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## A Glass Formation Study of Aqueous Tetraalkylammonium Nitrate Solutions

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Received July 18, 1995; revised January 31, 1996

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*The glass-forming composition regions of aqueous tetraalkylammonium nitrate solutions (alkyl = ethyl and n-propyl) were determined by a simple DTA method with a cooling rate of about 600 K·min<sup>-1</sup>. The glass transition temperatures  $T_g$  of these solutions vary in a different manner from those for simple inorganic salt solutions such as aqueous LiCl, MgCl<sub>2</sub>, and AlCl<sub>3</sub> solutions. Liquid-liquid immiscibilities are observed in these solutions at low temperatures.*

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**KEY WORDS:** Glass formation; aqueous solution; tetraalkylammonium nitrate; hydrophobic interaction; glass transition temperature.

### 1. INTRODUCTION

There have been a relatively large number of studies of aqueous tetraalkylammonium salt solutions of dilute and medium salt concentrations at ordinary temperatures<sup>(1-5)</sup> but only a few studies devoted to explore their thermodynamic properties at low temperatures.<sup>(6,7)</sup> In recent papers,<sup>(7,8)</sup> it is pointed out that hydrophobic interaction plays an important role in the glass formation of aqueous tetraalkylammonium chloride and bromide solutions.

Although  $T_g$  variation of an aqueous tetramethylammonium chloride solution with salt concentration is similar to that of an aqueous LiCl solution, those of other R<sub>4</sub>NCl solutions (R = C<sub>2</sub>H<sub>5</sub> and n-C<sub>3</sub>H<sub>7</sub>, X = Cl, Br) are totally different, reflecting the hydrophobic interactions between R<sub>4</sub>N<sup>+</sup> ions and water molecules.<sup>(8)</sup> Therefore, it would be interesting and important to study the glass-forming behavior of aqueous R<sub>4</sub>NNO<sub>3</sub> solutions since some

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new interesting information will be gained about the hydrophobic interaction in concentrated aqueous solutions.

## 2. EXPERIMENTAL

Aqueous tetraalkylammonium nitrate solutions were prepared by converting aqueous  $R_4NNO_3$  solutions ( $R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9$ ) into the nitrate solutions using anion exchange resin Dowex 1-X8 (100 ~ 200 mesh). An aqueous  $R_4NCl$  solution was passed over the anion exchange resin Dowex 1-X8 of the nitrate form and the eluent was collected. As no chloride ion was detected in the eluent, it was concluded that the ion-exchange was complete enough.

Adjustment of the salt concentration of the  $R_4NNO_3$  solution was made by heating the eluent at temperature below  $100^\circ C$  on a hot plate to a highly concentrated solution and adding distilled water to the concentrated  $R_4NNO_3$  solution to a predetermined salt concentration. The concentration of the prepared sample solutions was expressed by  $Y$  (= mol of water per mol of nitrate). The salt concentration was checked by the acid-base titration after the solution was passed over the anion exchange resin Dowex 1-X8 of the OH-form. We estimated that the accuracy of the solution concentration was better than  $\pm 2\%$ .

