Glass-forming ability of molten solvated salts
Glass transition temperatures of some systems salt—dimethylformamide

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Glass transition temperatures of the solutions of ammonium nitrate, silver nitrate, lithium nitrate, lithium chloride, calcium chloride, and zinc chloride in dimethylformamide have been determined as a function of salt concentration. All solutions were glass-forming in limited composition regions. Glass-forming composition limits of the solutions of these salts in dimethylformamide have been compared with those in dimethyl sulfoxide and in water.

Определены температуры застеклевания растворов нитрата аммония, нитрата серебра, нитрата лития, хлорида лития, хлорида кальция и хлорида цинка в диметилформамиде в зависимости от концентрации соли. Все растворы обладали свойством застеклеваться в ограниченном интервале по составу. Составные пределы застеклевания растворов этих солей в диметилформамиде были сопоставлены с соответствующими параметрами для растворов в диметилсульфоксиде и воде.

The glass-forming composition region and the influence of chemical composition on the glass transition temperature (T_g) were investigated for some salt — dimethyl sulfoxide (DMSO) systems in our previous paper [1]. The influence of salt concentration on the solvent-rich composition limit of the glass-forming region was assumed to be due to the possible change of liquid structure in such way that the structure entities for nucleus formation were not present in the solution in sufficient amount. The probability of the formation of the clusters of crystal-forming particles with long distance periodicity was thus reduced. This interpretation of the influence of composition on the glass-forming ability was suitable especially for solvent-rich glass-forming composition limit. If the equilibrium solid phase at the solvent-rich composition limit is solvent crystal then the low nucleation rate is conditioned by low probability of the clustering of unaffected solvent molecules. Increasing salt concentration can influence the structure of molecular solvent by ion—dipole interaction to such extent that the

concentration of unaffected solvent molecules is extremely reduced. Thus also the nucleation rate of solvent crystals is substantially reduced and the solution can be supercooled and glass can be formed by sufficiently fast cooling.

The x(solvent)/x(salt) ratio R at the solvent-rich glass-forming composition limit was in accordance with the aqueous solution structure [2, 3]. Also in systems salt—DMSO [1] the composition of the solvent-rich glass-forming composition limit did not surpass the possibility of formation of solvation spheres of the salts. The decrease of the unaffected solvent molecules concentration made it possible to interpret the solvent-rich glass-forming composition limit.

One of the reasons for the study of the glass-forming ability of the systems salt—dimethylformamide (DMF) was to verify or deny this hypothesis. DMF is an aprotic dipolar solvent and has, therefore, similar properties like DMSO. However, substantial difference is in their melting points (m.p.(DMSO) = = 18.55 °C, m.p.(DMF) = −61 °C). Therefore, the eutectic composition of the salt—DMF system can be expected at lower salt concentration than that of the salt—DMSO system. Solvent-rich glass-forming composition limits are usually in the vicinity of the eutectic point. The solvent-rich glass-forming composition limits can thus be expected to exist at a lower salt content than that of the salt —DMSO system. This fact can deny the hypothesis on the influence of unsufficient number of unaffected solvent molecules on the nucleation rate of solvent crystals.

Another reason for the study of the glass-forming ability of some salts solutions in DMF was the possibility to compare the glass-forming composition regions and the salt concentration dependence of glass transition temperatures with those in salt—DMSO and salt—H_2O systems.

Experimental

DMF, reagent grade (Merck), was used without additional treatment. Anhydrous lithium nitrate was prepared from trihydrate, reagent grade (Lachema, Brno), which was partly dehydrated by heating in an inert atmosphere and subsequently dried in vacuum at 160 °C under reduced pressure for 4 days. Anhydrous silver nitrate was prepared by remelting the product made by Kovohutě Vestec. Anhydrous ammonium nitrate and lithium chloride were vacuum dried. Anhydrous zinc chloride was prepared from reagent grade Merck's product by remelting in the stream of hydrogen chloride. Anhydrous calcium chloride was prepared by recrystallization of hexahydrate and subsequent drying at elevated temperature.

Working procedure

The samples for the determination of the glass transition temperature were prepared by dissolving a weighed quantity of anhydrous salt in a weighed quantity of DMF. The

lithium and ammonium nitrates content was determined spectrophotometrically after their weighing and dissolving in water. The silver nitrate content was determined by the Charpentier—Volhard method, the lithium chloride content argentometrically and the zinc and calcium chlorides content by means of EDTA titration.

