

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

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The glass transition temperatures (T_g) of the mixture calcium nitrate—water—dimethylformamide were determined in dependence on the content of calcium nitrate for the constant mole fraction of dimethylformamide in the mixed solvent. It was ascertained that this dependence can be approximated, in the framework of experimental errors, by a linear relation. On the basis of experimentally ascertained values of the glass transition temperature the dependence of T_g on the composition of the mixed solvent (y_{DMF}) was calculated. Maxima were ascertained on the curve representing this dependence, and the extents of the glass-forming regions were determined.

Определены температуры застеклевания (T_g) смеси нитрат кальция—вода—диметилформамид в зависимости от содержания нитрата кальция при постоянной мольной доле диметилформамида в смешанном растворителе. Показано, что эта зависимость может быть приближена в границах ошибки эксперимента посредством линейного соотношения. Исходя из опытно найденных значений температуры застеклевания, была рассчитана зависимость T_g от состава смешанного растворителя (y_{DMF}). На кривой, представляющей эту зависимость, обозначены максимумы и определены границы областей стеклообразования.

Previous papers were concerned with the influence of the solvent on the glass-forming ability of binary systems salt—solvent. In the capacity of solvent water and dimethyl sulfoxide (DMSO) were used [1, 2]. It was ascertained that the solutions of various salts differed in the magnitude of the glass-forming region as well as in the value of T_g according to the solvent used (water or DMSO). In order to explain these differences also the influence of the gradual replacement of H_2O with DMSO in the mixed solvent in ternary systems salt—water—DMSO was investigated. The gradual replacement of water with DMSO exerted considerable influence on the concentration extent of the glass-forming capacity of solutions of inorganic salts [3—8]. This influence of the composition of the mixed solvent, particularly at the boundary of the glass-forming capacity in the region of low salt content and high solvent content, was explained, on the basis of the aforementioned studies, by the change of the

structure of the liquid which had occurred due to the shortage of structural entities of the corresponding equilibrium crystalline phase, probably as a result of solvation or association equilibria of the individual components. Direct verification of this hypothesis is not possible; the hypothesis can be sustained only by a systematic study and statistical evaluation of various systems. Therefore, a new system was selected, in which dimethylformamide (DMF) was used as solvent [9]. DMF was selected as a dipolar, aprotic, good solvent for the salts under consideration with the characteristics similar to DMSO. Major differences can be observed only in the melting temperatures (DMF -61°C , DMSO $+18^{\circ}\text{C}$). It could be expected, therefore, that in the case of binary systems salt—DMF the eutectic compositions would be near the lower salt concentrations than in the case of the systems containing DMSO. The glass-forming region is usually situated in the proximity of the eutectic point; for this reason it was assumed that also the low concentration glass-forming boundary would be situated near the lower salt concentrations. This expectation was fulfilled with the binary systems salt—DMF. However, the high value of the solvent/salt ratio disproves the theory of the influence of insufficient quantity of uninfluenced solvent molecules on the nucleation rate and the growth of solvent crystals in the vicinity of the low concentration boundary. For the concept of a new explanation of the influence of the composition of the system on the glass-forming region and for the comparison of the glass-forming capacity with the ternary system salt—DMSO— H_2O the study of the glass-forming capacity of the system salt—DMF— H_2O proved to be useful. As the salt in the system the calcium nitrate was selected which is known to form easily the glass-forming solutions and which is easy to solve in DMF.

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.

DMF was the preparation of Merck and was used without any modifications.

The samples for the determination of T_g were prepared by weighing the necessary quantity of the mixed solvent and the necessary quantity of salt; 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 a previous paper [10].

The specimen quantity was 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 value of the DMF mole fraction in the mixed solvent y_{DMF} in dependence on the calcium nitrate mole fraction x in the solution are given in Table 1. Similarly with the system calcium nitrate—dimethyl sulfoxide—dimethylformamide, which was studied earlier [11], the relation between the glass transition temperature and the composition of the mixed solvent can be approximated by the linear expression

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

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

According to the works of *Sare* [1, 12] the extrapolation of the linear dependence T_g of binary aqueous solutions of inorganic salts to the zero salt concentration yields the values which are near the glass transition temperature of water. Analogously in a salt/solvent system the extrapolation to the zero salt content should yield the glass transition temperature of the pure solvent, and the values of the constant of the ternary system composition A obtained in this study should approach the values of the glass transition temperature of the H_2O —DMF systems of different compositions.