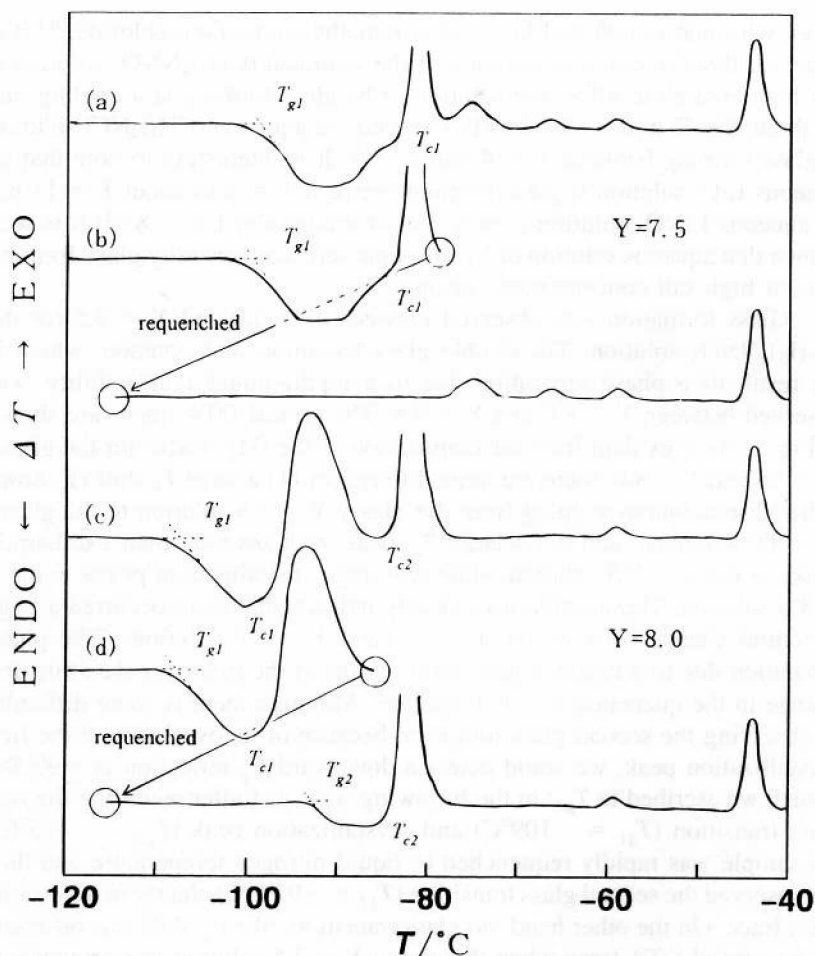
A simple DTA technique was employed to measure the glass transition temperatures  $T_g$  of these aqueous solutions. An aliquot of the sample solution in a 2mm inner-diameter glass tube with an end sealed, in which an alumel-chromel thermocouple junction was inserted, was vitrified in liquid nitrogen. The cooling rate of the solution was approximately  $600\text{ K}\cdot\text{min}^{-1}$ . Glass formation was checked visually as transparency of the solution is a good indicator for vitrification. Any incomplete vitrification is always associated with a loss of transparency and is easily detected visually. Benzene was used as a reference material. DTA measurements were carried out at a heating rate of about  $5\text{ K}\cdot\text{min}^{-1}$  in the glass transition temperature region. Reproducibility of the  $T_g$  determinations is better than  $\pm 1^\circ C$  and the accuracy of the  $T_g$  values was estimated to be about  $\pm 2^\circ C$  by the determination of the melting points of several organic compounds (toluene, methyl alcohol, and chloroform).

## 3. RESULTS AND DISCUSSION

Among four aqueous tetraalkylammonium nitrate solutions, only tetraethylammonium and tetrapropylammonium nitrate solutions are glass-forming in high salt concentration regions. As the solubility of tetramethylammonium nitrate is low (approximately  $7.9\text{ mol}\cdot\text{kg}^{-1(9)}$ ) as com-

pared with that ( $19.06 \text{ mol}\cdot\text{kg}^{-1}$ ) of tetramethylammonium chloride,<sup>(10)</sup> it is expected that the salt concentration of the saturated  $(\text{CH}_3)_4\text{NNO}_3$  solution is not high enough to allow the solution to be glass-forming at a cooling rate of about  $600 \text{ K}\cdot\text{min}^{-1}$ . As already reported, an aqueous  $(\text{CH}_3)_4\text{NCl}$  solution is glass-forming between  $Y = 4$  and  $Y = 7$ . It is interesting to note that an aqueous  $\text{LiCl}$  solution is glass-forming between  $Y = 3$  to about  $Y = 11$  but an aqueous  $\text{LiNO}_3$  solution is only glass-forming about  $Y = 8$ .<sup>(11)</sup> It is well known that aqueous solution of hygroscopic salts are generally glass-forming in their high salt concentration regions.<sup>(11)</sup>

