

Temperature of glass transitions and the glass-forming region in the system lithium nitrate—dimethyl sulfoxide—water

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The temperatures of glass transition of solutions of lithium nitrate in the mixed solvent dimethyl sulfoxide—water were determined at different $n(\text{DMSO})/n(\text{H}_2\text{O})$ ratios. It was found that the dependence of the temperature of glass transition on mole fraction of lithium nitrate at constant composition of solvent can be approximated by a linear relationship. Dependence of the temperature of glass transition on composition of the mixed solvent at constant concentration of lithium nitrate was found to be rather complex and it cannot be interpreted on the basis of contemporary theoretical conceptions. Limits of the glass-forming region in the ternary diagram are discussed on the basis of influence of the change in composition of solution on the induction period of nucleation of the corresponding equilibrium phase.

Определены теплоты остекления растворов нитрата лития в смеси растворителей диметилсульфоксид — вода при различных соотношениях $n(\text{ДМСО})/n(\text{H}_2\text{O})$. Обнаружено, что зависимость теплоты остекления от мольной доли нитрата лития при постоянном составе растворителя можно приблизить линейной формулой. Зависимость теплоты остекления от состава смеси растворителей при постоянной концентрации нитрата лития имеет сложный вид, который невозможно интерпретировать на основе имеющихся теоретических представлений. Рассматривается зависимость границ области стеклообразования в трехфазной диаграмме от изменения состава раствора и его влияния на индукционный период нуклеации, соответствующий равновесной фазе.

Recently it has been found that some inorganic salts can form aqueous and/or nonaqueous solutions which are glass-forming [1—4]. It is interesting to note that the glass-forming composition region in aqueous solutions and in dimethyl sulfoxide is for given salt usually different [4]. Also the concentration dependence of the temperatures of glass transition was found to be quantitatively different. In order to obtain experimental data for explanation of this phenomenon several ternary systems salt—DMSO—water have been investigated [5—7]. It was found that the gradual replacement of water by dimethyl sulfoxide influences both the glass-forming composition region and dependence of the temperature of glass transition on composition of the system.

The aim of this paper is to clarify the influence of composition on temperature of glass transition and the glass-forming composition region in the system lithium nitrate—dimethyl sulfoxide—water. Reason for choosing the system containing lithium nitrate follows from the former observation [4], namely that the glass-forming composition regions in water and dimethyl sulfoxide are remarkably different.

Experimental

Chemicals

DMSO, anal. grade (Merck) was used without further purification because it was found that traces of moisture have no relevant influence on the investigated properties. Anhydrous lithium nitrate was prepared from its trihydrate (Lachema, Brno). Substantial part of its water was evaporated by heating in an inert atmosphere. Residual water was removed by heating the sample 4 days in a vacuum drier at temperature not exceeding 160 °C.

Working procedure

The temperature of glass transition was determined by differential thermal analysis. The method and experimental equipment have been described in detail elsewhere [8]. Content of lithium nitrate in samples was checked by spectrophotometric determination [9]. It is expressed as a mole fraction x of salt in solution. Composition of mixed solvent is expressed by the mole fraction y of dimethyl sulfoxide (DMSO) defined as $y(\text{DMSO}) = n(\text{DMSO}) / n(\text{DMSO}) + n(\text{H}_2\text{O})$.

Results and discussion

Temperatures of glass transition

Results of determination of the temperatures of glass transition, T_g/K , as a function of mole fraction x of lithium nitrate (composition of mixed solvent defined by $y(\text{DMSO})$ being constant) are summarized in Table 1. The experimental data were treated by the methods of regression analysis. It was found that the dependence of the temperatures of glass transition on concentration of salt in the system can be approximated by a linear relationship

$$T_g = A + Bx \quad (1)$$

Table 1

Dependence of the temperature of glass transition (T_g /K) on mole fraction of lithium nitrate x at constant y (DMSO)

