

Glass transition temperatures and glass-forming region in the calcium nitrate—dimethyl sulfoxide—dimethylformamide system

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Received 8 September 1986

The glass transition temperatures (T_g) of the mixture calcium nitrate—dimethyl sulfoxide—dimethylformamide were determined in dependence on the concentration of calcium nitrate for the constant mole fraction of dimethylformamide in the mixed solvent. It was ascertained that this dependence can be approximated, within the framework of experimental errors, by a linear relation. The dependence of T_g on the composition of the mixed solvent y_{DMF} , calculated from the experimentally determined values of glass transition temperature, can be also described by a linear relation. From experimental data the glass-forming region of the system was constructed.

Определены температуры застекливания (T_g) смесей нитрат кальция—диметилсульфоксид—диметилформамид в зависимости от концентрации нитрата кальция при постоянной мольной доле диметилформамида в смешанном растворителе. Показано, что эту зависимость можно приблизительно выразить в границах ошибок эксперимента посредством линейного соотношения. Зависимость T_g от состава смешанного растворителя y_{DMF} , определенная исходя из экспериментально найденных величин температур застекливания, также может быть описана линейным соотношением. На основании опытных данных построена схема стеклообразующей области данной системы.

Earlier papers were concerned with the influence of the gradual replacement of water with dimethyl sulfoxide in the mixed solvent in the glass-forming salt—water—dimethyl sulfoxide systems on the glass transition temperature and on the range of the glass-forming region [1—6].

It was ascertained that in some cases (AgNO_3 , NH_4NO_3) the influence of this replacement can be approximated by a linear relation of T_g to the mole fraction of DMSO in the mixed solvent. In the systems containing CaCl_2 , LiNO_3 , and ZnCl_2 , however, considerable deviations of T_g appeared from the assumed additivity. Further it was ascertained that the gradual replacement of water with dimethyl sulfoxide exerts considerable influence on the concentration range of glass-forming capacity of inorganic salts solutions. Therefore, it was interesting to investigate the influence of the gradual replacement of one solvent by another

on the changes of the glass transition temperature and the concentration range of the glass-forming region in the glass-forming solutions of inorganic salts. In the capacity of mixed solvent the mixture of dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) was used, which belongs to the group of dipolar solvents. For model salt the calcium nitrate was selected which has been known to make glass-forming solutions in both solvents [7, 8].

Experimental

Anhydrous calcium nitrate was prepared by recrystallization of a commercial product with the elimination of the major part of water by evaporation above a burner and of the remainder in a vacuum drier.

DMSO and DMF were the preparations of Merck and were used without any modifications.

The samples for the determination of T_g were prepared by weighing the necessary quantity of salt and the necessary quantity of the mixed solvent.

The content of calcium ions was checked by chelatometry. The DMF content in the mixed solvent was expressed by the mole fraction of DMF (y_{DMF}).

The glass transition temperature was determined by the low-temperature differential thermal analysis with the indication of temperature and temperature difference of the specimen and the standard. The description of the method and of the experimental equipment was given in an earlier paper [9].

The samples quantity was about 0.2 cm^3 , the cooling rate $(15\text{ K}—17\text{ K})\cdot\text{s}^{-1}$. The reproducibility of T_g determination was 1%.

Results and discussion

The experimentally determined values of the glass transition temperature T_g for the constant values of the DMF mole fraction in the mixed solvent y_{DMF} and different mole fractions of calcium nitrate in the solution (x) are given in Table 1. It was ascertained by regression analysis that the dependence of the glass transition temperature on the composition of the solution can be approximated by the linear relation

$$T_g = A + B \cdot x \quad (1)$$

The computed values of the constants A and B are given in Table 2.

