

# Supercooling ability of lithium chloride solutions in ethylene glycol

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Received 3 October 1988

The dependence of the induction period of crystallization on the supercooling has been determined for the system lithium chloride—ethylene glycol over the composition range 0—8.6 mole % LiCl. This dependence may be described by a TTT (Time—Temperature—Transformation) curve. The addition of lithium chloride to ethylene glycol results in a substantial increase of the critical induction period of crystallization. The thermal stability of glasses is discussed in terms of the shape and position of the TTT curves.

Определена зависимость индукционного периода кристаллизации от сверхохлаждения в системе хлористый литий—этиленгликоль в интервале 0—8,6 мол. % LiCl. Эта зависимость может быть представлена посредством кривой ВТТ (Время—Температура—Трансформация). Добавление хлористого лития к этиленгликолю приводит к значительному увеличению критического индукционного периода кристаллизации. Тепловая устойчивость стекол обсуждается на основании формы и расположения кривых ВТТ.

In recent years, a number of laboratories in the world have been engaged in research on the application of halide glasses to the preparation of fibres for optical transmission systems [1, 2]. These glasses have the advantage of a lower optical attenuation compared with silica-based glasses. For this purpose, several hundred compositions have been proposed, mostly mixtures of fluorides, but also involving other halides. Such halide glasses are typically multicomponent systems, but their thermal stability is very low compared with silica-based glasses. The glasses that can be processed into fibres consist exclusively of a combination of several halides. The glass must first be converted into a plastic form by heating it above the glass transition temperature, and glass fibres are then drawn from a liquid in a supercooled, thermodynamically metastable state. Even a slight amount of crystallization during the fabrication process makes the product useless. Thus research on the supercooling ability of liquids is becoming of a great practical importance [3—5].

The question of the thermal stability of glass is one of the magnitude of the induction period of crystallization of a supercooled liquid in the range between

the liquidus temperature and the glass transition temperature. For one-component glasses, this subject has been elucidated by *Uhlmann* [6], and in the Czech scientific literature a very good treatise has been published by *Šatava* [7]. The dependence of the induction period of crystallization on the supercooling is characterized by the so-called TTT (Time—Temperature—Transformation) curve, which has a typical “nose” shape. Practically, this means that a plot of the induction period of crystallization against supercooling shows a minimum between the liquidus and glass transition temperatures. This minimum determines not only the critical rate of cooling of the liquid necessary to obtain glass, but also the thermal stability of the heated glass. In halide glass systems, the TTT curves are, however, difficult to establish, and other criteria of the thermal stability are insufficient for quantitative evaluation.

The effect of salt admixtures on the glass-forming ability can conveniently be studied for solutions of some electrolytes. The glass-forming ability has been demonstrated for solutions of various salts in dimethyl sulfoxide (DMSO) [8], dimethylformamide (DMF) [9], and dimethylacetamide (DMA) [10]. Induction periods of crystallization have also been studied for aqueous solutions of some electrolytes [4, 11]. Salt solutions are therefore convenient model systems on which to investigate the effect of salt admixtures on the glass-forming and supercooling abilities of liquids.

The aim of this work was to examine the effect of composition on the induction period of crystallization for the system ethylene glycol—lithium chloride.

## Experimental

Solutions were prepared by dissolving weighed amounts of dried chemicals of anal. grade. Samples of 100 mg to 2 g were pipetted into test tubes of 10 mm inner diameter with ground stoppers. The test tubes were immersed in a Dewar flask containing ethanol. The required temperature was maintained to within 0.5 K by controlled admission of liquid nitrogen into ethanol. The appearance of the first crystal was detected visually.

For each composition, 10 to 20 measurements were made at various temperatures, each repeated three or four times. The experimental results given below are averages for all the measurements.

The glass transition temperatures were determined by low-temperature DTA [10]. The liquidus temperatures were determined by the method of last crystal dissolution [12].