For the H_2O —DMF system the T_g values were ascertained within the concentration range of $y_{\text{DMF}} = 0.2$ — 0.9 . Their numerical values are given in Table 1 as the T_g values for $x = 0$.

The estimate of the glass transition temperatures of the H_2O —DMF system can be roughly based on the assumption of additivity of T_g in this system and on the values of T_g for H_2O and DMF, given in the work of *Sare* and *Angell* [13]. The concentration dependence of this approximation is $\{T_g\} = 139 - 10x$. The calculated $T_{g, \text{approx}}$ are also given in Table 2. In contradistinction to the DMSO—DMF system studied in [11] these values are noticeably higher than the values of the constant A in the majority of cases. The measured glass transition temperatures of the mixture of water with dimethylformamide approach the values of constants A rather than those of $T_{g, \text{approx}}$. The explanation can be sought, once again, in that the glass transition temperature of the mixture with organic solvents usually shows deviations from additivity.

Similarly with the system calcium nitrate—dimethyl sulfoxide—dimethylformamide [11] it is possible to compare the sum of constants ($A + B$) with the estimated experimentally undeterminable glass transition temperature of molten calcium nitrate. The values of the sum ($A + B$) are given in Table 2 and their arithmetic mean is (501 ± 23) K. The estimated glass transition temperature of calcium nitrate is 556 K. Although this temperature is by 55 K higher than the arithmetic mean of the values of ($A + B$), the approximate agreement is satisfac-

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
$y_{DMF} = 0.1$		$y_{DMF} = 0.2$		$y_{DMF} = 0.3$	
0.0590	167.3	0.0000	161.2	0.0000	158.2
0.0882	173.7	0.0299	167.4	0.0303	166.1
0.1191	184.0	0.0607	175.2	0.0591	172.6
0.1191	181.9	0.1008	183.5	0.0902	179.6
0.1484	192.0	0.1190	188.7	0.1202	185.0
0.1780	210.6	0.1482	200.2	0.1546	203.6
0.2078	222.3	0.1836	215.5	0.1759	210.9
0.2393	237.6	0.2058	222.7	0.2100	222.7
0.2629	245.4	0.2422	236.4	0.2384	234.8
0		0.2647	242.4	0.2750	246.7
				0.2883	255.0
$y_{DMF} = 0.4$		$y_{DMF} = 0.5$		$y_{DMF} = 0.6$	
0.0000	154.1	0.0000	149.5	0.0000	146.6
0.0254	162.5	0.0102	154.4	0.0301	156.1
0.0590	170.2	0.0590	166.3	0.0589	164.4
0.0891	178.9	0.0890	176.5	0.0886	172.7
0.1188	186.8	0.1197	186.0	0.1176	182.2
0.1476	198.9	0.1521	199.4	0.1521	196.5
0.1786	212.1	0.1668	203.6	0.1800	206.3
0.2072	224.2	0.2146	222.7	0.2195	222.1
0.2447	235.8	0.2483	231.9	0.2484	233.0
0.2781	249.0	0.3308	260.0	0.3184	256.1
0.2732	256.3			0.3279	258.6
0.2927	259.6				
		$y_{DMF} = 0.8$		$y_{DMF} = 0.9$	
$y_{DMF} = 0.7$		0.0000	143.0	0.0000	142.0
0.0000	143.8	0.0298	152.0	0.0280	148.1
0.0290	152.8	0.0673	159.1	0.0590	155.5
0.0603	162.0	0.0886	166.0	0.0728	158.5
0.0892	169.7	0.1240	178.6	0.1183	173.9
0.1187	178.6	0.1516	188.8	0.1466	181.9
0.1540	193.3	0.1819	200.2	0.1770	198.7
0.1802	204.6	0.2096	211.1	0.2105	214.0
0.2100	222.7	0.2450	222.5	0.2404	222.7
0.2368	227.0	0.2778	235.2	0.2650	231.4
0.2956	244.2	0.3298	255.0	0.3215	248.5
0.3377	256.5	0.3421	260.6		

tory, as the extrapolation from the measurable region of the relation of the glass transition temperature of calcium nitrate and the composition of mixed solvent is very distant.