It was ascertained [7, 8, 10] that in salt—solvent binary systems the extrapolation of the linear relation of the dependence of the glass transition temperature T_g to the zero salt concentration yields the value of T_g which is very near to the estimated value of T_g of pure solvent. The values of the constants A in a ternary system, therefore, should approach the T_g values of the DMSO—DMF system. In this work we succeeded in determining the experimental values of T_g of the DMSO—DMF system only for the composition of the mixed solvent charac-

Table 1

Dependence of the glass transition temperature, T_g/K , on the mole fraction of calcium nitrate, x , at different mole fractions of DMF, y_{DMF} , in mixed solvent

x	T_g/K	x	T_g/K	x	T_g/K
$y_{DMF} = 0.1$		$y_{DMF} = 0.2$		$y_{DMF} = 0.3$	
0.0831	177.0	0.0802	171.1	0.0536	161.8
0.1534	202.6	0.0994	173.1	0.1057	177.0
0.2075	223.7	0.1513	193.5	0.1494	199.5
0.3064	265.0	0.2016	216.6	0.1999	214.2
		0.2704	246.2	0.3010	254.5
		0.3199	263.8		
$y_{DMF} = 0.4$		0.3365	269.1	$y_{DMF} = 0.6$	
0.0344	157.5			0.0159	150.3
0.0580	166.5	$y_{DMF} = 0.5$		0.0308	151.6
0.1020	175.0	0.0519	158.2	0.0499	156.1
0.1518	193.0	0.1027	173.2	0.1014	169.7
0.2074	215.5	0.1332	184.0	0.1535	190.1
0.2664	239.5	0.2063	214.7	0.2002	210.2
0.3018	250.8	0.2586	233.7	0.3037	244.4
0.3311	259.2	0.3157	256.1	0.3363	259.7
		0.3388	260.8		
$y_{DMF} = 0.7$				$y_{DMF} = 0.9$	
0.0000	145.6	$y_{DMF} = 0.8$		0.0000	142.1
0.0267	149.7	0.0000	143.8	0.1013	166.8
0.0547	155.2	0.1025	168.2	0.2169	217.1
0.1018	169.5	0.2056	212.8	0.2593	232.3
0.2055	212.8	0.2685	234.2	0.3127	253.7
0.2601	231.4	0.3211	254.3	0.3339	264.7
0.3124	249.0	0.3312	255.7		
0.3346	259.6				

Table 2

Values of the constants A and B (eqn (1))

y_{DMF}	A/K	B/K	$(A + B)/K$	$T_{g,adit}/K$
0.0	149	363	512	150
0.1	142.6	397.9	540.5	148
0.2	135.7	399.8	535.5	146
0.3	140.2	378.1	518.3	144
0.4	143.1	352.5	495.6	142
0.5	136.7	372.1	508.8	140
0.6	139.7	347.7	487.4	138
0.7	139.5	352.3	492.0	136
0.8	139.3	352.6	492.0	134
0.9	136.4	374.3	510.7	132
1.0	124.8	402.4	527.2	129
			511 ± 18	

terized by $y_{\text{DMF}} = 0.7, 0.8, \text{ and } 0.9$. The glass transition temperature of the DMSO—DMF system can be roughly estimated on the basis of the assumption of additivity of T_g in this system and the T_g values of DMSO and DMF given in the work by *Sare and Angell* [8]. The dependence on composition in this approximation would be $\{T_g\} = 150 - 21y_{\text{DMF}}$; the approximate T_g values for the individual compositions of the mixed solvent are given also in Table 2. A comparison reveals that the values of A are somewhat lower than the estimated T_g of the mixed solvent in the majority of cases. That is in agreement, however, with the ascertained fact [11, 12] that the glass transition temperature of a mixture of organic solvents usually shows deviations from additivity.

The values of the sum of the constants ($A + B$) could be compared with the glass transition temperature of calcium nitrate. With the assumption of the validity of the linear relation between T_g and the mole fraction of the salt for every mixed solvent composition the value of ($A + B$) should indicate the glass transition temperature of molten calcium nitrate. Unfortunately, this temperature cannot be ascertained experimentally, as the molten calcium nitrate is not glass-forming. It is possible, however, to use the approximate relation of $T_g = (2/3) T_L$ (T_L — liquidus temperature) which is applicable to a number of pure substances. The values of ($A + B$) are also given in Table 2 and their arithmetic mean is (511 ± 18) K. The estimated glass transition temperature of calcium nitrate is 556 K. The approximate value is very good, if we take into account that the rule for estimating the glass transition temperature from the melting point of pure substances is more or less informative only and that the extrapolation from the measurable regions of the dependence of the glass transition temperature of calcium nitrate in a mixed solvent is very distant.