x	T_g /K	x	T_g /K
$y(\text{DMSO}) = 0.05$		$y(\text{DMSO}) = 0.3$	
0.0928	146.5	0.0000	142.6
0.1238	148.4	0.0496	150.3
0.1538	153.0	0.0980	158.7
$y(\text{DMSO}) = 0.1$		0.1482	166.8
		0.1980	170.7
0.0608	145.5	0.2271	176.6
0.0911	150.6	0.2559	178.6
0.1227	152.8	0.2994	184.3
0.1558	157.3	0.3468	190.6
0.1841	165.1	0.3734	192.7
0.2147	166.3	0.4007	196.9
0.2443	170.5	$y(\text{DMSO}) = 0.4$	
0.2753	175.5	0.0000	143.0
0.3144	180.9	0.0499	151.4
0.3455	187.6	0.0991	160.3
0.2502	170.5	0.1484	170.0
0.2721	173.5	0.1989	178.4
0.3070	180.9	0.2540	183.7
$y(\text{DMSO}) = 0.2$		0.2777	186.5
0.0000	139.7	0.2540	184.7
0.0496	144.8	0.3119	188.2
0.0991	152.5	$y(\text{DMSO}) = 0.5$	
0.1474	158.2	0.0000	144.0
0.1766	162.2	0.0499	153.1
0.2086	166.1	0.0985	162.0
0.2402	174.4	0.1477	171.1
0.2744	178.1	0.2002	181.5
0.2779	178.1	0.2539	186.8
0.3051	180.7	0.2866	190.8
0.3264	184.8	$y(\text{DMSO}) = 0.8$	
0.3493	187.0	0.0834	161.5
0.3845	192.7	0.1010	165.1
0.4186	197.8	0.1520	176.2
$y(\text{DMSO}) = 0.6$		0.1987	184.4
0.0264	148.6	0.2559	192.4
0.0321	150.8	0.2802	195.3
0.0602	156.3		
0.0617	156.8		
0.1014	163.8		
0.1494	173.3		

Table 1 (Continued)

x	T_g/K	x	T_g/K
0.1523	173.5	0.3037	202.5
0.1936	179.1	0.3209	204.0
0.1936	180.1		
0.2042	180.9		$y(\text{DMSO}) = 0.9$
0.2104	184.4	0.1163	168.2
0.2443	187.0	0.1859	183.0
0.2597	188.5	0.2155	182.4
0.2597	189.8	0.2448	189.8
0.2826	192.5	0.2784	193.9
0.2848	192.5	0.3099	203.7
	$y(\text{DMSO}) = 0.7$		
0.0318	153.5		
0.0597	155.0		
0.0896	161.5		
0.1189	168.8		
0.1714	179.0		
0.2303	188.6		
0.2623	191.5		

where A , B are the constants obtained at constant composition of the mixed solvent. Values of these constants for different mole fractions $y(\text{DMSO})$ are presented in Table 2.

The linear dependence of the temperatures of glass transition on composition of the liquid mixture is rather exception than a rule. It follows from an assumption of additive behaviour of this property in the corresponding binary systems. It is known that some mixtures of polymers, inorganic oxides, isomeric alcohols with water or of low-molecular organic liquids may show an additive behaviour of the temperatures of glass transition in their binary systems. Lesikar [10] reported deviation of T_g from additivity for some mixtures of lower alcohols. He proposed for representation of the concentration dependence of the parameter T_g the following equation

$$T_g = T_{g1}(1-x) + T_{g2}x + kx(1-x) \quad (2)$$

where T_{g1} and T_{g2} are the temperatures of glass transition of pure components and k is an adjustable parameter. It can be seen from the equation that the parameter k reflects the deviation from additivity. Eqn (2) can be transformed into the form

$$T_g = T_{g1} + bx - kx^2 \quad (3)$$

where $b = k + T_{g2} - T_{g1}$. At $k = 0$ and assuming that $A = T_{g1}$ we obtain the relation similar to eqn (1).

Table 2

Empirical constants A and B in eqn (1), number of experimental data (N), mean relative deviation of T_g (δ), and the temperature of glass transition of the mixed solvent $T_{g,s}$

$y(\text{DMSO})$	A/K	B/K	N	$\delta/\%$	$T_{g,s}/\text{K}$
0.00	134	176	7	0.41	
0.05	136.1	106.6	3	0.41	
0.1	136.3	142.5	13	0.65	
0.2	138.7	141.1	14	0.48	139.9
0.3	144.9	131.8	11	0.74	140.6
0.4	145.0	151.4	9	0.99	142.1
0.5	145.2	166.4	7	0.75	143.0
0.6	145.7	170.7	17	0.71	
0.7	146.5	178.4	7	0.86	
0.8	147.8	176.5	8	0.60	
0.9	148.3	171.1	6	0.91	
1.0	142.0	202.0	15	0.46	

Gordon *et al.* [11] have discussed in detail the formula

$$T_g = [xT_{g1} + c(1-x)T_{g2}] / [x + C(1-x)] \quad (4)$$

which also represents well the dependence of temperatures of glass transition on composition of binary mixtures. In the quoted paper main attention was paid to the physical meaning of the adjustable parameter C . It was found that according to the free volume model meaning of the parameter C corresponds to the ratio of heat capacities of components at the temperature of glass transition ($C = C(p_2)/C(p_1)$).

Temperatures of glass transition in the systems solvent—salt show, however, some specific features, which prevent using of relationships discussed above for this class of liquids. The temperature of glass transition of solvent is not usually experimentally accessible. Also the temperature of glass transition of anhydrous salt is unknown because these salts are not glass-forming. The third specific feature of the system solvent—salt is a limited glass-forming composition region. Therefore the observed linear dependence of the temperatures of glass transition of solution on concentration of salt is to be considered rather a result of the used mathematical approximation based on investigated region of the concentration dependence of T_g in the binary system than a proof of additivity of T_g in the system salt—solvent.