## Results and discussion

Typical variations in the induction period of crystallization as a function of temperature for ethylene glycol and for 4 mole % and 8.6 mole % solutions of

lithium chloride in ethylene glycol are shown in Fig. 1 in the form of TTT diagrams. The curves are very similar in shape, the main differing feature being the position of the minimum, which varies with the solution composition. The temperatures ( $T_N$ ) at which these minima occur and the minimum induction periods of crystallization for all the compositions investigated are listed in Table 1. Also included in the table are liquidus temperatures ( $T_L$ ) and glass transition temperatures ( $T_g$ ) for the investigated compositions.

The decrease in the liquidus temperature with increasing content of LiCl in

Fig. 1. Dependence of the induction period of crystallization  $\tau$  on the temperature  $T$  at different mole fraction of LiCl  $x$  in solution.

$\tau_N$  — critical induction period of crystallization,  $T_N$  — critical temperature of crystallization,  $T_U$  — upper crystallization temperature at  $\tau = 1800$  s,  $T_S$  — lower crystallization temperature at  $\tau = 1800$  s.  $x$ : 1. 0.000; 2. 0.040; 3. 0.076.

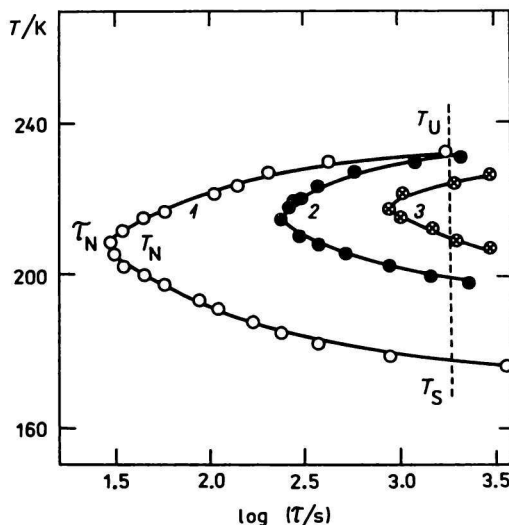


Table 1

Values of the 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 the mole fraction of lithium chloride  $x$  in solution

$x$	$\tau_N/s$	$T_L/K$	$T_U/K$	$T_N/K$	$T_S/K$	$T_g/K$
0.000	30	261	233	208	178	158
0.010	45	260	233	213	180	158
0.018	60	259	233	213	183	159
0.032	130	258	233	213	188	160
0.040	240	257	233	215	198	161
0.054	360	256	230	216	198	162
0.066	480	254	228	217	198	163
0.076	900	252	223	218	208	166

solution indicates that there is an eutectic composition above 8.6 mole % LiCl. At all the compositions investigated, crystalline ethylene glycol is the equilibrium solid phase. Clearly, the addition of LiCl to ethylene glycol hinders the nucleation of crystalline ethylene glycol, so increasing the induction period of crystallization. This phenomenon, also encountered with a number of other salt solutions [8–10], leads to the occurrence of the so-called solvent-rich glass-forming composition limit. This means that a salt solution which does not change into glass by the given mode of cooling (*e.g.* by liquid nitrogen) becomes glass-forming on increasing slightly the salt content. In our previous papers [9, 10] we have interpreted this phenomenon in terms of the formation of only inhomogeneous clusters in the nucleation process. This hypothesis is based on the assumption that for a crystal nucleus to be produced, a sufficiently large cluster of crystallizing particles with a long-range periodicity of arrangement must be formed. On addition of a salt to the solvent a situation may arise where the long-range periodical arrangement of each cluster is disturbed by inclusion of salt entities for example in the form of solvated ions, so that the cluster cannot become a crystal nucleus of the homogeneous phase.

Pure ethylene glycol is, however, glass-forming, so that the addition of LiCl to ethylene glycol increases the induction period of crystallization or in other words, it lengthens the time required for the formation of a large homogeneous cluster of ethylene glycol molecules which is to become a crystal nucleus.

As seen from Fig. 1, the increased lithium chloride content has an effect not only on the position of the TTT curve, but also on its shape. In order to facilitate the characterization of these changes, we use two additional numerical values to describe the narrowing of the crystallization region. These values have no theoretical significance, but are convenient from the practical point of view, because they bound the temperature ranges within which metastable supercooled liquids can be handled without the danger of crystallization.

