Stability of the Liquid State of Concentrated Aqueous Solutions of Lithium Salts at Low Temperatures

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The stability of the liquid state of aqueous lithium salt solutions was studied with a modified DTA technique. Aqueous solutions of LiCl and LiSCN in the concentration range 8–14 mol kg^{-1}, LiBr in the range 8–10 mol kg^{-1} maintain their liquid state for at least 50 hours at temperatures slightly above their glass transition points.

The study of liquid aqueous electrolyte solutions at low temperatures yields useful structural and dynamical information despite theoretical and experimental difficulties inherent in this region. Thermal and dynamic properties of aqueous solutions of LiCl at low temperatures have been well studied by methods such as DTA and NMR [1–7]. However, the stability of the liquid state of aqueous solutions of LiCl at low temperatures has not yet been investigated carefully. Our previous work, using DTA, revealed that aqueous lithium chloride solutions in the concentration range 8–14 mol kg^{-1} maintain their liquid state until the solutions vitrify, even when they are cooled down very slowly (0.5–0.8 K min^{-1}) [8, 9]. In this paper we describe the thermal behaviour of concentrated aqueous solutions of LiBr, $LiNO_3$ and LiSCN obtained from DTA, and we report on the stability of the liquid state of these solutions and those of LiCl at low temperatures, as determined by a modified DTA apparatus.

The thermal properties of aqueous solutions of LiBr and LiSCN are similar to those of aqueous LiCl solutions [8, 9]. Figure 1 represents thermograms of aqueous LiSCN solutions over a wide concentration range. Complicated thermal behaviour, indicating the formation or dissolution of ice or cryohydrates, is observed at concentrations lower than 7 mol kg^{-1} or higher than 14 mol kg^{-1}. However, the thermograms of the intermediate concentration range (8–14 mol kg^{-1}), exhibit no peak on cooling and heating except for a “kink” corresponding to a heat capacity change caused by the glass transition. In the case of aqueous LiBr solutions, the intermediate concentration range is from 8 to 10 mol kg^{-1}. No such concentration range is found for aqueous $LiNO_3$ solutions, though the highest concentration examined was 12 mol kg^{-1}, which is the solubility limit. It is interesting to note that among the lithium salts examined only $LiNO_3$ failed to stay in the liquid state at low temperatures at any concentration.

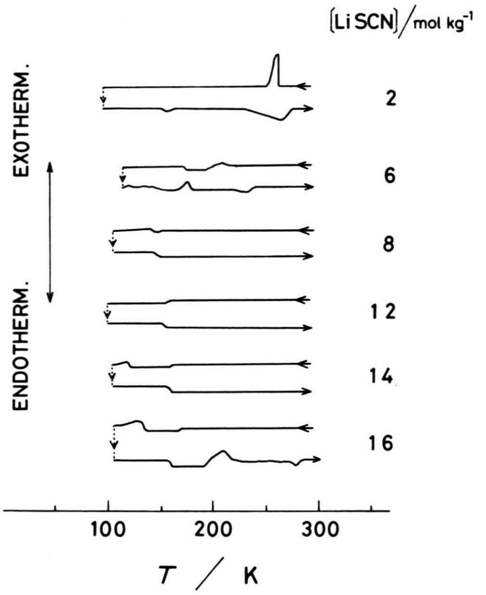

Fig. 1. Thermograms of aqueous LiSCN solutions.

The long-term stability of the liquid state of these solutions at low temperatures has been examined using a modified DTA apparatus. This is especially designed to hold the temperature of the sample solution constant but enabling giving controlled fluctuations of ±5 °C at one hour intervals together with recording of the exo- and/or endothermic heat changes of the sample solution [10]. Solutions of LiCl, LiBr and LiSCN, in the intermediate concentration ranges, where their thermograms have no peaks on heating and cooling except the heat capacity change due to the glass transition, are able to maintain the liquid state over 50 hours at low temperatures slightly above the

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glass transition point of each salt (153, 167 K for LiCl, 152, 165 K for LiBr and 170 K for LiSCN).

Our observations show that the stability of the liquid state of the lithium salt solutions is not very sensitive to the counter anions despite the difference in their size and shape. Lithium nitrate is an exception; the instability of the liquid state of aqueous $LiNO_3$ solutions at low temperatures may be related to the relatively low solubility of $LiNO_3$ compared with those of the other lithium salts. It is important to note that in those solutions of LiCl, LiBr and LiSCN whose liquid state is sufficiently stable at low temperatures, the hydration requirement of lithium ions is well satisfied without leaving an appreciable amount of free water molecules in the solution. We conclude that the hydration structure of lithium ions and the amounts of water taken up by hydrated cations relative to the amount of free water molecules may be mainly responsible for keeping the liquid state sufficiently stable down to the glass transition point. The structure and dynamics of hydrated lithium ions in such concentrated solutions are now the subject of investigations by the NMR method.

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