# Temperature of the glass transition of some systems of inorganic nitrates and chlorides with dimethyl sulfoxide

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The temperatures of the glass transition of solutions of lithium, silver, and ammonium nitrates as well as lithium, zinc, and calcium chlorides in dimethyl sulfoxide were determined. The formation of glass in a limited concentration region was observed with all solutions. In all cases, the concentration dependence of temperature of the glass transition was found to be linear.

Были определены температуры стеклования растворов нитратов лития, серебра и аммония и хлоридов лития, цинка и кальция в диметил-сульфоксиде. Все указанные растворы образовывали стекла в определен-ном интервале концентраций. Во всех случаях была обнаружена линейная зависимость температуры стеклования от концентрации.

The glass formation in the systems of hydrated inorganic salts is attributed to the role of water molecules in the hydration of anions and cations. The uncertainty in differentiating the cationic and anionic hydrations makes it impossible to apply the structural considerations in order to explain the glass-forming phenomenon on the basis of the experimentally determined changes of the physicochemical properties of systems consisting of inorganic salts and water effected by changing cations and anions. However, the undercooling and glass-forming abilities of inorganic salts were observed not only in aqueous systems [1, 2] but also in mixtures with some aprotic solvents [3]. The investigation of the physicochemical properties of those mixtures and their comparison with the properties of the corresponding aqueous systems [4] allow an additional approach to the explanation of the undercooling ability of those solutions.

Dimethyl sulfoxide (DMSO) which exhibits some properties similar and other quite different compared to water was chosen as the best suited solvent. DMSO, owing to its structure, solvates preferably the cations. Though DMSO is recently a favoured solvent, thus far only the temperature of glass transition in a sole system inorganic salt—DMSO, *viz.* calcium nitrate—DMSO, was determined [3].

In this investigation, temperature of the glass transition of lithium, ammonium, and silver nitrates as well as that of calcium, zinc, and lithium chlorides in DMSO was determined.

## Experimental

### Chemicals

DMSO, reagent grade, Merck, was used without any 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 a vacuum dry-box at 160°C under reduced pressure for 4 days. Anhydrous silver nitrate was prepared by melting the product made by Kovohutě Vestec. Anhydrous ammonium nitrate and lithium chloride were vacuum dried. Anhydrous zinc chloride, Merck, was used without any additional treatment. 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 temperatures were prepared by dissolving a weighed quantity of anhydrous salts in a weighed quantity of DMSO on heating in air. The lithium and ammonium nitrates content was determined spectrophotometrically after 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 the chelatometric method. The concentration of salts in the investigated systems was expressed in mole fractions $x$.

The glass transition temperature was determined by the method of differential thermal analysis. The method used and the experimental set-up were described in [5].

## Results and discussion

### Glass-forming composition regions

The experimental results are summarized in Tables 1—3. The low- and high-concentration limits of the glass formation of some aqueous solutions of salts are compared with corresponding DMSO solutions in Table 2. The glass-forming composition regions lie within those limits. With respect to the different mechanism of undercooling and, consequently, of the glass formation, the limiting values will be discussed independently.

For all the investigated salts, the low-concentration limit of glass formation in the DMSO solutions is higher than the corresponding value in aqueous systems. In case

of aqueous solutions of ammonium and silver nitrates, no glass was obtained when using the experimental technique described in [5]. For calcium nitrate, the low-concentration limit is close to eutonicom in crystallization region of the solvent in both aqueous solutions and DMSO [5]. The eutonic compositions in aqueous solution (7.7 mole % $Ca(NO_3)_2$) and in DMSO (9.4 mole % $Ca(NO_3)_2$) differ but slightly and the increase of the low-concentration limit of glass formation in DMSO (7.8 mole % $Ca(NO_3)_2$) as compared to aqueous solutions (6.7 mole % $Ca(NO_3)_2$) roughly corresponds to this difference. As the undercooling and consequently the