These new values are points of intersection of the coordinate of 1800 s with the upper ( $T_U$ ) and lower ( $T_S$ ) parts of the TTT curve. The time of 30 min was chosen because it is sufficiently long for both the manufacture of glass fibres and the experimental measurement of the properties of supercooled liquids to be accomplished. The points  $T_U$  and  $T_S$  are indicated in Fig. 1, and their numerical values are given in Table 1. In practice, the region between  $T_g$  and  $T_S$  covers the temperatures at which the heating of the glass does not induce crystallization within 30 min. In the region between  $T_L$  and  $T_U$ , experiments with supercooled liquids can be made provided that heterogeneous nucleation is excluded.

Extrapolation of the data for  $T_U$ ,  $T_N$ , and  $T_S$  as a function of the mole fraction of lithium chloride in ethylene glycol ( $x$ ) has shown that at  $x = 0.1$ ,  $T_U = T_N = T_S = 218$  K. This means that an about 10 mole % solution of LiCl in ethylene glycol will not crystallize within 30 min in the whole supercooling region.

The effects of the salt content in various solutions on the critical induction period of crystallization are compared in Fig. 2. The figure shows a plot of the critical induction period of crystallization in the systems  $\text{H}_2\text{O}-\text{Ca}(\text{NO}_3)_2$  [11],  $\text{H}_2\text{O}-\text{LiCl}$  [3], and ethylene glycol—LiCl as a function of the mole fraction of salt in solution. In aqueous solutions, a small change in the salt content results in a steep increase of the critical induction period of crystallization, so that at a certain rate of cooling (by liquid nitrogen) a water-rich glass-forming composition limit is encountered. In the system ethylene glycol—LiCl, the effect of the salt content is also pronounced, but all the solutions studied are glass-forming.

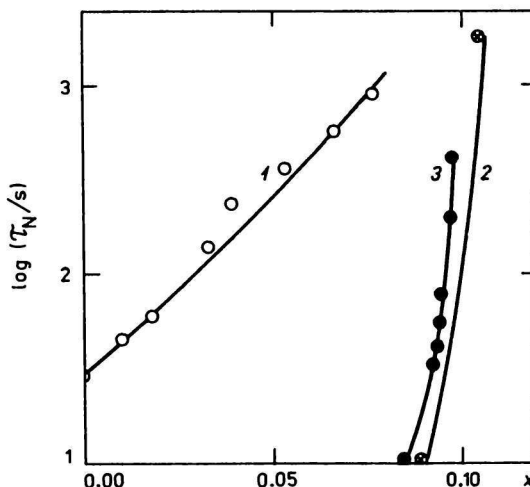


Fig. 2. Dependence of the critical induction period of crystallization  $\tau_N$  on mole fraction of salts  $x$  in solution: 1. Ethylene glycol—LiCl; 2.  $\text{H}_2\text{O}-\text{Ca}(\text{NO}_3)_2$  [11]; 3.  $\text{H}_2\text{O}-\text{LiCl}$  [3].

*Uhlmann* [6] has defined the critical rate of cooling at which the crystalline phase can no longer be detected as the ratio  $[dT/dt]_{\text{crit}} = \Delta T_N / \tau_N$ , where  $\Delta T_N = T_L - T_N$ . From our experimental data it can be deduced that this critical rate is lower than  $1.6 \text{ K s}^{-1}$  for all the samples investigated. The experimental cooling rate for solutions of other electrolytes is much higher, namely about  $16 \text{ K s}^{-1}$  [8—10]. Thus, the critical induction periods of crystallization for ethylene glycol and solutions of LiCl in ethylene glycol are much larger than would be necessary for the glass-forming composition limits to be encountered. In aqueous salt solutions, on the other hand, the critical induction periods of crystallization at low salt contents are so small ( $\tau_N < 3 \text{ s}$ ) that even rapid cooling of small samples in liquid nitrogen does not result in glass formation.

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Translated by M. Škubalová