Glass formation was observed between  $Y = 3.0$  and  $Y = 9.5$  for the  $(\text{C}_2\text{H}_5)_4\text{NNO}_3$  solution. The double glass transition phenomenon, which is the result of a phase separation due to a liquid-liquid immiscibility, was observed between  $Y = 8.0$  and  $Y = 9.5$ . The typical DTA traces are shown in Fig. 1. As is evident from the comparison of the DTA traces for the glassy  $Y = 7.5$  and  $Y = 8.0$ , there are large differences (1) a large  $T_g$  shift ( $T_g$  drops rather discontinuously going from the glassy  $Y = 7.5$  solution to the glassy  $Y = 8.0$  solution), and (2) a large  $T_{c1}$  peak with several small exothermic peaks in the  $Y = 7.5$  solution while two large crystallization peaks in the  $Y = 8.0$  solution. These differences clearly indicate that there occurred a large structural change between the  $Y = 7.5$  and  $Y = 8.0$  solutions. The phase separation due to a liquid-liquid immiscibility is the cause for the structural change in the quenched  $Y = 8.0$  solution. Although there is some difficulty in observing the second glass transition because of its overlap with the first crystallization peak, we could detect a downward  $C_p$  inflection at  $-92.5^\circ\text{C}$  (which we ascribed to  $T_{g2}$ ) in the following way: just after recording the first glass transition ( $T_{g1} = -109^\circ\text{C}$ ) and crystallization peak ( $T_{g1} = -105^\circ\text{C}$ ), the sample was rapidly reequenched to liquid nitrogen temperature and then we observed the second glass transition ( $T_{g2} = -92.5^\circ\text{C}$ ) clearly in the second DTA trace. On the other hand, no glass transition-like  $C_p$  shift was observed in the second DTA trace when the glassy  $Y = 7.5$  solution was reequenched just after observing the glass transition and the first exothermic peak  $T_{g1}$  at  $-90^\circ\text{C}$ . Therefore, we can conclude that observation of two glass transitions in the quenched  $Y = 8.0$  solution is ascribed to a liquid-liquid immiscibility. As the temperature is lowered, the homogeneous liquid solution becomes unstable and splits into two liquid phases (a water-rich phase and a salt-rich viscous one) to maintain thermodynamic stability. These two immiscible liquid phases are readily vitrified in the concentration range between  $Y = 8.0$  and  $Y = 9.5$  of the mother solution. Figure 2 shows the summarized  $T_g$  values for the  $(\text{C}_2\text{H}_5)_4\text{NNO}_3$  solution as a function of  $Y$ . As a typical  $T_g$  variation with  $Y$ , the  $T_g$  results for aqueous  $\text{LiCl}$  solution are shown in the inset of Fig. 2.  $T_g$  goes down in a downward concave way with increase in  $Y$ . On the other hand,  $T_g$  of the  $(\text{C}_2\text{H}_5)_4\text{NNO}_3$  solution falls rather linearly



**Fig. 1.** DTA traces for glassy aqueous  $(\text{C}_2\text{H}_5)_4\text{NNO}_3$  solutions of  $Y = 7.5$  and  $8.0$ . (a) and (b): DTA traces for the glassy  $(\text{C}_2\text{H}_5)_4\text{NNO}_3$  solutions of  $Y = 7.5$ . (c) and (d): DTA traces for the glassy  $(\text{C}_2\text{H}_5)_4\text{NNO}_3$  solutions of  $Y = 8.0$ . In the trace (b), it is confirmed that there is no second glass transition. Three exothermic peaks at  $-78$ ,  $-69$  and  $-63^\circ\text{C}$  maybe ascribed to the phase transitions associated with crystallized  $(\text{C}_2\text{H}_5)_4\text{NNO}_3$  hydrates.

with  $Y$ , and then discontinuously drops at  $Y = 8.0$  with the appearance of the second glass transition  $T_{g2}$ , indicating the abrupt compositional change of the solution. The  $T_{g2}$  value at  $Y = 8$  shows that the salt concentration of the salt-rich phase should be around  $Y = 4$ . The  $T_{g1}$  value of the water-rich phase falls linearly down to about  $-120^\circ\text{C}$  with increasing of  $Y$  in the mother solution and then the glass formation terminated due to the insufficient salt concentration of the water-rich phase as clearly shown by the opaqueness of

