

INDUCTION PERIOD OF CRYSTALLIZATION OF SILVER NITRATE SOLUTIONS IN ETHYLENE GLYCOL

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The dependence of the induction period of crystallization on supercooling was examined for the silver nitrate-ethylene glycol system over the concentration region of silver nitrate mole fraction of 0 to 0.12. Addition of AgNO_3 to ethylene glycol was found to increase considerably the critical induction period of crystallization, although to a lesser extent than $\text{Ca}(\text{NO}_3)_2$, CaCl_2 , ZnCl_2 , LiCl and LiNO_3 do. The effect of these salts on the critical induction period of crystallization in dimethyl sulfoxide, dimethylformamide, dimethylacetamide and methanol was compared in terms of the solvent-rich composition limit of the glass-forming ability. By using the TTT (Time-Temperature-Transformation) theory, it has been deduced that the effect of the salts on the critical induction period of crystallization of ethylene glycol is probably due to the different dependences of viscosity on their concentration in ethylene glycol in the supercooling region.

The effect of addition of some salts on the induction period of crystallization of ethylene glycol (EG) in the salt-EG systems has been examined previously¹⁻⁵, and a considerable increase in the critical induction period of crystallization has been established. The effect on this parameter increased in order $\text{LiCl} < \text{LiNO}_3 < \text{ZnCl}_2 < \text{CaCl}_2 \lesssim \text{Ca}(\text{NO}_3)_2$ (for 5 mole % solutions of the salts in ethylene glycol).

When studying the glass-forming ability of aqueous solutions of these salts⁶, all solutions were found glass-forming if a certain concentration limit was surpassed. This limit was referred to as the water-rich composition limit of glass-forming ability. The experimental values were obtained by rapid cooling of small samples of the solutions in liquid nitrogen, owing to which cooling rates of $15-17 \text{ K s}^{-1}$ could be applied.

From theoretical work in the field of supercooling^{7,8} it can be deduced that for the above cooling procedure the critical induction period of crystallization must be higher than 3 s for crystallization not to be observable in the glass. Thus, the water-rich composition limit of glass-forming ability roughly corresponds to the concentration of the salt in a solution whose critical induction period of crystallization is about 3 s.

For silver nitrate, its aqueous and methanolic solutions have not been found to be glass-forming⁹. Thus, it was of interest to examine how addition of silver nitrate

to ethylene glycol affects the induction period of crystallization of the latter. Quantitative investigation of this effect and its comparison with other glass-forming systems were the objectives of the present work.

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 liquidus temperatures were established by the last crystal dissolution method⁸.

RESULTS AND DISCUSSION

The values of the critical induction period of crystallization (τ_N), derived from the TTT (Time–Temperature–Transformation) diagrams of silver nitrate solutions⁹ in ethylene glycol, are given in Table I along with the values of the critical temperature of crystallization (T_N) at which the critical induction period was measured. The critical induction period of crystallization increases considerably on the addition of silver nitrate, e.g. 36-fold in the presence of 12 mole % AgNO_3 in the solution. Over the concentration region examined the critical temperature of crystallization increases by mere 7 K.

For comparing the effect of various salts on the critical induction period of crystallization of ethylene glycol, the common logarithm of this parameter was plotted

TABLE I

Critical induction period of crystallization τ_N , liquidus temperature T_L , upper and lower temperatures of crystallization at $\tau = 1800$ s (T_U and T_g , respectively), and critical crystallization temperature T_N at different AgNO_3 mole fractions in ethylene glycol solutions x

x	τ_N s	T_L K	T_U K	T_N K	T_g K
0.000	30	261	233	208	178
0.020	60	259	231	212	188
0.040	120	257	228	214	194
0.060	240	255	226	215	200
0.080	480	254	223	215	204
0.100	900	253	220	215	208
0.120	1 080	252	218	215	210

against the mole fractions of the salts in Fig. 1 using data from refs^{1,2,4,5}. The slopes of the tangents at a zero salt concentration in Fig. 1 can serve for a quantitative comparison of the effect of the various salts; for practical reasons, however, comparison at higher salt concentrations is more suitable. For solutions with 5 mole % of the salts, the τ_N value is approximately 200 s for AgNO_3 , 300 s for LiCl , 400 s for LiNO_3 , 780 s for ZnCl_2 , and 1 800 s for $\text{Ca}(\text{NO}_3)_2$ and CaCl_2 . Hence, in a 5 mole % solution of $\text{Ca}(\text{NO}_3)_2$ or CaCl_2 in EG the induction period of crystallization is nearly 10-fold as compared to a 5 mole % solution of AgNO_3 in EG.