The dependence of the glass transition temperature on the mixed solvent composition for constant salt concentration is plotted in Fig. 1. The diagram makes it obvious that this dependence generally fulfils well the assumption of additivity of the glass transition temperatures in the solvated salt melts systems which was found for the $\text{Ca}(\text{NO}_3)_2 \cdot \text{RH}_2\text{O}$ — $\text{Cd}(\text{NO}_3)_2 \cdot \text{RH}_2\text{O}$ system [13] as well as for the NH_4NO_3 —DMSO— H_2O system [2] and the AgNO_3 —DMSO— H_2O system [3]. Particularly satisfactory is the fulfillment of this assumption for lower calcium nitrate content (up to $x = 0.15$). With higher calcium nitrate concentrations deviations begin to appear in the region of $y_{\text{DMF}} = 0.1$ (positive deviations) and $y_{\text{DMF}} = 0.6$ (negative deviations). Approximately, however, it is possible to state that the gradual increase of the calcium nitrate content in the mixed solvent does not exert any substantial influence on the additivity of the glass transition temperatures of the mixed solvent which can be studied experimentally only in the region of $y_{\text{DMF}} = 0.7$ — 0.9 because of the glass-forming inability of other compositions.

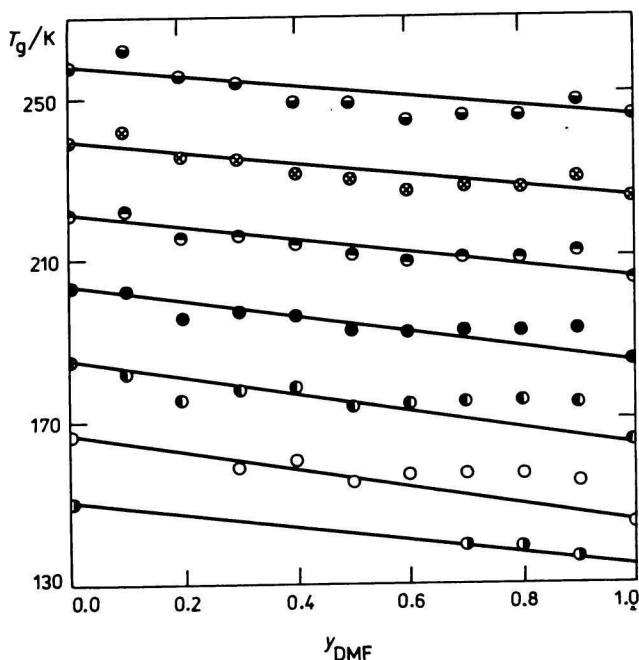


Fig. 1. Dependence of the glass transition temperature (T_g/K) on the composition of the mixed solvent (y_{DMF}) at a constant mole fraction of the calcium nitrate (x).

x : ○ 0.00; ○ 0.05; ● 0.10; ● 0.15; ● 0.20; ⊗ 0.25; ● 0.30.

Instead of the experimentally nonaccessible T_g value at $y_{DMF} = 0$ the $T_{g, \text{adit}}$ value from Table 2 was used, and the value at $x = 0.05$ was replaced by the extrapolated T_g value from the dependence of T_g on composition ($T_g(x)$) of the binary system $\text{Ca}(\text{NO}_3)_2$ —DMSO.

Glass-forming region

The extent of the glass-forming region of the $\text{Ca}(\text{NO}_3)_2$ —DMSO—DMF system is shown in the triangular diagram in Fig. 2. The plotted glass-forming region originates by the connection of the boundary glass-forming points of binary systems. The extent of glass-forming region of the $\text{Ca}(\text{NO}_3)_2$ —DMSO system was determined in a previous paper [8] as 7.8—33.5 mole % of $\text{Ca}(\text{NO}_3)_2$. The range of glass-forming region of the $\text{Ca}(\text{NO}_3)_2$ —DMF system was determined within the limits of 2.1—33 mole % of $\text{Ca}(\text{NO}_3)_2$ [14]. The range of glass-forming region of the DMSO—DMF binary system (approx. 70—95 mole % of DMF) has not been published yet.