*Table 1*

Dependence of temperatures of the glass transition $T_g$ of concentrated solutions of salts in DMSO on the mole fraction of salts ($x$)

| $x$ | $T_g/K$ | $x$ | $T_g/K$ | $x$ | $T_g/K$ |
|---|---|---|---|---|---|
| **LiNO₃** | | **NH₄NO₃** | | **ZnCl₂** | |
| 0.2008 | 183.7 | 0.2051 | 165.8 | 0.1371 | 175.2 |
| 0.2449 | 192.5 | 0.2304 | 169.0 | 0.1375 | 176.9 |
| 0.2469 | 193.6 | 0.2548 | 171.8 | 0.1584 | 183.6 |
| 0.2506 | 191.2 | 0.2817 | 174.5 | 0.1927 | 192.5 |
| 0.2506 | 191.7 | 0.2857 | 174.2 | 0.2235 | 205.9 |
| 0.2653 | 196.0 | 0.3149 | 179.2 | 0.2507 | 214.6 |
| 0.2653 | 197.0 | 0.3185 | 178.8 | 0.2827 | 222.9 |
| 0.2833 | 200.9 | 0.3760 | 185.1 | **LiCl** | |
| 0.2841 | 201.6 | 0.3817 | 185.2 | | |
| 0.2841 | 200.3 | 0.4052 | 187.5 | 0.1220 | 181.6 |
| 0.2857 | 201.3 | 0.4099 | 186.8 | 0.1327 | 184.7 |
| 0.2894 | 200.3 | 0.4377 | 190.5 | 0.1345 | 186.7 |
| 0.2994 | 203.0 | 0.4651 | 193.9 | 0.1498 | 190.6 |
| 0.2994 | 203.4 | 0.4938 | 196.4 | 0.1505 | 191.3 |
| 0.3180 | 206.6 | | | 0.1627 | 195.0 |
| 0.3185 | 204.5 | | | 0.1636 | 193.8 |
| | | **CaCl₂** | | 0.1737 | 196.2 |
| **AgNO₃** | | | | 0.1935 | 203.2 |
| | | 0.0558 | 162.8 | 0.2105 | 206.7 |
| 0.2064 | 181.2 | 0.0659 | 175.3 | 0.2155 | 207.2 |
| 0.2304 | 186.7 | 0.0759 | 179.1 | 0.2162 | 208.6 |
| 0.2625 | 192.7 | 0.1063 | 192.1 | | |
| 0.2853 | 194.4 | 0.1367 | 211.1 | | |
| 0.3190 | 202.3 | 0.1374 | 210.0 | | |
| 0.3460 | 206.2 | 0.1591 | 224.9 | | |
| 0.3799 | 209.2 | 0.1867 | 237.6 | | |
| 0.4040 | 212.5 | | | | |
| 0.4082 | 216.3 | | | | |

Table 2

Range of the glass-forming concentration region of investigated
systems in water and in DMSO

| Salt | in water | | in DMSO | |
|---|---|---|---|---|
| | Lower limit $(x)$ | Upper limit $(x)$ | Lower limit $(x)$ | Upper limit $(x)$ |
| Ca(NO₃)₂ | 0.0667[a] | 0.2564[a] | 0.0780[a] | 0.3352[a] |
| LiNO₃ | 0.1000[a] | 0.1300[a] | 0.2449 | 0.3104 |
| NH₄NO₃ | – | – | 0.2051 | 0.4938 |
| AgNO₃ | – | – | 0.2064 | 0.4082 |
| ZnCl₂ | 0.0625[a] | 0.4000[a] | 0.1371 | 0.2827 |
| CaCl₂ | 0.0526[a] | 0.0870[a] | 0.0558 | 0.1867 |
| LiCl | 0.0909[a] | 0.2667[a] | 0.1219 | 0.2167 |

a) Values based on data presented in [1].

