# Supercooling ability of lithium nitrate solutions in ethylene glycol

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The dependence of the induction period of crystallization on the super-cooling has been determined for the system lithium nitrate—ethylene glycol over the composition range of 0—8 mole % of $LiNO_3$. This dependence may be described by a TTT (Time—Temperature—Transformation) curve. The addition of lithium nitrate to ethylene glycol results in a substantial increase in the critical induction period of crystallization. The thermal stability of glasses is discussed in terms of the shape and position of the TTT curves.

In the preceding papers [1—4] a great attention has been paid to the glass--forming ability of solutions of salts both in water and in nonaqueous solvents. The glass-forming ability of liquids is in principle tied up with their supercooling ability, *i.e.* the induction period of their crystallization and its dependence on the temperature and the composition of the solution [5, 6]. The supercooling ability of salt solutions is of a great importance in the field of industrial crystallization, as it influences both the size and the shape of the crystals formed [7]. A new domain of application of both supercooling and glass-forming ability of ionic liquids has appeared recently. It is the application of new ionic glasses in the production of glass fibres for optoelectronics, *i.e.* the possibility of using halide glasses in the production of optical fibres [8, 9]. These glasses are said to have the advantage of a substantially reduced optical loss in comparison to the glasses based on $SiO_2$. However, they exhibit a very low thermal stability, and a significant reduction of the optical loss has not been attained as yet. The glass fibres are drawn from the liquid in supercooled, thermodynamically metastable state. Therefore, the investigation of the supercooling ability of ionic liquids is important also in this field [10—12].

The supercooling ability of some salt solutions has been already investigated previously [10, 13—15]. In the course of these studies it was found that salt solutions represent suitable model systems for the investigation of the effect of salts on both the supercooling and the glass-forming ability of the solutions. In our preceding papers we investigated the supercooling ability of the solutions of

lithium chloride and calcium nitrate in ethylene glycol [16, 17]. The aim of this paper was to determine the effect of the composition of the solution on the induction period of the crystallization in the system ethylene glycol—lithium nitrate.

## Experimental

The experimental technique was similar to that described in the preceding paper [16]. The investigated solutions were prepared by weighing dried anal. grade chemicals. The samples of the solutions (100 mg—2 g) were pipetted into test tubes with an internal diameter of 10 mm, sealed with ground-glass stoppers. The tubes were then immersed into a Dewar flask filled with cooled ethanol. The desired temperature was kept constant by controlled addition of liquid nitrogen to ethanol and measured with the accuracy of 0.5 K. The apparition of the first crystal was indicated visually. Each measurement was repeated 3—5 times. The experimental results presented below are the mean values of all measurements.

The temperatures of glass transition were determined by low-temperature DTA [8]. The temperatures of the liquidus were estimated by the method of the dissolution of the last crystal [14].

## Results and discussion

The dependence of the induction periods of crystallization on temperature for ethylene glycol as well as for the 4 and 6 mole % solutions of lithium nitrate in ethylene glycol is presented in Fig. 1 in the form of TTT (Time—Temperature —Transformation) diagrams. The numerical values of the critical induction period $\tau_N$ and those of the critical temperature of crystallization $T_N$ for all investigated systems are given in Table 1.

When the values of the critical induction period of the solutions of lithium chloride and of calcium nitrate in ethylene glycol are compared with those given in the preceding papers [16, 17] it is evident that the effect of the addition of lithium nitrate to ethylene glycol on the critical induction period of crystallization is greater than the similar effect of the addition of lithium chloride; it is, however, smaller than that of the addition of calcium nitrate. A more detailed comparison is presented in Fig. 2, where the values of log $\tau_N$ are plotted against the mole percentage of the salt for the systems ethylene glycol—$LiNO_3$, ethylene glycol—$Ca(NO_3)_2$, and ethylene glycol—LiCl.

