THE SUPERCOOLING ABILITY OF CALCIUM NITRATE SOLUTIONS IN ETHYLENE GLYCOL

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The dependence of the induction period of crystallization on the supercooling was determined for the $Ca(NO_3)_2$–ethylene glycol system at mole fractions of the former from 0 to 0·049, and treated in terms of the TTT (Time–Temperature–Transformation) diagram. Addition of $Ca(NO_3)_2$ to ethylene glycol brings about 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 our previous work, the glass forming ability of solutions of salts in nonaqueous solvents has been studied[1−3], following up the work of Angell and Sare[4] who employed the method of rapid cooling of concentrated solutions of some salts. In this manner the glass transition temperatures have been determined for some aqueous and nonaqueous solutions of electrolytes. The glass forming ability of liquids is basically conditioned by their supercooling ability, i.e. by the occurrence of an induction period of crystallization and its dependence on the temperature and composition of the solution[5,6]. Affecting the size and shape of newly formed crystals, the supercooling ability of solutions of salts is of great importance in industrial crystallization[7]. Recently, the supercooling and glass forming ability has found application in the manufacture of glass filaments for optoelectronics, where the use of halide glasses has also been found feasible[8,9]; these glasses are superior to SiO_2 based glasses with respect to their considerably lower optical attenuation, their temperature stability, however, is very low. Glass filaments are drawn from the liquid in the supercooled, thermodynamically metastable state. Thus the study of the supercooling ability of ionic liquids is of importance in this field as well[10−12].

The supercooling ability of solutions of some salts has been examined recently[10,13−15]; these solutions emerged as suitable model systems on which the effect of salts on the supercooled and glass forming ability can be conveniently studied. Previously we investigated the supercooling ability of solutions of LiCl in ethylene glycol[16]. The aim of the present work was to establish the effect of composition on the induction period of crystallization in the $Ca(NO_3)_2$–ethylene glycol system.

EXPERIMENTAL

The method used was similar as in ref.[16]. The solutions were prepared by weighing-in the dry chemicals of reagent grade purity. Aliquots $0.1-2$ g in weight were pipetted into test tubes 10 mm i.d. fitted with ground-in stoppers, and these were submerged in a Dewar vessel containing cool ethanol. The desired temperature was attained by adding to the ethanol an appropriate amount of liquid nitrogen, and was measured with an accuracy of 0.5 K. The appearance of the first crystal was indicated visually. Each measurement was repeated $3-5$ times. The data reported are averages of all measurements.

The glass transition temperature was determined by low temperature DTA measurements[8], the liquids temperature, by using the last crystal dissolution method[14].

RESULTS AND DISCUSSION

The temperature dependences of the induction period of crystallization for ethylene glycol and for solutions of $Ca(NO_2)_2$ in this solvent at mole fractions of the former $x = 0.02$ and 0.04 are shown in Fig. 1 in the form of the TTT (Time–Temperature––Transformation) curves. The numerical data are given in Table I.

Comparing critical induction periods of crystallization for the $Ca(NO_3)_2$–ethylene glycol system with those for the system where LiCl served as the salt[16] we observe that the effect of addition of $Ca(NO_3)_2$ on the critical induction period of crystallization is considerably more marked than the effect of addition of LiCl: for instance, whereas for LiCl in ethylene glycol at a mole fraction of 0.01 the critical induction period is 45 s, for $Ca(NO_3)_2$ at the same mole fraction it is as long as 120 s. A more detailed comparison of the two salts in ethylene glycol is presented in Fig. 2 in the form of plots of the critical induction period of crystallization on the salt content of the system. Since the curve for $Ca(NO_3)_2$ bends towards the x axis, the growth of the difference between the critical induction periods of crystallization with increasing mole fraction of the salts is not dramatic.

TABLE I

x^a	τ_N s	$\log \tau_N$	T_N K
0·000	30	1·477	208
0·010	120	2·079	215
0·020	300	*2·477	218
0·030	500	2·699	220
0·040	1 200	3·079	218
0·049	1 800	3·255	215

^{a} $Ca(NO_3)_2$ mole fraction.

Fig. 2 also shows the dependences of the critical induction periods of crystallization on the mole fractions of the two salts in their aqueous solutions[10,13]. In this case, small change in the salt content of the aqueous system brings about a dramatic increase in the critical induction period, to the extent that at a certain cooling rate (about 16 K s^{-1}) a water-rich glass forming composition limit appears. Although in the solutions of the two salts in ethylene glycol the effect of the salts on the critical induction period is also marked, the liquids examined are all glass forming.