Table 3

Constants of eqn ($1$) approximating the concentration dependence
of temperature of the glass transition

| Salt | in water | | in DMSO | |
|---|---|---|---|---|
| | A | B | A | B |
| Ca(NO₃)₂ | 141[a] | 383[a] | 149[a] | 372[a] |
| LiNO₃ | 134[a] | 176[a] | 142 | 202 |
| NH₄NO₃ | – | – | 144.9 | 104.8 |
| AgNO₃ | – | – | 149 | 161 |
| ZnCl₂ | 140.6[a] | 202.6[a] | 130.9 | 329.1 |
| CaCl₂ | 123[a] | 471[a] | 135.6 | 549.5 |
| LiCl | – | – | 149.3 | 273.3 |

a) Values based on data presented in [1].

glass-forming ability of solutions of electrolytes in this region is conditioned by low rate of nucleation of the solvent, it may be assumed that a comparable addition of calcium nitrate into water and DMSO effects a similar influence on the structure of the respective solutions. Presumably, the molecules of solvents are influenced by the ions of salts and form their solvation spheres so that there are no greater clusters of unaffected molecules which might form the nucleation centres of the solvent crystals. The ratio R of the amount of solvent to that of salt, calculated from the composition of solutions, was found to be 10—14 which means that the solvation sphere of ions in both water and DMSO is formed by approximately 12 molecules of solvent.

Similar considerations may be applied to calcium chloride. Here, the low-con-

210

centration limit in water (5.2 mole % $CaCl_2$) and in DMSO (5.5 mole % $CaCl_2$) is virtually the same. In this case, however, the average value of $R = (1 - x)/x$ ($x$ is the mole fraction of salt) is 18 which means that each molecule of salt would be solvated by 18 molecules of solvent in both water and DMSO.

Somewhat greater difference between the values of the low-concentration limit of glass formation was found for lithium chloride (9.1 mole % LiCl in aqueous solutions and 12.2 mole % LiCl in DMSO). In aqueous solutions, the value of the low-concentration limit is within the region of crystallization of ice. The phase diagram of the system lithium chloride—DMSO is not known and it may only be assumed that the low-concentration limit of glass formation is within the region of DMSO crystallization. In this case, the ions of the salt would exert their influence in average upon 10 molecules of water and only 7 molecules of DMSO in the respective solutions which means that the hydration of lithium chloride would be markedly more pronounced than its solvation by dimethyl sulfoxide.

Still greater difference between the low-concentration limits of glass formation was observed with zinc chloride (6.2 mole % $ZnCl_2$ in aqueous solutions and 13 mole % $ZnCl_2$ in DMSO). In aqueous solutions, the low-concentration limit of glass formation is within the region of crystallization of ice. The phase diagram of the system zinc chloride—DMSO is not known. Assuming the low-concentration limit of glass formation is in the region of DMSO crystallization, there should be a significant difference between hydration (15 molecules of water) and solvation (7 molecules of DMSO), similarly as in case of lithium chloride.

The greatest difference between the values of the low-concentration limits of glass formation was determined for lithium nitrate (10 mole % $LiNO_3$ in aqueous solutions compared to 24.4 mole % $LiNO_3$ in DMSO). The low-concentration limit of glass formation in aqueous solutions is in the region of the eutonic composition, however, the phase diagram of the system $LiNO_3$—DMSO was not published thus far. Assuming at least a certain similarity between the phase diagrams of the two systems, the low-concentration limit of glass formation should be in the region of the congruently melting trisolvate $LiNO_3 \cdot 3DMSO$. This would indicate, however, that there is no undercooling in the eutonic region and, consequently, lithium nitrate cannot decrease the nucleation rate of dimethyl sulfoxide in the region of DMSO crystallization.

The entirely anomalous behaviour of ammonium nitrate and silver nitrate in aqueous solutions where undercooling and glass formation do not take place might be explained by a small effect of those salts on the molecules of water. This assumption is supported by the fact that no congruently melting hydrates were determined in the respective phase diagrams. The phase diagrams of the corresponding systems with DMSO are not yet known, so that the interpretation of differences between the aqueous and nonaqueous systems with respect to the solvate formation is impossible at the time being.