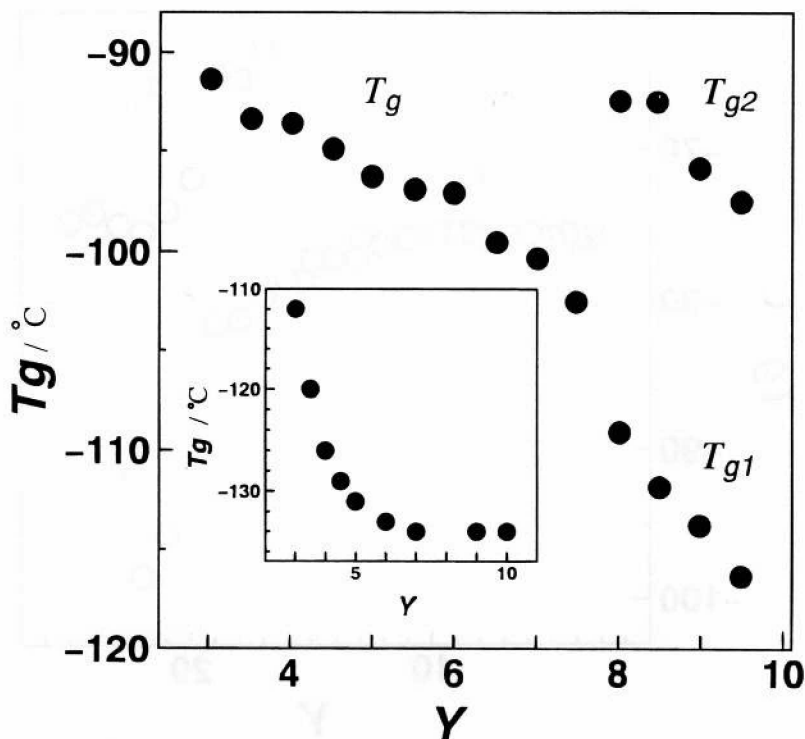


Fig. 2. The glass-forming composition region for an aqueous  $(\text{C}_2\text{H}_5)_4\text{NNO}_3$  solution. The inset shows the glass-forming composition region for an aqueous  $\text{LiCl}$  solution. ( $T_g$  data from Ref. 11 and our unpublished data.)

the quenched sample solution. In this connection, it is important to point out that the salt-rich phase is still glass-forming as evidenced by the high  $T_{g2}$  value. Comparison of the  $T_g$  results for the  $\text{LiCl}$  and  $(\text{C}_2\text{H}_5)_4\text{NNO}_3$  solution indicates that  $T_g$  of the later solution is much higher than the former one at the same  $Y$  value. This behavior is common for all the  $(\text{C}_2\text{H}_5)_4\text{NX}$  solutions ( $X = \text{Cl}, \text{Br}$  and  $\text{NO}_3$ ) as discussed later in more detail.

As is seen in Fig. 3, the glass-forming composition region is much wider for the  $(n\text{-C}_3\text{H}_7)_4\text{NNO}_3$  solution than for the  $(\text{C}_2\text{H}_5)_4\text{NNO}_3$  solution. An interesting feature is that there is a wide composition region where  $T_g$  is almost invariant despite of the salt concentration changing from  $Y = 4$  to  $Y = 14$ . The similar behavior has been observed for  $(n\text{-C}_3\text{H}_7)_4\text{NCl}$  and  $(n\text{-C}_3\text{H}_7)_4\text{NBr}$  solutions.<sup>(8)</sup> As the viscosity of a glass-forming liquid is well expressed by the so-called WLF formula<sup>(12)</sup>