The glass transition temperature was determined by the method of low-temperature differential thermal analysis. The method used and the experimental set-up were described in [4].

Results and discussion

Glass transition temperature

Results for the variation in glass transition temperature (T_g) with salt concentration are shown in Figs. 1 and 2. At first sight, there are great differences in the salt concentration dependence of the glass transition temperatures of individual salts. Some dependences can be regarded as nearly linear (NH_4NO_3, $AgNO_3$, $LiNO_3$, and $CaCl_2$) while for the others ($ZnCl_2$, $LiCl$) the dependences are distinctly curved. In $ZnCl_2$—DMF system the curve is convex, while in the salt-richer part of LiCl—DMF system the curve is concave to the x axis.

In the case of the linear dependence of the glass transition temperatures on salt concentration, the extrapolation of the glass transition temperature to the
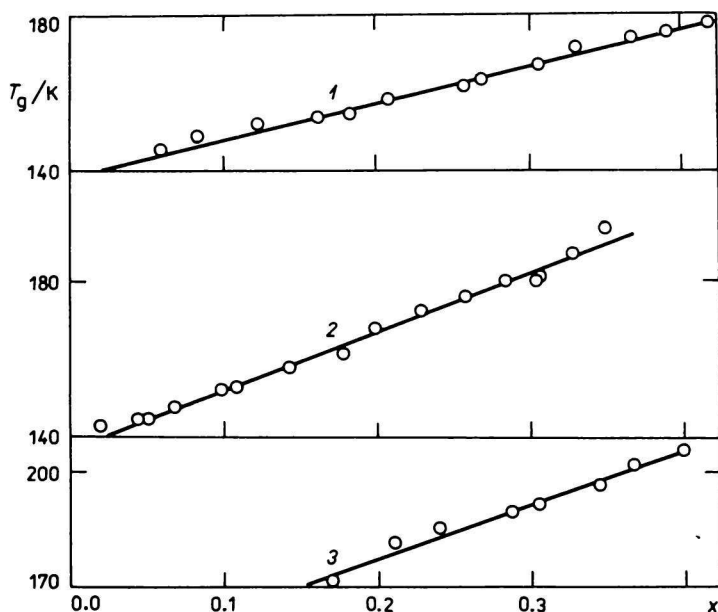

Fig. 1. Glass transition temperatures, T_g, of some nitrates as a function of the mole fraction of salts, x. 1. NH_4NO_3; 2. $AgNO_3$; 3. $LiNO_3$.

zero salt concentration gives values 135—150 K. These values are somewhat higher than the glass transition temperature for DMF = 129 K [5]. The linear extrapolation of T_g values is, therefore, not possible.
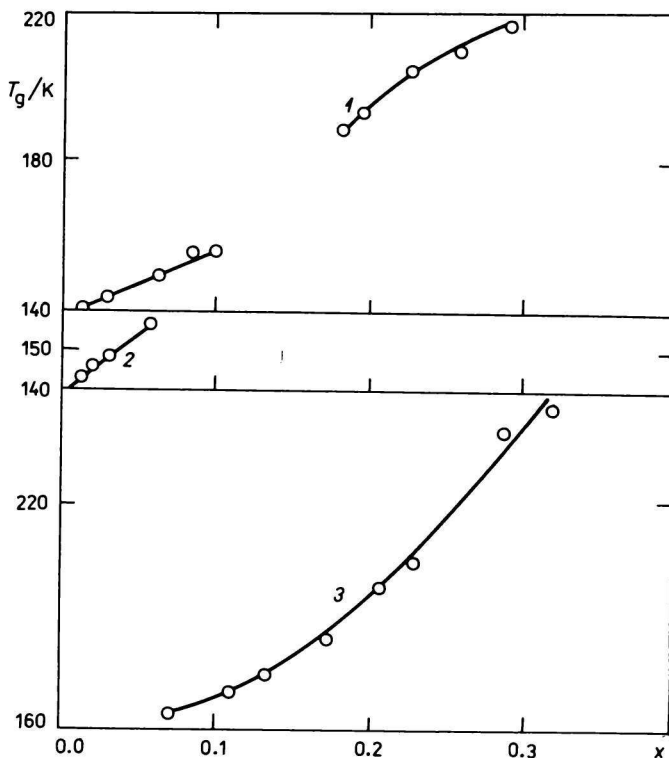

Fig. 2. Glass transition temperatures, T_g, of some chlorides as a function of the mole fraction of salts, *x*. *1.* LiCl; *2.* CaCl$_2$; *3.* ZnCl$_2$.

