

Induction period of crystallization of calcium chloride solutions in ethylene glycol

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*Dedicated to Associate Professor K. Matiašovský, DrSc.,
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The dependence of the induction period of crystallization on supercooling was determined for the system calcium chloride—ethylene glycol over the composition range 0—5 mole % CaCl_2 . This dependence can be described by a TTT (time—temperature—transformation) curve. The addition of calcium 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.

Supercooling of liquids is a phenomenon the nature of which is not yet fully understood. The existence of a liquid in thermodynamically unstable state at the temperature lower than is its equilibrium temperature of solid—liquid transition can be explained by an anomalous slow-down of nucleation of crystals. A quantitative measure of supercooling is the induction period of crystallization [1]. This induction period corresponds to the time at which the first observable crystal forms in the liquid at given supercooling. Generally it holds that the induction period shortens when supercooling increases. At the critical temperature of supercooling it reaches its minimum value, the so-called critical induction period of crystallization. If the temperature is further decreased the induction period of crystallization starts to increase as a result of increasing viscosity of the liquid.

Ability of some salt solutions for supercooling has been studied by several authors [1—3]. It has been found that salt solutions are suitable model systems for investigation of the influence of salts on supercooling and glass-forming ability of solutions. In our previous works [4—6] we have investigated supercooling of solutions of lithium chloride, calcium nitrate, and lithium nitrate in ethylene glycol. The aim of this work is to present the results of investigation of the influence of composition on the induction period of crystallization in the system ethylene glycol—calcium chloride.

Experimental

The same experimental method as in the previous work [4] was used. Solutions were prepared of dried chemicals of the anal. grade by weighing. Samples of solutions (from 100 mg to 2 g) were pipetted into test tubes having inner diameter 10 mm and equipped with ground-in stopper. The test tubes were immersed into the Dewar flask containing cooled ethanol. The required temperature was kept constant within ± 0.5 K by adding controlled amount of liquid nitrogen into ethanol. Appearance of the first crystal was indicated visually. The presented experimental data are the arithmetic mean of 3—5 measurements.

The temperature of glass transition was determined by a low-temperature DTA [4]. The equilibrium temperatures of liquidus were determined by the method of dissolution of the last crystal [2].

Results and discussion

Dependence of the induction period of crystallization on temperature for ethylene glycol and for 2 and 4 mole % solution of calcium chloride in ethylene glycol is presented in Fig. 1 as the TTT (time—temperature—transformation) diagram. Numerical values of the critical induction period τ_N and the critical temperature of crystallization T_N are summarized in Table 1 for all the investigated compositions of solutions.

When we compare the values of critical induction periods for solutions of lithium chloride, calcium nitrate, and lithium nitrate in ethylene glycol which

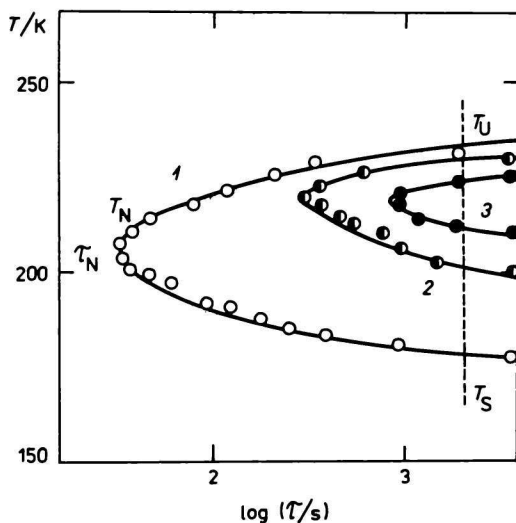


Fig. 1. Dependence of the induction period of crystallization τ on the temperature T at different mole fraction x of CaCl_2 in solution.

τ_N — critical induction period of crystallization, T_N — critical temperature of crystallization, T_U — upper temperature of crystallization, T_S — lower temperature of crystallization.

x : 1. 0.000, 2. 0.020, 3. 0.040.