Physical meaning of the empirical constant A in eqn (1) cannot be a priori identified with the temperature of glass transition of the solvent. In despite of that Angell and Sare [1] found that extrapolation of concentration dependence of T_g to zero concentration of salt in glass-forming aqueous solutions can give values which

are close to the temperature of glass transition of water. This observation is interesting because it allows an approximate estimation of the temperatures of glass transition of solvent. It should be pointed out again that this extrapolation can give only a rough estimate of this parameter as at low concentrations of salts the parameter T_g is usually not accessible to direct experimental determination. In the binary system water—DMSO the parameter T_g could be determined in the glass-forming composition region [12]. Experimental values of this parameter (it is denoted as $T_{g,s}$) are presented in Table 2. It is seen that they are in good agreement with the parameters A in the corresponding ternary system. Comparison of parameters B is also interesting. Assuming validity of the relationship (3) and additivity in the system (*i.e.* $k = 0$) the value B should correspond to the difference of temperatures of glass transition of anhydrous salt and temperature of glass transition of solvent. Thus the concentration dependence of the temperatures of glass transition could be used for estimation of the temperature of glass transition of the anhydrous salt. However, well-founded objections can be raised against this method of evaluation of temperature of glass transition of anhydrous salt: Too far extrapolation of the linear relationship is needed, the additivity of the temperatures of glass transition in the system salt—solvent is not theoretically proved and finally, the estimate of T_g cannot be verified experimentally.

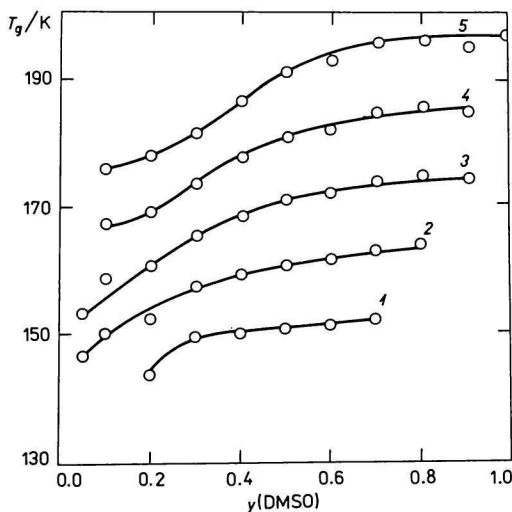


Fig. 1. Dependence of the temperature of glass transition (T_g/K) on mole fraction $y(\text{DMSO})$ in the mixed solvent at constant concentration of lithium nitrate.

The curves correspond to the following concentrations of LiNO_3 : 1. 3 mole %; 2. 9 mole %; 3. 15 mole %; 4. 21 mole %; 5. 27 mole %.

The influence of mixed solvent on the temperature of glass transition of mixtures at constant mole fractions of lithium nitrate in solution is presented in Fig. 1. It is seen that the curves have a monotonously increasing character without a conspicuous extremum. This type of temperature dependence of glass transition on composition of the mixed solvent differs remarkably from a similar function in the systems ammonium nitrate—DMSO—water and silver nitrate—DMSO—water where a linear dependence of the temperature of glass transition on composition of the mixed solvent at constant salt concentration has been observed. Behaviour of the system discussed in this paper is, however, similar to that observed in the system calcium chloride—DMSO—water [7]. Common feature of the system ammonium nitrate—DMSO—water and silver nitrate—DMSO—water consists in the experimental fact that aqueous solutions of ammonium nitrate and silver nitrate are not glass-forming. Explanation of different shape of the dependence of temperatures of glass transition in both types of systems can be found in different hydration of cations. Physical meaning of this difference and its manifestation in the studied phenomenon is, however, still unexplained. It is interesting that in the case of molten mixture of hydrates $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ — $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ a linear dependence of the temperatures of glass transition on composition has been found [11]. Thus we may formulate hypothesis that a mixture of hydrates behaves ideally, which means that in these systems the dependence of the temperature of glass transition on composition is a linear one. On the other hand, the mixtures of solvates and hydrates do not show this property, probably as a result of complicated hydration and solvation equilibria.

Glass-forming region

On the basis of limit concentration values of lithium nitrate at given composition of solvent (these data are summarized in Table 1) the glass-forming composition region PSEJKLMNP has been defined as it is shown in the triangular diagram in Fig. 2. The most interesting are the boundaries of the glass-forming region. At composition corresponding to these boundaries substantial changes in structure of solution must occur. Small change in composition causes that at standard cooling rate in liquid nitrogen an amorphous glassy solid substance instead of a crystal phase is formed. The boundary composition of the glass-forming region cannot be considered constant because it depends on conditions under which it was determined. Especially the rate of cooling plays an important role in this respect.