For an easy assessment of the shape of the TTT curves, the T_U and T_S temperatures were used in earlier papers¹⁻⁵. These values have no theoretical background but they characterize well the shape of the curves. T_U and T_S are temperatures at which the induction period of crystallization is 1 800 s at temperatures higher and lower than T_N , respectively. At temperatures between T_L (the temperature of the liquidus) and T_U the properties of the supercooled liquid can be measured for half an hour, which is a time sufficient for experimental investigation. Between the temperatures T_S and T_g (the glass transition temperature) the basic parameters of glass-forming supercoolable liquids can be determined. The T_L , T_U and T_S values are also given in Table I and shown in Fig. 2. The $T_L - T_U$ region grows slightly wider with increasing concentration of AgNO_3 in the solution, which implies that supercooled solutions of AgNO_3 in ethylene glycol can be examined experimentally at lower

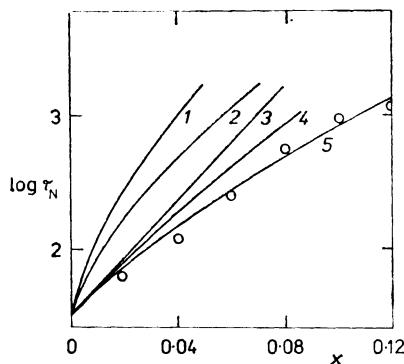


FIG. 1

Dependence of the critical induction period τ_N (in s) on the mole fraction x of the salt in the salt-ethylene glycol system. Salt: 1 $\text{Ca}(\text{NO}_3)_2$ and CaCl_2 , 2 ZnCl_2 , 3 LiNO_3 , 4 LiCl , 5 AgNO_3

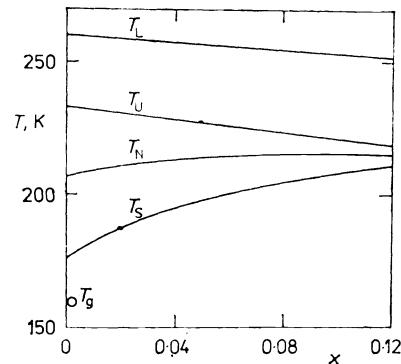


FIG. 2

Dependence of the characteristic temperatures on the AgNO_3 mole fraction x in the ethylene glycol solution. T_L liquidus temperature, T_U and T_S upper and lower, respectively, temperatures of crystallization at $\tau = 1\ 800$ s, T_N critical temperature of crystallization, T_g glass transition temperature

temperatures than pure ethylene glycol. The $T_U - T_S$ region grows narrower at higher concentrations of AgNO_3 but it is not zero even at 12 mole % AgNO_3 . This is in contrast with the systems studied previously, where this difference was zero at 10 mole % LiCl , 8.5 mole % LiNO_3 , 7.5 mole % ZnCl_2 , 5.5 mole % CaCl_2 and mere 5 mole % $\text{Ca}(\text{NO}_3)_2$ in ethylene glycol. Thus, addition of AgNO_3 to ethylene glycol has the lowest effect not only on the induction period of crystallization but also on the $T_U - T_S$ temperature difference with respect to all the systems hitherto examined.

The effect of salts on the supercoolability of their solutions in various solvents can be compared semiquantitatively based on the solvent-rich composition limit of glass-forming ability. For many solutions of salts in water or in nonaqueous solvents it has been found that at a certain concentration of the salt, glass can be obtained by rapid cooling of small samples in liquid nitrogen⁶⁻¹⁴. This implies that at a certain concentration of the salt in solution the critical induction period of crystallization attains a value higher than 3 s. Hence, the solvent-rich composition limit of glass-forming ability is a measure of the effect of the salt on the critical induction period of crystallization⁹. For the salts under study, the solvent-rich composition limits of glass-forming ability in various solvents are given in Table II. The salt concentrations in water at these limits decrease in order LiNO_3 , LiCl , ZnCl_2 , CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, which roughly coincides with the increasing order of the effect of the salts on the critical induction period of crystallization in the salt-EG systems. No glass-forming ability was found for the $\text{AgNO}_3-\text{H}_2\text{O}$ system, which is consistent with the lowest dependence of τ_N on the salt concentration in the AgNO_3 -EG system. In the other solvents used, the salt orders with respect to their effect on the

TABLE II
Solvent-rich composition limits of glass-forming ability for various salt-solvent systems

Salt	Concentration, mole %, in				
	water ^{6,10,14}	DMSO ^{6,10,14}	DMF ¹⁴	DMA ¹⁴	CH_3OH ¹⁴
AgNO_3	no glass	20	2	12	no glass
LiCl	9	12	1	7	5
LiNO_3	10	25	17	8	4
ZnCl_2	6	14	7	7	2
CaCl_2	5	6	1.4	—	1
$\text{Ca}(\text{NO}_3)_2$	6	8	2	4	4

DMSO dimethyl sulfoxide, DMF dimethylformamide, DMA dimethylacetamide.

glass-forming ability limit exhibit many exceptions. This indicates that specific ion–solvent interactions exist, affecting the critical induction period of crystallization and thereby the solvent-rich composition limit of glass-forming ability.

