

INDUCTION PERIOD OF CRYSTALLIZATION OF ZINC CHLORIDE SOLUTIONS IN ETHYLENE GLYCOL

Ivo SLÁMA and Jarmila MALÁ

Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, 160 00 Prague 6

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The dependence of the induction period of crystallization on the supercooling was examined for the ZnCl_2 -ethylene glycol system at mole fractions of the salt from 0 to 0.07, and treated in terms of the TTT (Time-Temperature-Transformation) diagram. The critical induction period of crystallization increases substantially on the addition of ZnCl_2 to ethylene glycol. The thermal stability of supercooled liquids is discussed in terms of the shape and position of the TTT curves.

The glass-forming of solutions of salts in various solvents has been examined in our previous papers¹⁻⁴. With the cooling procedure used, glass-forming has been found to take place only after reaching a certain concentration of the salt in the solution. This solvent-rich limit of the glass-forming composition region was known to exist for some aqueous solutions of salts^{5,6}, and its existence was interpreted in terms of the formation of inhomogeneous clusters of various entities in the liquid near the liquidus temperature, these failing to constitute crystallization nuclei^{3,4}. During the investigation of the supercooling of solutions of salts in ethylene glycol⁷⁻¹⁰, lithium and calcium salts were observed to induce an appreciable increase in the critical induction period of crystallization of ethylene glycol.

The effect of zinc chloride on the solvent-rich composition limit of glass-forming has also been studied in various solvents¹⁻⁴. The aim of the present work was to examine the effect of this salt on the induction period of crystallization of ethylene glycol.

EXPERIMENTAL

The experimental methodology was as in our earlier work¹. Solutions were prepared from reagent grade chemicals by weighing. Samples of the solutions (0.1–2 g) were pipetted into test tubes 10 mm i.d. fitted with ground-in stoppers, and the test tubes were submerged in a Dewar vessel filled with cool ethanol. Temperature was held constant to within ± 0.5 K by adding liquid nitrogen to the ethanol. The appearance of the first crystal was indicated visually. Each measurement was repeated 3 to 5 times; the data reported are averages of all measurements.

The glass transition temperature was determined by low-temperature DTA measurements¹. The liquidus temperatures were established by the last crystal dissolution method¹¹.

RESULTS AND DISCUSSION

The values of the critical induction period of crystallization (τ_N) and of the critical temperatures of crystallization (T_N), derived from TTT (Time–Temperature–Transformation) diagrams^{7–10}, are given in Table I. The dependence of the critical induction period of crystallization (in the logarithmic scale) on the salt mole fraction for the zinc chloride–ethylene glycol system is compared with those for ethylene glycol solutions of lithium chloride⁷, calcium nitrate⁸, lithium nitrate⁹, and calcium chloride¹⁰ in Fig. 1. This diagram demonstrates that zinc chloride has an appreciable effect on the critical induction period of crystallization of ethylene glycol – higher than lithium salts, although lower than calcium salts.

This effect can be interpreted in terms of the hypothesis^{3,4} that heterogeneous clusters of various entities form in the liquid in the liquidus temperature range. The critical induction period of crystallization of ethylene glycol is 30 s at the critical temperature of 208 K, i.e. at a supercooling of 53 K. Below the liquidus temperature, spontaneous crystallization of ethylene glycol sets in only after a very long time. The cause of this should be sought in the nucleation, the rate of ethylene glycol crystal growth being unable to affect the crystallization to such an extent.

The fact that clusters of the same molecules of ethylene glycol do not form crystallization nuclei rapidly enough may be due to the molecules in the clusters being not oriented in the crystal-forming positions. Only in a longer period of time, a cluster can form a structure with a long periodicity and thus become a crystal nucleus. The heterogeneity of the clusters is affected by the addition of a salt to ethylene glycol, namely so that the heterogeneity increases. This is consistent with the induction period of crystallization increasing with increasing concentration of the salt in the solution. The fact that different salts in ethylene glycol exhibit different dependences of the critical induction period of crystallization can be explained in terms of the different interactions of the salts with the solvent.