The high-concentration limit of glass formation for solutions of calcium nitrate, lithium nitrate, and calcium chloride in DMSO is by 8—18 mole % higher than in the corresponding aqueous solutions. Similarly as in case of the low-concentration limits of glass formation, it only can be stated that the composition of the solution is not favourable for the nucleation of an equilibrium solid phase. In case of the high-concentration limit of glass formation, however, a subsequent addition of the electrolyte into the system results in structural changes which effect a positive influence on the nucleation of an equilibrium solid phase.

In case of calcium nitrate, it is interesting that undercooling and glass-forming abilities were observed even with a melt corresponding to the composition of the congruently melting tetrasolvates [6]. In aqueous solutions of calcium nitrate, the glass formation was observed up to the concentration of 25.6 mole % $Ca(NO_3)_2$ exceeding the composition of the congruently melting trihydrate. In DMSO, the high-concentration limit of glass formation is even higher which may be explained by a presumable existence of a eutecticum in the subsystem trisolvate—calcium nitrate [6].

In case of zinc chloride and lithium chloride, the high-concentration limit of glass formation in DMSO apparently is lower than it is in water. Unfortunately, the values reported for DMSO are those for solutions with a maximum concentration of salts which could be prepared by the experimental technique used while the real values of the high-concentration limit may be higher. Thus it is obvious that the knowledge of phase diagrams of the systems salt—DMSO is inevitable as a basis for the discussion of differences in the glass-forming abilities.

### Influence of salts on temperature of the glass transition

Conformably to [4], it was found that the concentration dependence of the glass transition temperatures can be in the first approximation described by the relation

$$T_g = A + B\,x \qquad (1)$$

where $T_g$ is the glass transition temperature in K, $A$ and $B$ are the constants and $x$ is the mole fraction of the salts. The data from Table 1 were processed by the method of least squares and the calculated parameters $A$ and $B$ are presented in Table 3 together with analogous values for aqueous solutions. The standard relative deviation for $T_g$ was 0.6 %. Though the relation (1) holds in the narrow region of the determined glass formation, it is interesting to discuss the parameters $A$ and $B$ from the point of view of far extrapolations.

Provided that the relation (1) hold for the whole concentration range, the value of parameter $A$ should have the significance of the undeterminable $T_g$ of pure solvent. In aqueous solutions, these values are close to each other and correspond

to $T_g$ of water of about 140 K [7]. In case of DMSO, the values of $A$ also are fairly similar, the average being by *ca.* 10 K higher than that for aqueous solutions. This might agree with the likely value of $T_g$ of DMSO which, unfortunately, also cannot be determined experimentally. This presumption is supported by the melting temperature of DMSO which is by 19 K higher than that of water.

Contrary to the parameter $A$, the values of parameter $B$ are widely different (*e.g.*, for solutions of ammonium nitrate and calcium chloride in DMSO, the values of $B$ are 104.8 and 549.5, respectively). The values of $B$ determine the slope of the concentration dependence of $T_g$ and in the determinable region they usually are comparable to the slopes of tangents to the liquidus curves corresponding to congruently melting solvates [6]. In case of the systems salt—DMSO, this, however, cannot be verified as the corresponding phase diagrams are not known thus far.

## References

1. Sare, E. J., *Ph.D. Thesis.* Purdue University, Lafayette, 1971.
2. Angell, C. A. and Sare, E. J., *J. Phys. Chem. 52,* 1058 (1970).
3. Sare, E. J. and Angell, C. A., *J. Solution Chem. 2,* 53 (1973).
4. Malá, J. and Sláma, I., *Collect. Czech. Chem. Commun. 44,* 1877 (1979).
5. Malá, J., Novák, J., Kodejš, Z., and Sláma, I., *Collect. Czech. Chem. Commun. 43,* 183 (1978).
6. Pacák, P. and Sláma, I., *Collect. Czech. Chem. Commun.,* in press.
7. Angell, C. A. and Tucker, J. C., *J. Phys. Chem. 84,* 266 (1980).