The addition of lithium nitrate to ethylene glycol affects not only the position but also the shape of the TTT curve. For an easier characterization of these changes two numerical values were used in the preceding papers which may

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characterize the diminution of the range of the crystallization zone. Although these values have no theoretical foundation, they are of practical importance as they give the limits of the temperature ranges where the manipulations with the metastable supercooled liquid may be performed without any danger of crystallization.
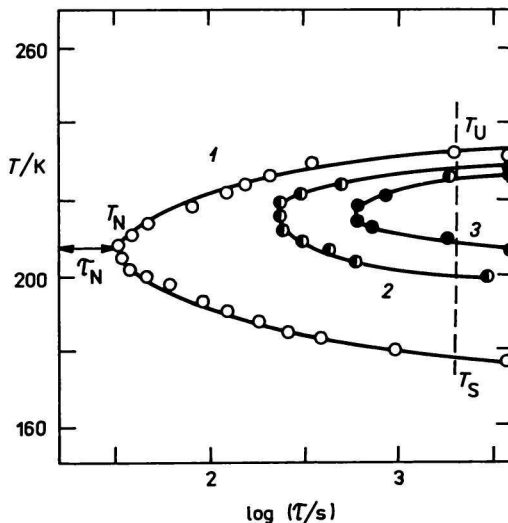


Fig. 1. Dependence of the induction period of crystallization $\tau$ on temperature $T$ at various mole fractions $x$ of LiNO₃ in solution.
$\tau_N$ — critical induction period of crystallization, $T_N$ — critical temperature of crystallization, $T_U$ — upper temperature of crystallization, $T_S$ — lower temperature of crystallization. *1.* 0.000, *2.* 0.040, *3.* 0.060.

*Table 1*

Critical induction period of crystallization $\tau_N$, liquidus temperature $T_L$, upper crystallization temperature $T_U$ at $\tau = 1800$ s, critical crystallization temperature $T_N$, lower crystallization temperature $T_S$ at $\tau = 1800$ s, and glass transition temperature $T_g$ for different values of mole fraction $x$ of lithium nitrate in solution

|  | $\tau_N / s$ | $T_L / K$ | $T_U / K$ | $T_N / K$ | $T_S / K$ | $T_g / K$ |
|---|---|---|---|---|---|---|
| 0.000 | 30 | 261 | 233 | 208 | 178 | 158 |
| 0.020 | 100 | 258 | 230 | 215 | 193 | 161 |
| 0.040 | 240 | 255 | 227 | 215 | 202 | 163 |
| 0.060 | 600 | 253 | 224 | 217 | 210 | 165 |
| 0.080 | 1700 | 250 | 219 | 217 | 215 | 168 |

The newly introduced points are the points of intersection of the TTT curves with the coordinate 1800 s. This time has been selected as both in the drawing of glass fibres and in the experimental measurement of the properties of supercooled liquids 30 min represent a sufficiently long time for the realization of the process in question. The point $T_U$ is the point of intersection of the coordinate
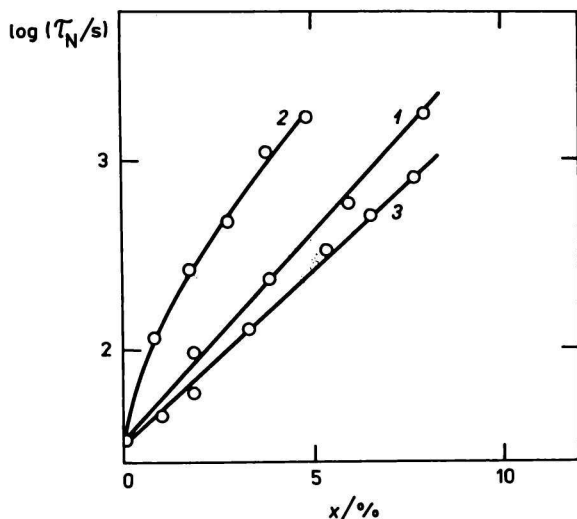
Fig. 2. Dependence of the critical induction period of crystallization $\tau_N$ on mole fraction $x$ of salt in solution.
1. Ethylene glycol—$LiNO_3$; 2. ethylene glycol—$Ca(NO_3)_2$ [17]; 3. ethylene glycol—$LiCl$ [16].

1800 s with the upper part of the TTT curve, the point $T_S$ is the point of intersection of this coordinate with the lower part of the TTT curve.