Table 1

Values of the critical induction period of crystallization τ_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 calcium chloride in solution

$x(\text{CaCl}_2)$	τ_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	120	259	231	220	195	160
0.020	300	257	229	221	202	162
0.030	540	255	227	222	208	164
0.040	960	253	224	221	213	166
0.050	1800	251	218	218	218	167

were obtained in the previous works [4–6] with the data for calcium chloride solutions presented in this paper it follows that the influence of calcium chloride on the critical induction period is greater than the influence of the addition of lithium chloride and/or lithium nitrate and it is the same as the influence of calcium nitrate. A more detailed comparison of these data can be seen from Fig. 2 where the values of $\log \tau_N$ vs. the content of salts are plotted.

The addition of calcium chloride into ethylene glycol influences not only the position of the TTT curve in the diagram but also its shape. For easier characterization of these changes two numerical values which can describe the shrinkage of the region of crystallization can be used in a similar way as it has been done in the previous papers [4–6]. These values have no theoretical meaning

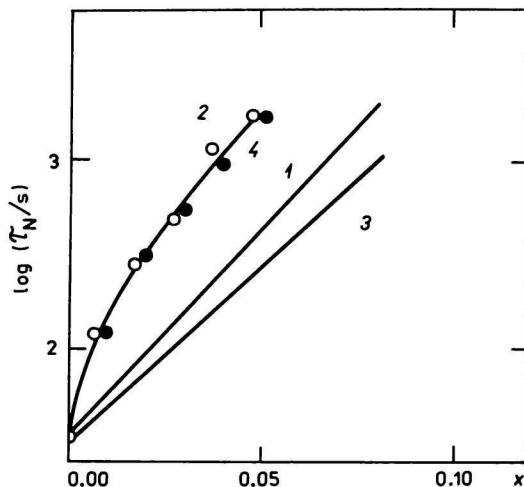


Fig. 2. Dependence of the critical induction period of crystallization τ_N on mole fraction of salt x in solution.

1. Ethylene glycol—LiNO₃;
2. ethylene glycol—Ca(NO₃)₂ (O);
3. ethylene glycol—LiCl;
4. ethylene glycol—CaCl₂ (●).

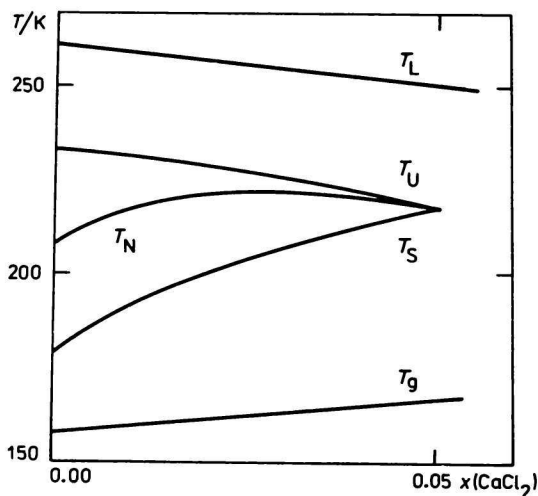


Fig. 3. Dependence of the characteristic temperatures on mole fractions x of CaCl_2 in solution.

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.

but they can be useful from the practical point of view because they delimit the temperature regions in which the supercooled liquid can be used without danger of its crystallization.

These points are defined as intersections of the TTT curves with the coordinate 1800 s. The time 1800 s has been chosen because it is sufficient for drawing of glass fibres as well as for experimental measurement of properties of supercooled liquids. The point T_U is the intersection of given coordinate with the upper part of the TTT curve. The point T_S is its intersection with the lower part of this curve.

In Fig. 3 the dependences of the coordinates of the points T_U , T_N , T_S and of the liquidus temperature T_L and the temperature of glass transition T_g are plotted as a function of mole fraction of salts in solution for the system ethylene glycol—calcium chloride. For a clear view the experimental points are omitted. The difference $T_L - T_g$ gives the extent of supercooling. It can be seen that this extent decreases with increasing content of salt in ethylene glycol. From the practical point of view the difference between T_g and T_S defines the conditions under which the heated glass does not crystallize within 30 min. Conditions defined by the temperatures T_L and T_U give the possibility to make experiments with supercooled liquids at least for half an hour. The difference $T_U - T_S$ marks the region in which the crystallization can start within 30 min. This extent of crystallization is remarkably diminished with the increasing content of CaCl_2 in ethylene glycol. At 5 mole % it disappears completely. This means that 5 mole % solution of CaCl_2 in ethylene glycol will not crystallize within half an hour in the whole supercooled region.

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