

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

Tooru Hasebe, Rie Sato, Kazuko Tanaka *, and Reita Tamamushi

Department of Chemistry, Faculty of Education, Fukushima University, Matsukawa, Fukushima 960-12, Japan

Z. Naturforsch. **47a**, 543–544 (1992);
received November 27, 1991

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, LiNO₃ 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

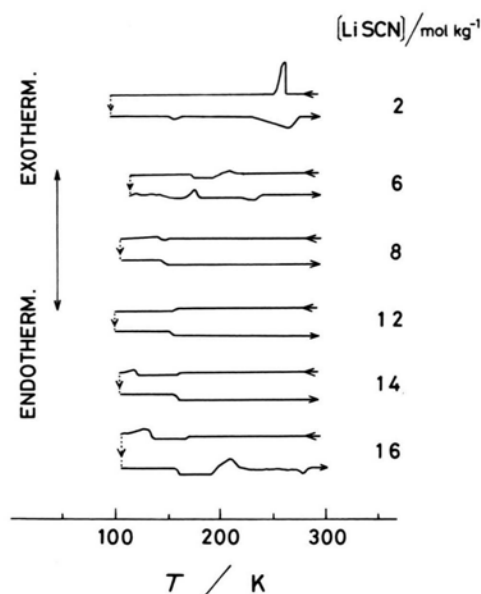


Fig. 1. Thermograms of aqueous LiSCN solutions.

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 LiNO₃ 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 LiNO₃ failed to stay in the liquid state at low temperatures at any concentration.

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

* The Institute of Physical and Chemical Research, Hirose, Wako, Saitama 351-01, Japan.

Reprint requests to Dr. Tooru Hasebe, Department of Chemistry, Faculty of Education, Fukushima University, Matsukawa, Fukushima 960-12, Japan.

0932-0784 / 92 / 0300-0543 \$ 01.30/0. – Please order a reprint rather than making your own copy.



Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition “no derivative works”). This is to allow reuse in the area of future scientific usage.

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.

The authors acknowledge the support of the Grant-in-Aid for Scientific Research on Priority Area of "Molecular Approaches to Non-Equilibrium Process in Solutions" from the Ministry of Education, Science and Culture, Japan.

- [1] C. A. Angell and E. J. Sara, *J. Chem., Phys.* **52**, 1058 (1970).
- [2] C. A. Angell, E. J. Sara, J. Donnelly, and D. R. MacFarlane, *J. Phys. Chem.* **85**, 1461 (1981).
- [3] E. J. Sutter and J. F. Harmon, *J. Phys. Chem.* **79**, 1958 (1975).
- [4] N. Boden and M. Mortimer, *J. Chem. Soc. Faraday Trans. II*, **74**, 353 (1978).
- [5] E. W. Lang and H. D. Luedemann, *Ber. Bunsenges. Phys. Chem.* **89**, 508 (1985).
- [6] E. W. Lang and F. X. Prielmeier, *ibid.* **92**, 717 (1988).
- [7] E. W. Lang, W. Fink, H. Radkowsch, and Girlich, *ibid.* **94**, 342 (1990).
- [8] T. Hasebe, K. Tanaka, and R. Tamamushi, 8th International Symposium on Solute-Solute-Solvent Interactions at Regensburg, Germany 1987.
- [9] T. Hasebe, K. Tanaka, and R. Tamamushi, submitted for publication.
- [10] T. Hasebe, R. Sato, K. Tanaka, and R. Tamamushi, in preparation.