Higher Ca(NO$_3$)$_2$ contents of the system with ethylene glycol affect not only the position of the TTT curve but also its shape. For a convenient characterization of
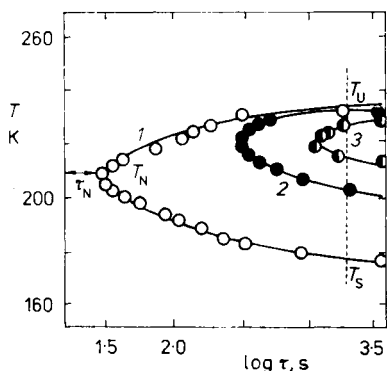

FIG. 1

Dependence of the induction period of crystallization τ_N on temperature T for Ca(NO$_3$)$_2$–ethylene glycol systems. T_U and T_S are the upper and lower crystallization temperatures at τ = 1 800 s. Ca(NO$_3$)$_2$ mole fraction: *1* 0·00, *2* 0·02, *3* 0·04
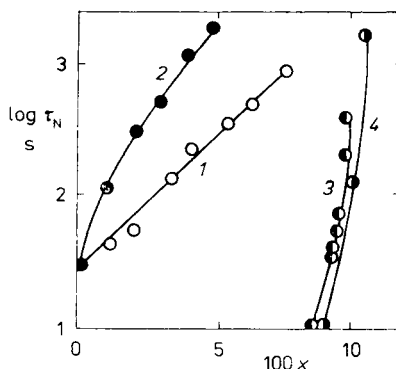
FIG. 2

Dependence of the critical induction period of crystallization τ_N on the mole fraction of salt in solution x. Curves: *1* LiCl–ethylene glycol[16], *2* Ca(NO$_3$)$_2$–ethylene glycol, *3* LiCl–water[10], *4* Ca(NO$_3$)$_2$–water[13]

FIG. 3

Dependences of characteristic temperatures of Ca(NO$_3$)$_2$–ethylene glycol systems on the Ca(NO$_3$)$_2$ mole fraction x. T_L is the liquidus temperature, T_U and T_S are the upper and lower temperatures of crystallization at τ = 1 800 s, respectively, T_N is the critical temperature of crystallization and T_g is the glass transition temperature
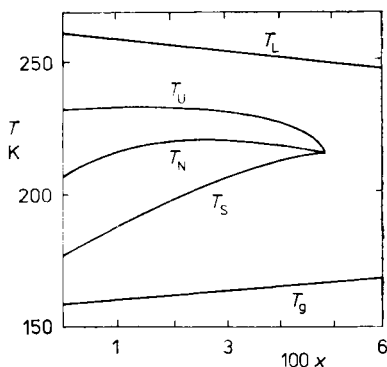
these changes, two numerical values, viz. the points of intersection of the upper and lower branches of the TTT curve with the 1 800 s coordinate (points T_U and T_S, respectively), were used in our previous work. These values have no theoretical background but they are useful in practice because they indicate the temperature regions where the metastable supercooled liquid can be handled without the hazard of crystallization. The time of 1 800 s has been chosen in view of the fact that for glass filament drawing, as well as for the experimental measurement of properties of supercooled liquids, a time of 30 min is long enough for the processes to be accomplished.

Fig. 3 shows the plots of the T_U and T_S values and of the liquidus temperature T_L and the glass transition temperature T_g vs the composition of the $Ca(NO_3)_2$–ethylene glycol system (the experimental points are omitted for the sake of clarity). The region between the T_g and T_L curves is the supercooled region. In the region between T_U and T_L the supercooled liquid can be handled provided that heterogeneous nucleation is prevented. On heating the glass, crystallization will not occur within half an hour if the temperatures lie between T_g and T_S, whereas at temperatures between T_S and T_U crystallization within this period of time is possible. The latter region grows considerably narrower with increasing $Ca(NO_3)_2$ content and vanishes altogether at a mole fraction about 0·05. Hence, solution of $Ca(NO_3)_2$ in ethylene glycol at this concentration of approximately 5 mol. % will not crystallize within half an hour over the entire supercooling region. Such liquids can be regarded as well supercoolable.

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