The influence of composition of ionic liquids on glass-forming is not yet explained. Necessary condition for glass formation is supercooling of liquid, which means that neither at temperature of solid—liquid equilibrium nor at lower temperatures a corresponding crystalline phase is immediately formed. The ability of metastable existence of liquid under its equilibrium temperature without

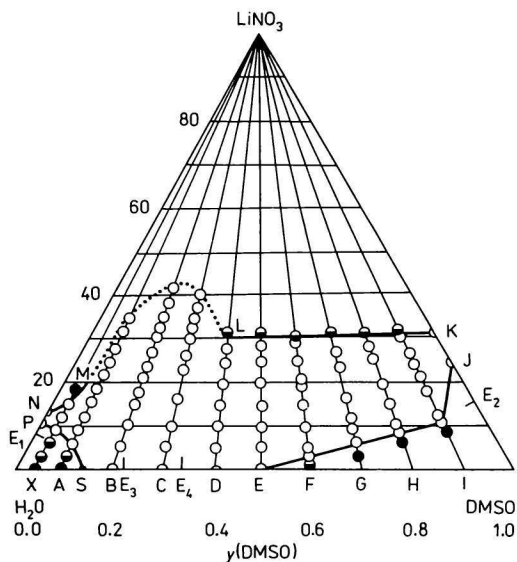


Fig. 2. Glass-forming composition region in the system lithium nitrate—DMSO—water.
 ○ Solutions which form after cooling a glassy phase; ◐ solutions which partially crystallize after cooling; ● solutions which crystallize well after cooling.

detectable crystal formation is caused by a low nucleation rate and/or by low growing rate of crystals. This phenomenon has been theoretically thoroughly studied in pure substances [13] and in the case of industrial crystallization [14].

The most important for glass-forming is the induction period of nucleation and the influence which can even a small change in composition of solution have on this parameter. From this point of view we may presume that small change in composition of solution causes such structural changes that the conditions for formation of a critical nucleus are disadvantageous. It can be caused by a rapid decrease of concentration of the structural entities which are necessary for formation of nucleus or by change of conditions which are favourable for clustering of nucleus-forming entities. It is obvious that these changes will depend on composition of the crystalline phase which is in equilibrium with solution. Owing to this fact we shall discuss separately the solvent rich composition limit PSEK and the salt rich composition limit KLMN of glass formation.

At the point P the equilibrium crystalline phase in the binary system lithium nitrate—water is lithium nitrate trihydrate. It can be assumed that the change of ratio of total number of water molecules to lithium nitrate in solution from $R_{\text{H}_2\text{O}} = 10$ to $R_{\text{H}_2\text{O}} = 8$ makes the nucleation of lithium nitrate trihydrate more difficult.

Point S represents the equilibrium of ice with binary solution DMSO—water. As the solution begins to be glass-forming at this concentration one may conclude that the mean ratio of DMSO molecules to one molecule of water changes from 7 to 6. This influences negatively the formation of critical nuclei of ice. Oppositely at the ratio $n(\text{DMSO})/n(\text{H}_2\text{O}) \geq 1$ the conditions in the solution dimethyl sulfoxide—water begin to be favourable for an easy nucleation of crystalline dimethyl sulfoxide (point E).

At the point J the equilibrium solid phase is formed by crystalline $\text{LiNO}_3 \cdot 3\text{DMSO}$ [15]. An increase of concentration of lithium nitrate in the region of the mole ratio $n(\text{DMSO}):n(\text{LiNO}_3) = 3$ makes therefore the nucleation of crystals $\text{LiNO}_3 \cdot 3\text{DMSO}$ more difficult.

Point K lies at the high-concentration boundary in the region of equilibrium of binary solution of lithium nitrate in DMSO with solid lithium nitrate [15]. The ratio $n(\text{DMSO}):n(\text{LiNO}_3) = 2$ already makes in solution favourable conditions for nucleation of lithium nitrate.

Ternary diagram of the system lithium nitrate—DMSO—water is not yet known. However, we may reasonably assume that in the region K—L the equilibrium solid phase consists of crystalline lithium nitrate. Thus the conditions should be similar like in the binary system when the nucleation of lithium nitrate crystals takes place.

At the mole fraction $y(\text{DMSO}) = 0.2$ the glass-forming composition region in pseudo-binary system lithium nitrate—mixed solvent is the most extended. It can be concluded that this composition of the mixed solvent is not favourite for nucleation of crystalline lithium nitrate up to the mole ratio $n(\text{LiNO}_3):n(\text{mixed solvent})$ equal to one.

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