$$\eta = \eta_0 \exp[A/(T - T_0)]$$

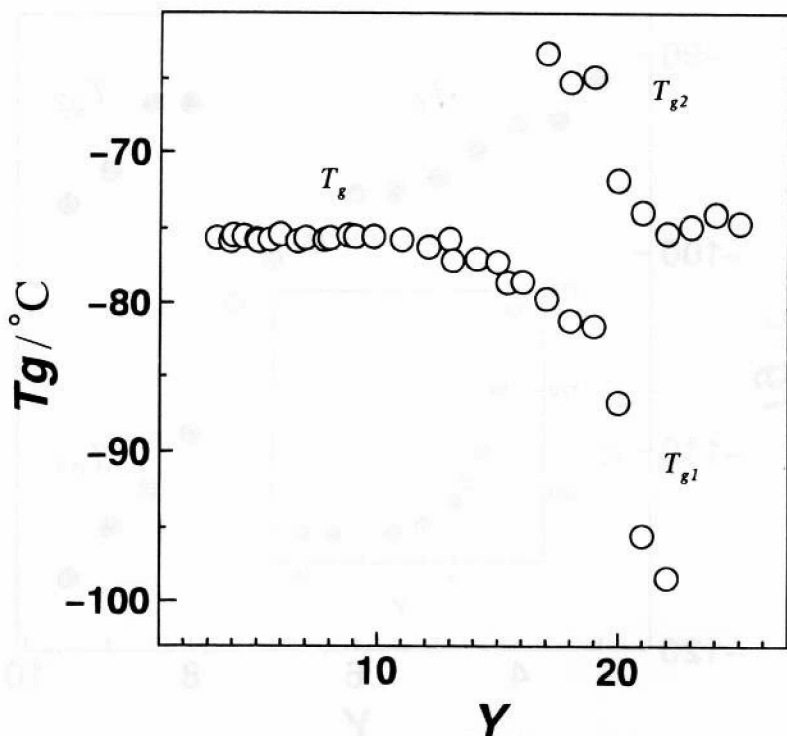


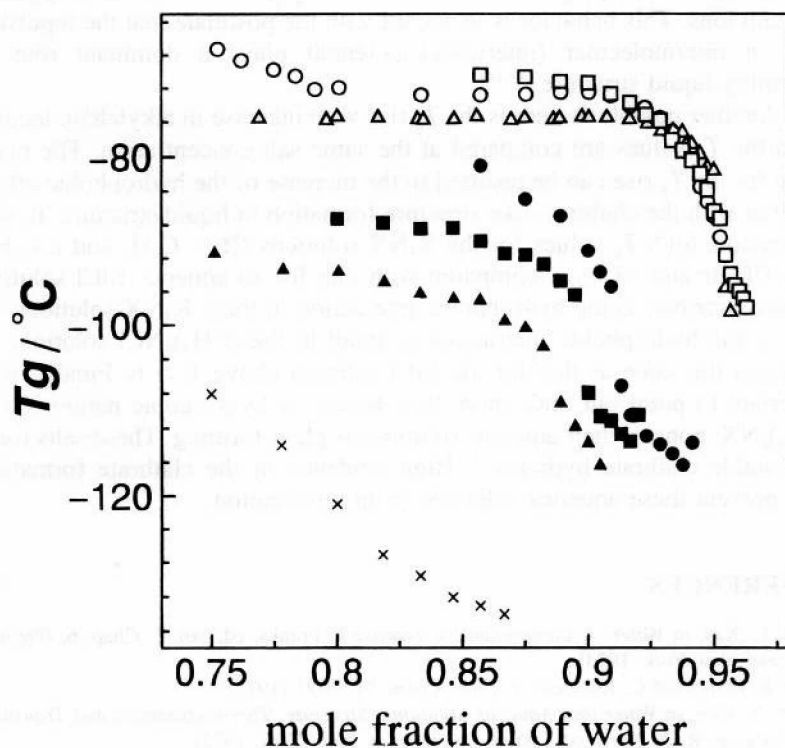
Fig. 3. The glass-forming composition region for an aqueous  $(n\text{-C}_3\text{H}_7)_4\text{NNO}_3$  solution.

where  $\eta$  is the viscosity at  $T$ ,  $T_0$  is a constant and is considered to be near  $T_g$ , and  $\eta_0$  and  $A$  are constants for the system. It is inferred from this formula that the isothermal viscosity of the  $(n\text{-C}_3\text{H}_7)_4\text{NNO}_3$  solution is invariant from  $Y = 3$  to  $Y = \sim 14$  at temperatures just above  $T_g$ . It is considered that clathrate-like structure formation is the major cause for the invariant  $T_g$  behavior with the salt concentration. As an  $(n\text{-C}_3\text{H}_7)_4\text{N}^+$  ion is smaller than an  $(n\text{-C}_4\text{H}_9)_4\text{N}^+$  ion, which is well known for its stable clathrate hydrate formation, water structure around an  $(n\text{-C}_3\text{H}_7)_4\text{N}^+$  ion should resemble the structure of an aqueous  $(n\text{-C}_4\text{H}_9)_4\text{NCl}$  solution. It is also expected that the structure of the  $(n\text{-C}_3\text{H}_7)_4\text{NNO}_3$  solution may resemble those of molten states of the simple clathrate such as  $(\text{CH}_3)_3\text{CNH}_2/9(3/4)\text{H}_2\text{O}$  and  $(\text{C}_2\text{H}_5)_2\text{NH}_2/6(2/3)\text{H}_2\text{O}$ . The clathrate-like structure might develop with increase in water content by sharing of water molecules with adjacent cage-like structures. The extensive sharing of water molecules between adjacent clathrate-like structures should develop in the constant  $T_g$  region from  $Y = 3$  to  $Y = 14$ . The normal  $T_g$  behavior with salt concentration is that  $T_g$  falls smoothly with

increase in water content, as well represented by the  $T_g$  curve of an aqueous LiCl solution (the inset in Fig. 1).

Above  $Y = 14$ , two glass transitions are observed, indicating that a phase separation occurred in the quenching process. High  $T_{g2}$  value suggests that the salt concentration of the phase-separated salt-rich phase should be higher than that of the solution of  $Y = 4$ . The rapid  $T_g$  rise toward higher salt concentration (decreasing in  $Y$  value) is a common phenomenon for every aqueous binary solution.<sup>(11)</sup> Thus, if an aqueous  $(n\text{-C}_3\text{H}_7)_4\text{NNO}_3$  solution of  $Y < 4$  was vitrified,  $T_g$  should be higher than  $-75^\circ\text{C}$ . The rather invariant  $T_{g2}$  value for the solution of  $Y > 22$  indicates that the salt content in the salt-rich phase is in the  $4 < Y < 14$  range of the mother solution. Therefore, it is expected that the salt-rich phase will behave the same way as the mother solution when we quenched the solution with changing the salt concentration.