Generally speaking it can be stated that the influence of the composition of the electrolyte solutions on their glass-forming capacity has not been elucidated

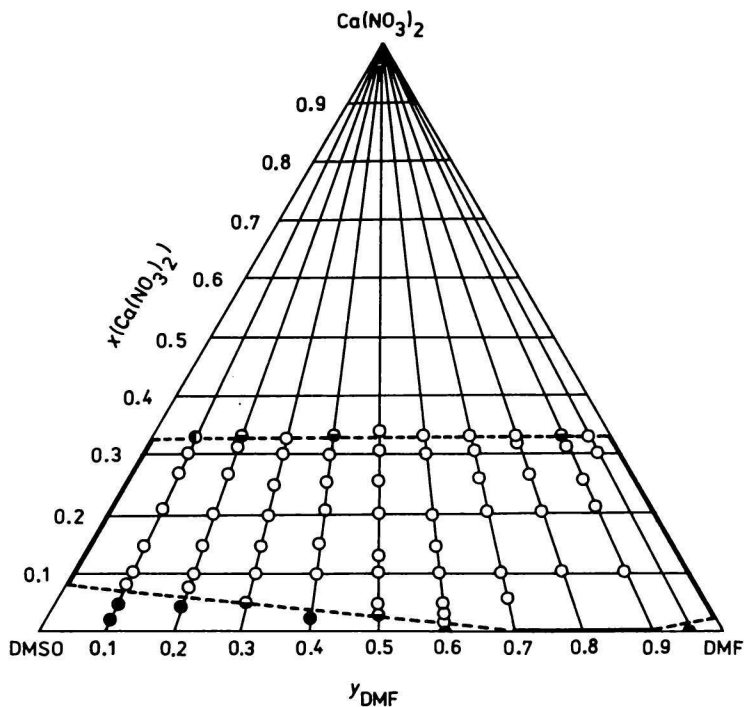


Fig. 2. The glass-forming composition region in the system calcium nitrate—dimethyl sulfide—dimethylformamide. The content of dimethylformamide in mixed solvent was expressed by the mole fraction of dimethylformamide y_{DMF} , the content of calcium nitrate by the mole fraction of calcium nitrate in the solution (x).

so far. In a recent work [14], however, some hypotheses have been formulated which will be used also in the discussion of the concentration limits of the studied system.

The joint condition of the origin of a supercooled liquid and glass is the prevention of the crystallization process below the liquidus temperature. The crystallization process consists of nucleation, *i.e.* the formation of a critical cluster of crystal-forming entities with long-range periodicity of arrangement, and of the growth of crystals. The necessary prerequisite for forming of glass is the retardation of the origin of the nucleus in the course of cooling from the liquidus temperature to the glass transition temperature. The rate of this retardation is the nucleation induction period.

The boundaries of the glass-forming composition can be determined experimentally. For these compositions substantial change of the nucleation induction period must take place. The explanation of this phenomenon must be sought in the influence exerted on the solution structure by a minute change of its

composition which results in a more difficult, *i.e.* from the kinetic point of view slower, nucleus formation.

One of the possible influences of the solution composition on nucleus formation consists in the interaction of the solvated substance with the solvent in the course of which associates or solvates originate to such an extent that the concentration of crystal-forming entities is substantially reduced. This hypothesis is applicable to the explanation of the low-content glass-forming boundary, when the equilibrium solid phase is represented by the solvent crystal. For example, the bond of the molecules of water in the ion coordination spheres reduces the concentration of the "free" molecules of water as a result of which the nucleus formation of crystalline ice is limited.

The application of this assumption necessitates the knowledge of the phase equilibrium of the investigated system. Experimental data of this type have not been found in literature for the DMSO—DMF system. Therefore, it is only possible to assume that at low DMF concentrations in the mixed solvent the equilibrium solid phase will consist of the crystalline DMSO. As the mixed solvent is not glass-forming up to 70 mole % of DMF, it can be concluded that the DMF/DMSO interaction does not produce an associate with several DMF molecules, or at least not such associate as would reduce substantially the concentration of the "free" DMSO and thus limit its nucleation.

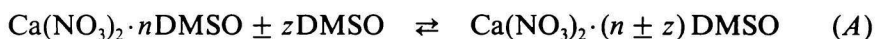
Different situation arises in the DMSO—DMF system in respect of its glass-forming capacity in the region of high DMF concentrations. In this study we have succeeded in preparing, by the given method, glasses from the solutions of 5 mole % of DMSO. If we assume that the equilibrium solid phase consists of the crystalline DMF, it means that already a small quantity of DMSO in the mixed solvent exerts significant influence on the induction period of DMF crystallization. Provided the structure is influenced so as to reduce substantially the concentration of the "free" DMF, it would mean that the associate $\text{DMF} \cdot n\text{DMSO}$ should originate in the DMSO—DMF system, where n should be high. The confirmation of this assumption, however, necessitates detailed information on the properties of the DMSO—DMF system which, unfortunately, is not yet available in literature.