The slopes of the linear concentration dependence of T_g values can be compared with those in aqueous and DMSO systems [1]. It was found that in the case of NH$_4$NO$_3$ and AgNO$_3$ the slopes in DMF solutions are comparable with those in DMSO solutions. The slopes for LiNO$_3$ and CaCl$_2$ in DMF are distinctly lower than those in DMSO and in water.

Glass-forming composition regions

The solvent-rich and salt-rich glass-forming composition limits of some salts in DMF solutions are compared with corresponding aqueous and DMSO solutions in Table 1. The glass-forming composition regions lie within these limits. From Table 1 it can be seen that the aqueous solutions of ammonium nitrate and silver nitrate are not glass-forming.

Table 1

Solvent-rich and salt-rich glass-forming composition limits of some solutions of salts in water, DMSO, and in DMF in mole fractions (x)

Salt	In water [2]		In DMSO [1]		In DMF	
	solvent-rich x(limit)	salt-rich x(limit)	solvent-rich x(limit)	salt-rich x(limit)	solvent-rich x(limit)	salt-rich x(limit)
NH_4NO_3	—	—	0.2051	0.4938	0.060	0.421
$AgNO_3$	—	—	0.206	0.408	0.018	0.353
$LiNO_3$	0.100	0.130	0.245	0.310	0.173	0.403
$LiCl$	0.091	0.267	0.122	0.216	0.013—0.100	0.141—0.300
$CaCl_2$	0.053	0.087	0.056	0.187	0.014	0.057
$ZnCl_2$	0.063	0.400	0.137	0.283	0.073	0.323

The solvent-rich glass-forming composition limits of mole fractions x_1 of calcium nitrate solutions are in the following order: x_1 (in DMF) $< x_1$ (in H$_2$O) $< x_1$ (in DMSO). This order corresponds to the order of melting points of the solvents. In the case of DMF solution the ratio R is 49 at the solvent-rich glass-forming composition limit. That is much more than the assumed number of molecules in the solvation spheres of ions of calcium nitrate (18). It is obvious that the possibility of interpretation of the influence of salt concentration on the nucleation rate by means of "bonding" all the solvent molecules in the solvation sphere of ions cannot be applied in this case. The salt-rich glass-forming composition limits of calcium nitrate solutions rise in the following order: x_1 (in H$_2$O) $< x_1$ (in DMF) $= x_1$ (in DMSO). The DMF solution of Ca(NO$_3$)$_2$ has the greatest glass-forming composition region ($x = 2$—33 mole % of salt).

Calcium chloride has following solvent-rich glass-forming composition limits: x_1 (in DMF) $< x_1$ (in H$_2$O) $< x_1$ (in DMSO). The order is again comparable with the solvent melting points. At the solvent-rich glass-forming composition limits $R = 70$, which is again much more than it corresponds to the number of solvent molecules in the solvation sphere of CaCl$_2$ (18). The salt-rich glass-forming composition limits are: x_1 (in DMF) $< x_1$ (in H$_2$O) $< x_1$ (in DMSO). The greatest extent of glass-forming composition region was found in DMSO ($x = 5.6$—18.7 mole % CaCl$_2$).

The solvent-rich glass-forming composition limits of lithium chloride in the studied solutions are: x_1 (in DMF) $< x_1$ (in H$_2$O) $< x_1$ (in DMSO). This sequence is again comparable with the solvent melting points. R is 76 at the solvent-rich glass-forming composition limit in DMF solution, *i.e.* much more than the assumed number of solvent molecules in solvation sphere of LiCl (6—8). The salt-rich glass-forming composition limits are: x_1 (in DMSO) $< x_1$ (in H$_2$O) $< x_1$ (in DMF). The greatest extent of glass-forming composition region was found in DMF ($x = 1.3$—30 mole % LiCl). The glass-forming region of this system is somewhat different from the other ones. In the composition region 10—14 mole % LiCl, the glass transition temperature could not be experimentally determined. Small peaks appeared on the DTA trace, both in exo- and endothermal directions, which makes the determination of glass transition temperature impossible. Solutions in the composition range 10—14 mole % LiCl were vitreous after quenching, but the glass became suddenly opaque. It was not possible to distinguish whether some crystals or small crackers were formed in the solution. The effect of liquid—liquid immiscibility is also possible.

