# Glass-forming ability and glass transition temperatures of some systems salt—methyl alcohol

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The glass transition temperature of ammonium nitrate, silver nitrate, lithium nitrate, lithium chloride, calcium chloride, and zinc chloride in methanol has been studied as a function of composition. Except ammonium nitrate—methanol and silver nitrate—methanol, all the above systems are glass-forming, but only over limited composition ranges. The glass-forming composition limits for these systems have been compared with those for solutions of the same salts in water, dimethyl sulfoxide, dimethylformamide, and dimethylacetamide. The glass-forming ability has been interpreted in terms of the formation of inhomogeneous clusters.

Изучена зависимость температур остеклевания нитрата аммония, нитрата серебра, нитрата лития, хлорида лития, хлорида кальция и хлорида цинка в метиловом спирте от состава. За исключением нитратов аммония и серебра, все остальные системы были в метаноле стеклообразующими, правда, в области, ограниченной по составу. Составные пределы стеклообразования растворов этих солей в метаноле были сопоставлены с подобными пределами в воде, диметилсульфоксиде, диметилформамиде и диметилацетамиде. Способность к стеклообразованию объясняется с позиции гипотезы об образовании негомогенных кластеров.

A number of studies have been concerned with the glass-forming ability of solutions of some salts in various solvents, namely of lithium nitrate, lithium chloride, ammonium nitrate, silver nitrate, calcium chloride, and zinc chloride in dimethyl sulfoxide (DMSO) [1], dimethylformamide (DMF) [2], dimethyl-acetamide (DMA) [3], and water [4]. It has been found that the glass-forming composition range differs considerably from one system to another. For example, silver nitrate in DMSO is glass-forming over the range 20—40 mole % of salt, while in DMF the glass-forming composition range extends from 2 to 35 mole % of AgNO<sub>3</sub>. For lithium nitrate, the glass-forming ability has been

observed over the range 8–-40 mole % LiNO<sub>3</sub> in DMA and only 25–31 mole % LiNO<sub>3</sub> in DMSO.

In order to interpret the glass-forming ability of salt solutions in nonaqueous solvents, a hypothesis of inhomogeneous cluster formation has been advanced [2, 3], which is based on the following assumptions. Crystallization of the solid phase at the liquidus temperature requires the formation of the so-called critical nuclei, *i.e.* sufficiently large clusters of crystallizing entities with a long-range periodical ordering corresponding to the structure of the nascent crystal. If cooling of the solution in the vicinity of the liquidus temperature does result in the formation of large clusters which, however, do not have a long-range periodical ordering, crystal nuclei will not be formed.

Inhomogeneous clusters in solutions of some salts probably form as a result of incorporation of non-crystal-forming entities into clusters of crystallizing particles. A sufficiently large cluster cannot alone serve as a crystal nucleus. If the incorporation becomes so extensive that not a single homogeneous crystal--forming cluster of the equilibrium primary crystallizing phase remains below the liquidus temperature, the solution is capable of undercooling, persisting as a liquid in a metastable undercooled state. Crystallization cannot occur until the incorporated species is removed, probably by diffusion, and at least one cluster attains the crystal structure of the equilibrium solid phase. Experimentally, the time for this to occur is the so-called induction period of crystallization or nucleation. This period depends not only on the undercooling, but also on the solution composition. Besides the crystallizing entities, the solution must also contain other species capable of being incorporated in the homogeneous clusters. In concentrated salt solutions, the most likely non-crystal-forming entities are ions solvated by solvent molecules in a number different from that involved in the coexisting solid phase. On this basis it is possible to interpret both the solvent-rich and salt-rich glass-forming composition limits.

The glass-forming ability is especially pronounced in systems involving several solvates with various numbers of solvent molecules. The phase diagram of such a system shows the existence of several congruently and/or incongruently melting compounds. A large number of crystalline solvates are known to exist in concentrated solutions of salts in methyl alcohol. Attention has therefore been focused on the glass-forming ability of these systems.