The glass-forming limit at high calcium nitrate content is practically constant in the whole ternary system and amounts to 33 mole % of $\text{Ca}(\text{NO}_3)_2$.

More detailed information is available only about the $\text{Ca}(\text{NO}_3)_2$ —DMSO system for which the liquidus temperature and the supercooling temperature have been found [15]. The existence of a congruently melting compound $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{DMSO}$ and of two eutectic points at approximately 8 mole % and 19 mole % of $\text{Ca}(\text{NO}_3)_2$ was ascertained in the system. Therefore, the hypothesis of the influence of the shortage of crystal-forming entities in the solution on the limitation of nucleus forming cannot be used to explain the glass-forming

capacity in the region below 33 mole % of salt. For example, in the case of melt composition with 20 mole % of $\text{Ca}(\text{NO}_3)_2$ it is necessary to assume that the solution will contain a prevailing quantity of crystal-forming entities of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{DMSO}$. However, it is impossible to exclude the possibility that in the liquid phase also the particles of $\text{Ca}(\text{NO}_3)_2 \cdot (4 \pm z)\text{DMSO}$ will be present, where z may be 1, 2, 3, and 4. In this case the hypothesis of non-homogeneous, non-crystal-forming clusters can be used for the interpretation of the influence of solution composition on glass forming [14]. This hypothesis is based on the assumption that even though the solution contains a sufficient number of crystal-forming entities for nucleus formation, the non-crystal-forming particles are built into the cluster in the course of nucleation. If a sufficient number of non-crystal-forming particles is present in the cluster, the cluster cannot form the basis for crystal growth even after it has achieved critical size, as the built-in non-crystal-forming particles cancel the long-range periodicity of the cluster. A non-homogeneous cluster of above-critical size, however, can become a crystallization nucleus, when the majority of non-crystal-forming particles has been forced out of the cluster into the solution. Such process, however, is of diffusion character and its course is time-dependent. This view induces the kinetic factor into the nucleation process which can be used for the interpretation of the increase of the nucleation induction period.

In the studied $\text{Ca}(\text{NO}_3)_2$ —DMSO system the particles of the $\text{Ca}(\text{NO}_3)_2 \cdot (4 \pm z)\text{DMSO}$ type can play the role of the afore mentioned non-crystal-forming entities. Their frequency distribution depends on a number of solvation equilibria of the type



the equilibrium constants of which have not been determined experimentally so far. The high-content glass-forming limit in the $\text{Ca}(\text{NO}_3)_2$ —DMSO system, therefore, can be interpreted as follows: At the $\text{Ca}(\text{NO}_3)_2$ concentration in DMSO of some 33 mole % the frequency representation of non-crystal-forming particles markedly changes, as a result of which homogeneous clustering of crystal-forming particles can take place which form a perfect nucleus, *i.e.* a cluster of crystal-forming particles of critical size with crystal periodicity.

The limit salt concentration for the salt-rich composition glass-forming limit cannot be predicted, unfortunately, because of our ignorance of the course of solvation equilibria. In spite of that, however, this hypothesis affords so far the only logical explanation of the induction period of nucleation of crystalline solvates. Moreover, it incorporates the kinetic factor (diffusion of non-crystal-forming particles from the cluster), which can explain the longer nucleation induction period.

It is obvious that the hypothesis of the origin of non-homogeneous non-crystal-forming clusters would be applicable to pure mixed solvent. The associates of molecules of two solvents would represent the non-crystal-forming entities in such a case. In this way the hypothesis of non-homogeneous clusters becomes more general for the interpretation of the influence of composition on super-cooling and glass-forming.

The hypothesis of non-homogeneous clusters can be applied also to the $\text{Ca}(\text{NO}_3)_2$ —DMF system, although experimental data on this system have not been published so far. The case of interpretation of the glass-forming limit in the whole $\text{Ca}(\text{NO}_3)_2$ —DMSO—DMF ternary system is similar.

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Translated by S. Kadečka