Theoretical calculation of the dependence of the induction period of crystallization on temperature and on the composition of ionic liquids has been presented previously⁸. The volume of crystals (v) formed in 1 cm³ of the liquid phase in time t can be expressed by the equation

$$v = (1/3) \pi I_0 u^3 t^4, \quad (1)$$

where I_0 is the nucleation frequency and u is the linear velocity of crystal growth. In the supercooled state, the latter can be written as

$$u = [f\mathbf{k}T/(3\pi a_0^2 \eta)] [1 - \exp(-\Delta H_m \Delta T_r/RT_m)], \quad (2)$$

where f is the fraction of positions at the crystal surface to which the molecule can be attached, a_0 is the diameter of the molecule, \mathbf{k} is the Boltzmann constant, T is absolute temperature, η is viscosity of the solution, ΔH_m is the heat of melting of the crystal, $\Delta T = T_m - T$ is supercooling, T_m is the liquidus temperature, T_r is the reduced temperature, $\Delta T_r = T/T_m$ is reduced supercooling, and R is the gas constant.

The nucleation frequency I_0 can be expressed by the relation

$$I_0 = [n\mathbf{k}T/(3\pi a_0^3 \eta)] \exp [(-16\pi\alpha^3\beta)/(3T_r(\Delta T_r)^2)], \quad (3)$$

where α and β are dimensionless parameters defined by the equations

$$\alpha = (NV_m^2)^{1/3} \sigma/\Delta H_m \quad (4)$$

$$\beta = \Delta H_m/RT.$$

In the equations, n is the number of molecules in 1 cm³ of the crystal, N is Avogadro's constant, V_m is molar volume of the crystal phase and σ is interfacial tension.

Experimental data are unavailable for concrete calculation of the TTT curves based on this theoretical approach. However, by combining Eqs (1)–(3) and rearranging, we can obtain an expression for the induction period of crystallization, viz.

$$t = \left\{ \frac{n\mathbf{k}}{9a_0^3 v} \exp \left(\frac{-16\pi\alpha^3\beta}{3T_r(\Delta T_r)^2} \right) \left[\frac{f\mathbf{k}}{3\pi a_0^2} \left(1 - \exp \left(\frac{-\Delta H_m \Delta T_r}{RT_m} \right) \right) \right]^3 \right\}^{-1/4} \frac{\eta}{T}. \quad (6)$$

This equation demonstrates that the induction period of crystallization depends mainly on the solution viscosity and temperature. Applying Eq. (6) to the critical

induction period of crystallization τ_N we obtain

$$\tau_N = \left\{ \frac{nk}{9a_0^3 v} \exp \left(\frac{-16\pi\alpha^3\beta}{3T_r(T_r)^2} \right) \left[\frac{fk}{3\pi a_0^2} \left(1 - \exp \left(\frac{-\Delta H_m \Delta T_r}{RT_m} \right) \right) \right]^3 \right\}^{-1/4} \frac{\eta}{T_N}. \quad (7)$$

Since T_N of ethylene glycol varies only slightly with additions of salts (and this applies also to the other systems examined), the expression in braces can be regarded as constant when comparing various salt-EG systems. Thus, it is likely that the differences in the dependences of $\log \tau_N$ on the salt concentration for the various salt-EG systems are due to different dependences of viscosity on the concentration of salt in these systems.

REFERENCES

1. Sláma I., Malá J.: *Chem. Papers* **43**, 507 (1989).
2. Sláma I., Malá J.: *Collect. Czech. Chem. Commun.* **54**, 2711 (1989).
3. Sláma I., Malá J.: *Chem. Papers*, in press.
4. Sláma I., Malá J.: *Chem. Papers*, in press.
5. Sláma I., Malá J.: *Collect. Czech. Chem. Commun.* **55**, 2428 (1990).
6. Angell C. A., Sare E. J.: *J. Chem. Phys.* **52**, 1058 (1970).
7. Uhlmann D. R.: *J. Non-Cryst. Solids* **7**, 337 (1972).
8. Pacák P., Horská I., Sláma I.: *Krist. Tech.* **14**, 741 (1979).
9. Sláma I., Malá J.: *Chem. Papers* **43**, 353 (1989).
10. Sare E. J., Angell C. A.: *J. Solution Chem.* **2**, 53 (1973).
11. Malá J., Sláma I.: *Chem. Zvesti* **35**, 207 (1981).
12. Malá J., Sláma I.: *Chem. Papers* **42**, 139 (1988).
13. Sláma I., Malá J.: *Chem. Papers* **42**, 467 (1988).
14. Sláma I.: *Chem. Listy* **80**, 565 (1986).

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