Table 2

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

y_{DMF}	A/K	B/K	$(A + B)/\text{K}$	$T_{\text{g, approx}}$
0.0	141	383	524.0	139
0.1	137.2	408.1	545.3	138
0.2	156.0	319.3	475.0	137
0.3	152.6	339.0	491.6	136
0.4	149.1	365.3	514.4	135
0.5	148.2	336.4	484.6	134
0.6	144.1	350.2	494.3	133
0.7	141.2	346.9	488.1	132
0.8	138.0	349.7	487.7	131
0.9	137.9	343.7	481.6	130
1.0	124.8	402.4	527.2	129
			501 ± 23	

The dependence of the glass transition temperatures on the composition of the mixed solvent is shown in Fig. 1. The diagram makes it obvious that this dependence shows considerable deviations from additivity of glass transition temperatures. In the H_2O —DMF system these deviations from additivity have their maximum at $y_{\text{DMF}} = 0.2$ and attain as many as 20 K. With the growing content of calcium nitrate these maxima drop considerably and shift to the region of $y_{\text{DMF}} = 0.4$. However, for the highest studied calcium nitrate contents of $x = 0.25$ and 0.3 the negative deviations from the additivity of glass transition temperatures begin to appear in the region of $y_{\text{DMF}} = 0.2$. This influence of the calcium nitrate content on the glass transition temperature deviation in the system calcium nitrate—water—dimethylformamide cannot be explained on the basis of our contemporary knowledge.

Glass-forming region

The range of the glass-forming region of the $\text{Ca}(\text{NO}_3)_2$ — H_2O —DMF system is presented in the triangular diagram in Fig. 2. The scope of the glass-forming region in the system of the mixed solvent H_2O —DMF is relatively large (20—90 mole % of DMF). The range of the glass-forming region of the $\text{Ca}(\text{NO}_3)_2$ — H_2O binary system was determined within the limits of 6.7—25.6 mole % of $\text{Ca}(\text{NO}_3)_2$ [12]. The composition range of the

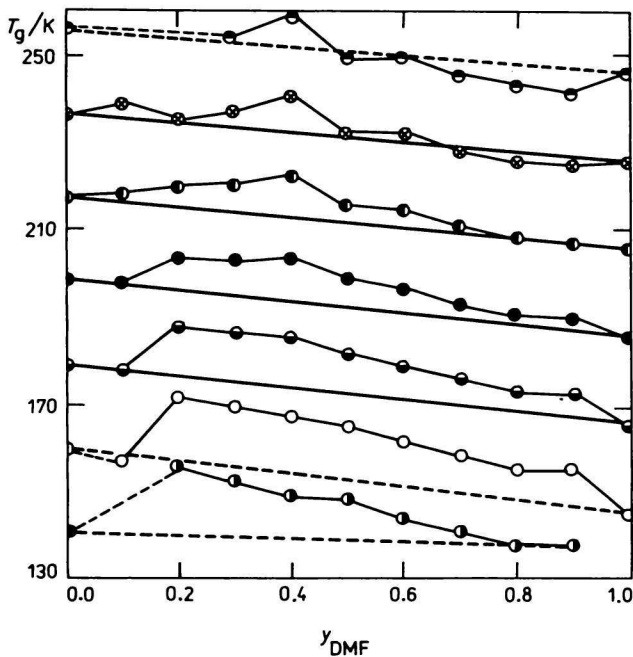


Fig. 1. Dependence of the glass transition temperature (T_g/K) on the composition of the mixed solvent (y_{DMF}) at a constant mole fraction of calcium nitrate (x).

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

The dashed line indicates the systems, in which the T_g values could not be determined at $y_{DMF} = 0$, and therefore the extrapolated values were used.

$\text{Ca}(\text{NO}_3)_2$ —DMF binary system (2.1—33 mole % of $\text{Ca}(\text{NO}_3)_2$) was studied in our previous paper [9]. The low-content boundary of the glass-forming capacity of the $\text{Ca}(\text{NO}_3)_2$ — H_2O system can be approximated, consequently, by the line connecting the low-content boundaries of the $\text{Ca}(\text{NO}_3)_2$ — H_2O and $\text{Ca}(\text{NO}_3)_2$ —DMF binary systems with the boundaries of the glass-forming capacity of the H_2O —DMF system. The high-content boundary of glass-forming capacity of the $\text{Ca}(\text{NO}_3)_2$ — H_2O —DMF system is characterized by gradual increase in the regions of $y_{DMF} = 0$ —0.5 from 25.6 mole % of $\text{Ca}(\text{NO}_3)_2$ to some 33 mole % of $\text{Ca}(\text{NO}_3)_2$ and by the generally constant value of 33 mole % of $\text{Ca}(\text{NO}_3)_2$ in the region of $y_{DMF} = 0.5$ —1.