Another interesting phenomenon is the effect of composition on the shape of curves in the TTT diagram. In our earlier work, additional two points on the TTT curves, T_U and T_S , were employed for this purpose. T_U is the point of intersection of the upper branch of the TTT curve with the 1 800 s coordinate. Actually, this time of 1 800 s has no theoretical background; it was chosen for practical reasons, half an hour being a sufficiently long time allowing all the basic physico-chemical measurements in the supercooled liquid to be performed. T_S is the point of intersection of the lower branch of the TTT curve with the 1 800 s coordinate; again, half an hour is sufficient for handling the glasses heated to above their glass transition temperature. The T_U and T_S values, along with the liquidus temperatures T_L and glass transition temperature T_g , are given in Table I for the various solution compositions.

From the practical point of view, the differences between the temperature parameters are of importance since they determine the applicability regions. For instance,

TABLE I

Critical induction period of crystallization τ_N , liquidus temperature T_L , upper and lower temperatures of crystallization at $\tau = 1\,800$ s (T_U and T_S , respectively), critical crystallization temperature T_N , and glass transition temperature T_g at different ZnCl_2 mole fractions in ethylene glycol solutions x

x	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	260	231	214	184	160
0.020	180	259	231	216	189	162
0.030	300	257	231	218	194	164
0.040	480	256	231	220	199	166
0.050	780	255	230	220	205	167
0.060	1 200	254	227	220	210	170
0.070	1 620	252	222	220	217	170

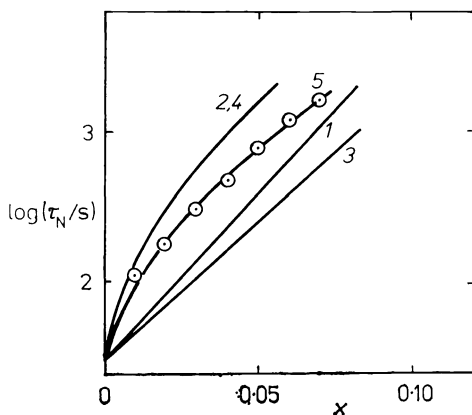


FIG. 1

Dependence of the critical induction period of crystallization, τ_N , on the mole fraction, x , of the salt in the salt-ethylene glycol system. Salt: 1 LiNO_3 , 2 $\text{Ca}(\text{NO}_3)_2$, 3 LiCl , 4 CaCl_2 , 5 ZnCl_2

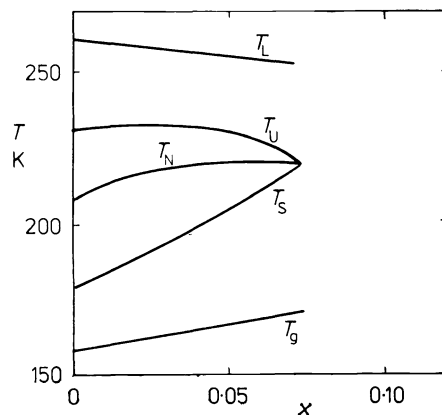


FIG. 2

Dependences of the characteristic temperatures on the ZnCl_2 mole fraction, x , in the ethylene glycol solution. T_L liquidus temperature, T_U upper temperature of crystallization at $\tau = 1\,800$ s, T_N critical temperature of crystallization, T_S lower temperature of crystallization at $\tau = 1\,800$ s, T_g glass transition temperature

the $T_L - T_g$ region corresponds to the existence of the supercooled liquid. Fig. 2 demonstrates that this region grows narrower as the ZnCl_2 content of the solution is increased. Increase in the glass transition temperature with increasing salt content is a general feature of solvent-salt systems¹⁰. A decrease in the liquidus temperature with increasing salt concentration can also be expected in the range of crystallization of the solvent, i.e. to the eutectic composition of the solution. As a result, the region of existence of the supercooled liquid grows narrower with increasing concentration of the salt in the solution.

The $T_L - T_U$ difference determines the region within which the supercooled liquid can be sustained in the metastable existence for at least half an hour. In the ethylene glycol-salt systems so far examined, this region grows narrower and ultimately vanishes at a certain concentration of the salt⁷⁻¹⁰. For the ZnCl_2 -ethylene glycol systems, this concentration limit is 7.5 mole % ZnCl_2 (Fig. 2).

The $T_S - T_g$ difference corresponds to the region within which the glass can be handled for at least half an hour without the hazard of its crystallization. In the ethylene glycol-salt systems examined previously⁷⁻¹⁰, this region grows wider with increasing salt content; Fig. 2 documents that this also applies to the ethylene glycol-zinc chloride system.

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