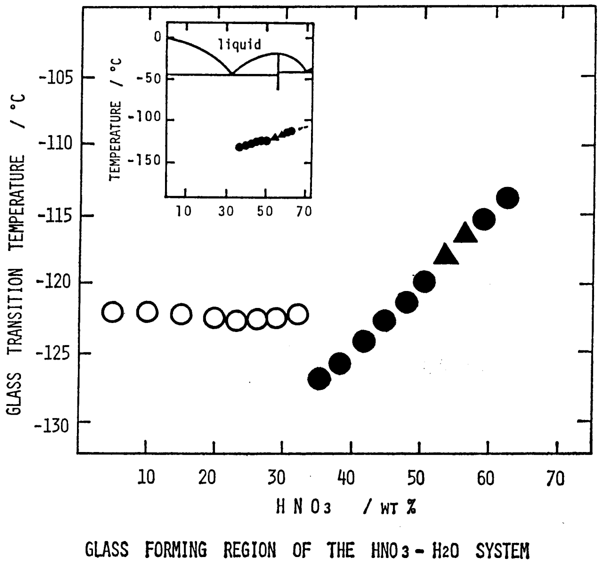

Fig. 1. Variation of T_g with solution composition. The inset shows the phase diagram of the HNO_3–H_2O system [from J. Timmermans, "Physico Chemical Constants of Binary Systems," Interscience Publishers, Inc., New York (1960), Vol. 4, p. 466]. ●: T_g in the glass-forming composition region, ○: T_g of the portion remained uncrystallized in the non-glass-forming composition region, ▲: the expected glass transition temperature if the solution was glass-forming.

The results obtained are plotted in Fig. 1 together with the phase diagram as an inset. Glass formation was visually checked and it began from the composition of about 35 wt% HNO_3 up to about 62 wt% HNO_3 (above which measurements were not made because of non-availability of a higher cocentration in this study). The solutions having the composition of less than 35 wt% HNO_3 are only partially glass-forming, therefore giving a glass transition as seen in the DTA trace A in Fig. 2.

An interesting point is the existence of a very narrow window (≈54 wt% HNO_3 region) where no glass transition is observed, indicating that the whole body of the solution crystallizes in the quenching rate of about 10^3 K/min. This is peculiar because most aqueous solutions which have a glass forming composition region are partially glass forming even in the non-glass forming composition region.[4,5] As the composition of the non-glass forming solution is very near 54 wt%, we consider that an additive compound of the composition $HNO_3 \cdot 3H_2O$ was formed in the cooling process. This is supported by the DTA trace C shown in Fig. 2. The fact that an appreciable part (about 5%) of the 53.8% HNO_3 solution crystallized in the eutectic composition, as evidenced with

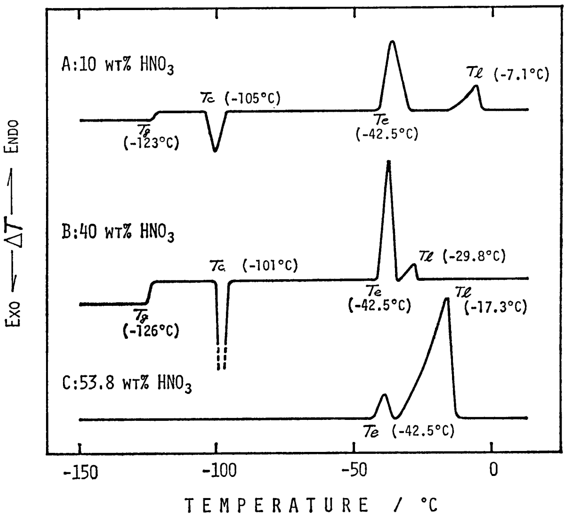

Fig. 2. DTA traces of several quenched HNO_3 solution.
T_c: Crystallization temperature, T_e: eutectic temperature of the HNO_3–H_2O system, T_l: liquidus temperature of the HNO_3–H_2O solution.

the DTA peak at −42 °C, suggests that there exists a considerable concentration fluctuation about 53.8 wt% HNO_3 in the solution in the liquid state.

Linear variation of T_g with solution composition indicates that the structure of the HNO_3 solution varies smoothly with the composition in the glass-forming composition region (≈35 to 62 wt% HNO_3). Thus, the existence of the narrow non-glass forming region can not be ascribed to a sudden change of the solution structure. It is considered that whether or not a given liquid crystallizes during cooling before a glass transition is reached is purely a kinetic problem.[6–8] Taking account of various factors appearing in the kinetic theories of glass formation developed by Turnbull *et al.*[7,9] and Uhlmann,[8] we consider that a geometrical factor, which has not been properly incorporated in the current kinetic theories despite of the fact that its importance has often been noted in various qualitative criteria for the glass-forming of a liquid,[10,11] is a main cause for the anomalous crystallization behavior. In other words, the structure of the ≈54 wt% HNO_3 solution at low temperature is expected to resemble that of the $HNO_3 \cdot 3H_2O$ crystal so that the barrier to nucleation is low as compared with that in other glass-forming concentration region.

Estimation of T_g for a pure non-glass forming liquid has often been made by the extrapolation of T_g data for binary mixtures.[1,2,12] A simple least-squares curve fitting for the present T_g data yields the following formula for the concentration dependence of T_g for the HNO_3 solution:

$$T_g = 0.48X - 144, \tag{1}$$

where X in HNO_3 wt% and T_g in °C. From Eq. 1, we estimate that the T_g value for a glassy bulk water will be −144±2 °C if water is successfully made a glassy state by a rapid cooling. This value is a little lower than those (−134—−138 °C) estimated from other T_g data for several aqueous solutions[1,12] and that (−139 °C) obtained for amorphous ice made by a vapor deposition method.[13] We consider that this low value is presumably due to hydronium ions in the glassy HNO_3 solution though an explicit interpretation is at present difficult. However, a plausible, though indirect, evidence for the above speculation comes from the observation that the mobility of H_3O^+ ions in ice is faster than that in aqueous solution (at room temperature) by about two order of magnitude.[14] Another supporting experimental evidence is that glass transition in a glassy crystal ice, which is claimed to be related to proton disordering, occurs at −173 °C.[15]

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