The zinc chloride solutions have the solvent-rich glass-forming composition limits in the order: x_1 (in H$_2$O) $< x_1$ (in DMF) $< x_1$ (in DMSO). The limit of the solvent-rich glass-forming composition region in DMF solution corresponds to $R = 13$, which is in reasonable agreement with the maximum number

of solvent molecules in the solvation sphere of $ZnCl_2$ (18). The salt-rich glass-forming composition limits are: x_1 (in H_2O) $<$ x_1 (in DMF) $<$ x_1 (in DMSO). Aqueous solutions of zinc chloride have the greatest glass-forming composition region ($x = 6$—40 mole % $ZnCl_2$).

The solvent-rich glass-forming composition limits in lithium nitrate solutions are: x_1 (in H_2O) $<$ x_1 (in DMF) $<$ x_1 (in DMSO). The salt-rich glass-forming composition limits have the following order: x_1 (in H_2O) $<$ x_1 (in DMSO) $<$ $<$ x_1 (in DMF). The solutions of lithium nitrate in DMF have the greatest glass-forming composition range ($x = 17.3$—40 mole % $LiNO_3$).

In ammonium nitrate solutions the solvent-rich glass-forming composition limits were found in the following order: x_1 (in DMF) $<$ x_1 (in DMSO), which corresponds to the order of solvent melting points. The salt-rich glass-forming composition limits are: x_1 (in DMF) $<$ x_1 (in DMSO). The solution of ammonium nitrate in DMF has the greatest glass-forming composition region ($x =$ $= 6$—42 mole % NH_4NO_3).

Very low solvent-rich glass-forming composition limit was found for the solution of silver nitrate in DMF: x_1 (in DMF) $\ll$ x_1 (in DMSO). The salt-rich glass-forming composition limits are: x_1 (in DMF) $<$ x_1 (in DMSO). The solution of silver nitrate in DMF forms the most extensive glass-forming composition range ($x = 1.8$—35.3 mole % $AgNO_3$).

From this comparison it can be concluded that some salts have at the solvent-rich glass-forming composition limits much higher R than it corresponds to the maximum number of solvent molecules in solvation spheres of ions. The hypothesis on the influence of salt concentration on the substantial decrease of the concentration of the "unaffected" solvent molecules in the solution cannot thus be used for the interpretation of solvent-rich glass-forming composition limit.

More general hypothesis for the interpretation of the glass-forming ability could be as follows:

Let us assume that below the liquidus temperature not only homogeneous but also heterogeneous clusters or aggregates are formed in the solution. The homogeneous clusters can form a crystal nucleus. The heterogeneous cannot. This assumption is very probable in molten solvated salt systems. There is quite enough of crystal-forming particles but also a large number of non-crystal-forming ones present in the salt solution near the liquidus temperature. All ions solvated with another number of the solvent molecules than it corresponds to the number of solvent molecules forming the crystal solvate can be regarded as non-crystal-forming particles. In the process of aggregation or clustering, the noncrystallizing entities could be incorporated in clusters of crystallizing entities to such extent that the long range periodicity is substantially disordered and the

cluster cannot form a nucleation centre. At certain composition the probability of formation of "homogeneous" clusters can be substantially suppressed. This fact can cause significant reduction of nucleation rate and thus the increased possibility of solution supercooling and glass-forming at high cooling rate. This assumption could explain even the supercooling and glass-forming of the melts of some crystal solvates, *e.g.* hexahydrate of calcium nitrate.

This hypothesis is also in accordance with the experimental fact that the addition of some dipolar solvents (DMSO) to the concentrated aqueous solutions of some salts broadened substantially the glass-forming composition range in ternary systems [6—11]. The number of noncrystallizing ions in mixed solvent is much higher than that in aqueous solution due to the probability of not only hydrated ions but also solvated and mixed ions formation. Thus the probability of formation of heterogeneous clusters can be much higher.

The effect of addition of some dipolar solvents to the concentrated aqueous solutions on the nucleation rate can be also employed in the field of industrial crystallization. Thus the possibility of controlling the nucleation rate in the supercooled or supersaturated region enables to obtain the desired size and shape of crystals produced.

The glass-forming ability of molten solvated salts is interesting also for another reasons. In the last years, new types of ionic glasses were studied as the materials for optoelectronics in infrared region [12, 13]. Halide glasses are regarded as the most promising solution of this problem. However, the glass--forming ability of inorganic halides is very limited and only some multicomponent systems can be used. The research into the glass-forming ability of molten solvated salts represents an inspiring way how to search for the new types of ionic glasses.

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