The influence of electrolyte composition in various solvents on their glass-forming capacity has not been fully elucidated so far. For qualitative interpretation, however, it is possible to use some assumptions formulated in an earlier work [11].

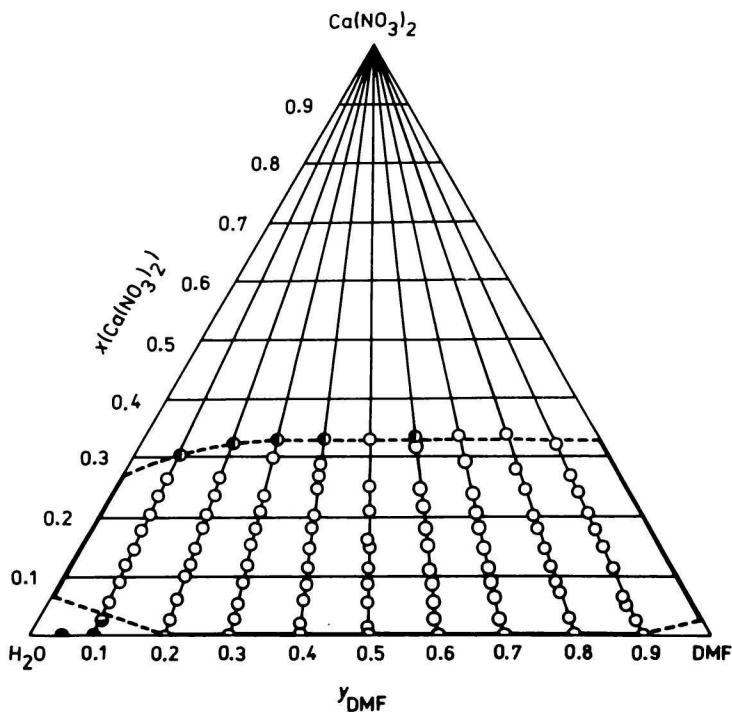


Fig. 2. Glass-forming composition region of the system calcium nitrate—water—dimethylformamide.

The concentration of dimethylformamide in the mixed solvent was expressed by the mole fraction of dimethylformamide y_{DMF} , the concentration of calcium nitrate by the mole fraction of calcium nitrate x .

One of the possible influences of solution composition on nucleation consists in the interaction of the solvated substance with the solvent giving rise to associates or solvates. This interaction can result in a substantial reduction of concentration of crystal-forming particles. This hypothesis could be used for the interpretation of the low-content boundaries of the glass-forming capacity. In the $\text{Ca}(\text{NO}_3)_2$ — H_2O binary system the crystalline ice represents the equilibrium solid phase up to the eutectic composition of 7.7 mole % of $\text{Ca}(\text{NO}_3)_2$. The bonding of water molecules in the ion hydration spheres may result even for a low-content boundary of the glass-forming capacity of the H_2O — $\text{Ca}(\text{NO}_3)_2$ system (6.7 mole % of $\text{Ca}(\text{NO}_3)_2$) in a considerable reduction of the “free” water content, which would limit the nucleation of crystalline ice, as a result of which the solution could be glass-forming.

For the H_2O —DMF binary system no experimental data on phase equilibria have been found in literature. However, it is possible to assume that the

equilibrium solid phase in the region of $y_{\text{DMF}} = 0-0.2$ in the mixed solvent will be represented, once again, by crystalline ice. Raman spectroscopy made it possible to ascertain [14] that an addition of DMF to water results in the fission of hydrogen bonds. In accordance with other authors [15-17] we have come to the conclusion that the DMF molecule creates hydrogen bridges with the H_2O molecule across the carbonyl oxygen and partly also across the nitrogen. However, so far there is no uniform opinion about the stoichiometry of originating associates. Some authors give *e.g.* $\text{DMF} \cdot 2\text{H}_2\text{O}$ [18, 19], other $\text{DMF} \cdot 3\text{H}_2\text{O}$ [20] or $\text{H}_2\text{O} \cdot 2\text{DMF}$ [21]. *Emons et al.* [22] proved by Raman spectrometry the existence of mixed ligand complexes the composition of which depends on DMF content in the mixed solvent. With the assumption of origin of associate of the $\text{DMF} \cdot n\text{H}_2\text{O}$ type, where n may equal 1-6, once again, a considerable reduction of the "free" water content and, consequently, the limitation of crystalline ice nucleation and the limitation of the glass-forming capacity could take place in the case of the 20 mole % of DMF content in the mixed solvent.