Figure 4 shows the summarized  $T_g$  data for tetraalkylammonium salt solutions so far reported together with the  $T_g$  data obtained in this work.



**Fig. 4.** The summarized  $T_g$  data for glassy aqueous  $R_4NX$  solutions. (x):  $(\text{CH}_3)_4\text{NCl}$ , (●):  $(\text{C}_2\text{H}_5)_4\text{NCl}$ , (■):  $(\text{C}_2\text{H}_5)_4\text{NBr}$ , (▲):  $(\text{C}_2\text{H}_5)_4\text{NNO}_3$ , (○):  $(n\text{-C}_3\text{H}_7)_4\text{NCl}$ , (□):  $(n\text{-C}_3\text{H}_7)_4\text{NBr}$ , (△):  $(n\text{-C}_3\text{H}_7)_4\text{NNO}_3$



Here all the  $T_{g2}$  data are excluded from plottings for avoiding complexity. As to the  $(\text{CH}_3)_4\text{NX}$  solutions ( $\text{X} = \text{Cl}, \text{Br}$  and  $\text{NO}_3$ ) only the chloride solutions is glass-forming so that it is impossible to discuss the anionic effect on the glass-forming behavior. Comparison of the  $T_g$  results for the  $(\text{C}_2\text{H}_5)_4\text{NX}$  solutions shows that the  $T_g$  values are in the order:  $T_g(\text{chloride}) > T_g(\text{bromide}) > T_g(\text{nitrate})$ , at the same salt concentration. On the other hand, the  $T_g$  values for aqueous inorganic salt solutions are in the order:  $T_g(\text{nitrate}) > T_g(\text{chloride}) > T_g(\text{bromide})$ . There is a clear tendency that  $T_g$  becomes lower for an aqueous solution of a larger structure breaking ion. It is difficult, at present, to give a plausible explanation about the low  $T_g$  values for the  $(\text{C}_2\text{H}_5)_4\text{NNO}_3$  solution. However, it is interesting to note that the  $T_g$  values of  $(\text{C}_2\text{H}_5)_4\text{NX}$  solutions are in the same increasing order as viscosity  $B$  coefficient.<sup>(1)</sup> As is evident from Fig. 4, the anionic effect becomes small for the  $T_g$  behavior of the  $(\text{C}_2\text{H}_5)_4\text{NX}$  solutions as all the solutions give similar  $T_g$  values. As tetrapropylammonium ion is much larger than an  $\text{X}^-$  ion ( $\text{X}^- = \text{Cl}^-, \text{Br}^-$  and  $\text{NO}_3^-$ ), solution properties are predominantly governed by tetrapropylammonium ions. This behavior is in accord with the postulate that the repulsive term in intermolecular (interionic) potential plays a dominant role in determining liquid structure.<sup>(13,14)</sup>

Another notable feature is the  $T_g$  rise with increase in alkylchain length, when the  $T_g$  values are compared at the same salt concentration. The main cause for the  $T_g$  rise can be resorted to the increase of the hydrophobic effect together with the clathrate-like structure formation in liquid structure. In this connection, high  $T_g$  values for the  $\text{R}_4\text{NX}$  solutions ( $\text{R} = \text{C}_2\text{H}_5$  and  $n\text{-C}_3\text{H}_7$ ,  $\text{X} = \text{Cl}, \text{Br}$  and  $\text{NO}_3$ ) as compared with that for an aqueous  $\text{LiCl}$  solution are also ascribed to the hydrophobic interaction in these  $\text{R}_4\text{NX}$  solutions. In fact, as the hydrophobic interaction is small in the  $(\text{CH}_3)_4\text{NCl}$  solution,  $T_g$  is almost the same as that for the  $\text{LiCl}$  solution above  $Y > 6$ . Finally, it is important to point out once more that despite of hygroscopic nature of  $(n\text{-C}_4\text{H}_9)_4\text{NX}$ , none of their aqueous solutions is glass-forming. These salts form very stable clathrate hydrates.<sup>(3)</sup> High tendency of the clathrate formation may prevent these aqueous solutions from vitrification.

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