Fig. 3 shows the dependence of the points $T_U$, $T_N$, and $T_S$, of the liquidus temperature $T_L$ and of the glass transition temperature $T_g$ on the mole percentage of the salt in the solution. For the sake of simplicity, the experimental points have been omitted. The difference $T_L - T_g$ indicates the range of the supercooling zone. It is clear that this range decreases only a little with the increasing content of salt in ethylene glycol. For practical purposes, the temperature range
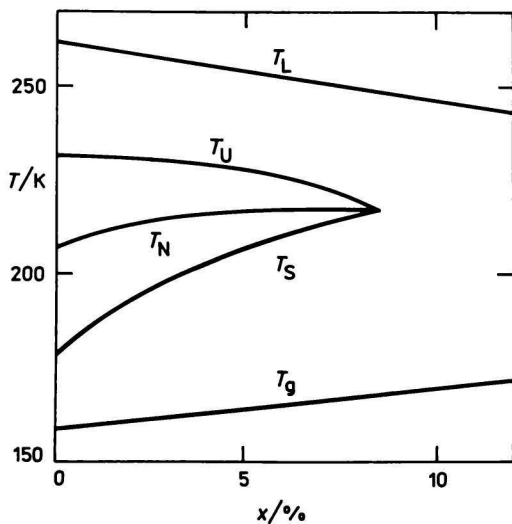


Fig. 3. Dependence of the characteristic temperatures on mole fraction $x(LiNO_3)$ in solution.
$T_L$ — liquidus temperature, $T_U$ — upper temperature of crystallization at $\tau = 1800$ s, $T_N$ — critical temperature of crystallization, $T_S$ — lower temperature of crystallization at $\tau = 1800$ s, $T_g$ glass transition temperature.

between $T_g$ and $T_S$ indicates the temperatures between which no crystallization of the glass takes place within half an hour. The temperature range between $T_L$ and $T_U$ gives the possibility of experimenting with supercooled liquids for at least half an hour. The difference $T_U - T_S$ indicates the range where the crystallization in the course of 30 min is possible. The latter range of crystallization decreases to a high extent with the increasing content of $LiNO_3$ in ethylene glycol and disappears completely at 8.5 mole % of $LiNO_3$. This means that an approximately 8.5 mole % solution of $LiNO_3$ in ethylene glycol will not crystallize within half an hour in the whole zone of supercooling. Such liquids may be considered as possessing a very good supercooling ability.

## References

1. Malá, J. and Sláma, I., *Chem. Zvesti 35,* 207 (1981).
2. Malá, J. and Sláma, I., *Chem. Papers 42,* 139 (1988).
3. Sláma, I. and Malá, J., *Chem. Papers 42,* 467 (1988).
4. Angell, C. A. and Sare, E. J., *J. Chem. Phys. 52,* 1058 (1970).
5. Uhlmann, D. R., *J. Non-Cryst. Solids 7,* 337 (1972).
6. Šatava, V., *Czech. J. Phys. A23,* 565 (1973).
7. Nývlt, J., *Industrial Crystallization, The State of the Art.* 2nd Edition. Verlag Chemie, Weinheim, 1982.
8. Kodejš, Z., Pacák, P., and Sláma, I., *Chem. Listy 82,* 113 (1988).
9. Lucas, J., *J. Non-Cryst. Solids 80,* 83 (1988).
10. Angell, C. A. and Choi, I., *J. Microsc. Spectrosc. Electron. 141,* 251 (1986).
11. Senepati, H. and Angell, C. A., *Proceedings of the 4th International Symposium on Halide Glasses,* p. 367. California, 1987.
12. MacFarlane, D. R. and Moore, L. J., *Proceedings of the 4th International Symposium on Halide Glasses,* p. 371. California, 1987.
13. Pacák, P., Horsák, I., and Sláma, I., *Krist. Tech. 14,* 741 (1979).
14. Pacák, P. and Sláma, I., *Collect. Czechoslov. Chem. Commun. 46,* 1629 (1981).
15. Pacák, P. and Sláma, I., *J. Solution Chem. 8,* 529 (1979).
16. Sláma, I. and Malá, J., *Chem. Papers 43,* 507 (1989).
17. Sláma, I. and Malá, J., *Collect. Czechoslov. Chem. Commun. 54,* 2711 (1989).