In the $\text{Ca}(\text{NO}_3)_2-\text{H}_2\text{O}-\text{DMF}$ ternary system the bond of molecules into the ion hydration spheres and into associates would proceed simultaneously which could explain the gradual reduction of the low-content boundary of the glass-forming capacity in the region of $y_{\text{DMF}} = 0-0.2$.

In the $\text{Ca}(\text{NO}_3)_2-\text{DMF}$ binary system no experimental data on phase equilibria have been found in literature. However, it is possible to assume that in the composition range of 0-2.1 mole % of $\text{Ca}(\text{NO}_3)_2$ the equilibrium phase will be represented by crystalline DMF. The bond of the DMF molecules into the ion solvation spheres could result in a considerable reduction of the "free" DMF content in the case of the low-content boundary of the $\text{Ca}(\text{NO}_3)_2-\text{DMF}$ system. This would limit the nucleation of the DMF crystals and the solution would have the necessary prerequisites for glass-forming.

In the $\text{H}_2\text{O}-\text{DMF}$ binary system it can be also only assumed that in the region of $y_{\text{DMF}} = 0.9-1.0$ the equilibrium solid phase is represented by the crystalline DMF. Under the assumption of the origin of an associate in the mixed solvent a substantial reduction of the content of the "free" DMF molecules could take place, which would reduce the nucleation of crystalline DMF and, consequently, enable glass-forming.

In the $\text{Ca}(\text{NO}_3)_2-\text{H}_2\text{O}-\text{DMF}$ ternary system the bond of DMF into the ion solvation spheres and into the associates would exist simultaneously. This could explain the gradual reduction of the low-content glass-forming boundary in the region of $y_{\text{DMF}} = 0.9-1.0$.

In the $\text{Ca}(\text{NO}_3)_2-\text{H}_2\text{O}$ binary system the existence of two congruently melting compounds, *viz.* $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, was ascertained [23]. For the explanation of glass-forming in the region of up to 25 mole % of $\text{Ca}(\text{NO}_3)_2$, consequently, it is not possible to use the hypothesis about the

influence of the shortage of crystal-forming entities in the solution on the limitation of nucleus forming. For instance, for the melt composition even with 25 mole % of $\text{Ca}(\text{NO}_3)_2$ it must be assumed that the solution will contain the prevailing quantity of crystal-forming entities $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. From the viewpoint of dissociation of congruently melting compounds, however, it is possible to assume that also particles of general composition of $\text{Ca}(\text{NO}_3)_2 \cdot (3 \pm z)\text{H}_2\text{O}$ will originate in the liquid phase, where $z = 1, 2, \text{ and } 3$. In this case it is possible to use for the interpretation of the influence of solution composition on glass-forming the hypothesis of the origin of non-homogeneous, non-crystal-forming clusters [11].

In the $\text{Ca}(\text{NO}_3)_2\text{—H}_2\text{O}$ system the particles of the $\text{Ca}(\text{NO}_3)_2 \cdot (3 \pm z)\text{H}_2\text{O}$ type can play the role of the aforementioned non-crystal-forming entities. Their distribution would depend on a number of hydration equilibria of the type



the equilibrium constants of which have not been experimentally determined so far.

The high-content glass-forming boundary in the $\text{Ca}(\text{NO}_3)_2\text{—H}_2\text{O}$ system, consequently, can be interpreted as follows: in the case of the $\text{Ca}(\text{NO}_3)_2$ concentration in water in excess of 25 mole % of $\text{Ca}(\text{NO}_3)_2$ the frequency of representation of non-crystal-forming particles markedly changes. This may result in homogeneous clustering of crystal-forming particles which form a perfect nucleus, *i.e.* a cluster of crystal-forming particles of critical size with crystal periodicity.

As we have shown in the $\text{Ca}(\text{NO}_3)_2\text{—DMSO—DMF}$ system [11] the hypothesis of non-homogeneous clusters can be used also for the interpretation of low-content boundaries of binary systems and for ternary systems as well. Thus this hypothesis has become so far the only logical explanation of the influence of composition on glass-forming ability which enables the interpretation of even anomalous glass-forming capacity of solvated melts.

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