The aim of this work was to determine the glass-forming composition ranges for solutions of some salts in methyl alcohol, to compare the ranges with those for the same salts in other solvents, and to measure the dependence of the glass transition temperature of glass-forming solutions on the solution composition.

#### Experimental

#### Chemicals

Methyl alcohol of anal. grade (Lachema, Brno) was used as received. The other chemicals, sample preparation, and analytical methods used to check the salt content of samples were the same as described previously [5].

## Procedure

The glass transition temperature was determined by low-temperature differential thermal analysis. The apparatus and procedure have been described previously [5].

Experimental evidence for the existence of crystalline solvates as an equilibrium solid phase in glass-forming solutions was obtained by precipitating the solid phase from solutions undercooled for a long time and by comparing the crystals with those of the anhydrous salt under a microscope.

## **Results and discussion**

#### Glass transition temperatures

The experimentally obtained glass transition temperatures of solutions of chosen salts are summarized in Table 1. The variation in the glass transition temperature with the mole fraction of salt in methanol is different for different systems (Figs. 1 and 2). The data for calcium chloride, for example, can be fitted, as a first approximation, to a linear equation. Extrapolation to zero concentration yields a glass transition temperature for methanol by about 10 K lower than that reported by *Lesikar* (104 K) [6].

The plots of the glass transition temperature as a function of salt content for the systems lithium nitrate—methanol and lithium chloride—methanol are concave with respect to the x axis. For the system zinc chloride—methanol, the plot has a well-defined S-shape. The glass transition temperatures found for the salt solutions in methanol are the lowest of all values observed for systems so far studied by us.

## Glass-forming composition range

The glass-forming composition ranges of the above systems are bounded by the lowest and highest salt contents of solutions at which glass is formed on

#### Table 1

x	$T_{g}/K$	X	$T_{ m g}/ m K$
NH <sub>4</sub> NO <sub>3</sub> CH <sub>3</sub> OH	less soluble	le ZnCl <sub>3</sub> CH <sub>3</sub> OH	
	non-glass-forming		
		0.0205	106.4
		0.0263	107.1
AgNO <sub>3</sub> CH <sub>3</sub> OH	non-glass-forming	0.0508	111.5
		0.1011	124.1
LiNO <sub>3</sub> —CH <sub>3</sub> OH		0.1018	126.4
		0.1519	146.8
0.0354	108.1	0.2013	178.0
0.0544	108.6	0.2024	174.1
0.0851	110.1	0.2037	177.8
0.1004	113.7	0.2376	192.6
0.1589	122.1	0.2958	207.3
0.1928	131.5	0.3400	215.9
0.2106	135.4	0.3400	216.6
0.2524	144.4	0.3482	216.9
0.2668	149.3	0.4562	228.5
LICI-CH.OH		0.4930	233.1
2101 011,011		CaCl <sub>2</sub> CH <sub>2</sub> OH	
0.0477	107.1		
0.0862	112.0	0.0138	102.4
0.1188	118.1	0.0139	110.3
0.1411	125.7	0.0208	106.6
0.2097	156.8	0.0391	121.2
0.2249	159.5	0.0448	130.4
0.2302	160.4	0.0472	129.9
0.2323	161.6	0.0545	129.2
0.2353	160.2	0.0729	141.1
0.2399	162.1	0.0770	145.7
		0.0839	146.8
		0.0888	149.0
		0.0986	158.5
		0.1016	155.5
		0.1022	160.8
		0.1083	161.4

Dependence of the glass transition temperature  $T_g$  on the mole fraction of salt in the solution

quenching. The limits depend on the mode of cooling: the range becomes somewhat narrower as the rate of cooling is decreased.

Experimentally determined values of these limits are listed in Table 2, along with values for solutions of the salts in water, DMSO, DMF, and DMA.

As seen from the table, ammonium nitrate solutions in methanol and water

are not glass-forming. The solubility of ammonium nitrate in methanol is very low. Homogeneous solutions with a maximum of 6 mole % of salt could be prepared, but no glass was obtained on quenching them. The phase diagram for ammonium nitrate in methanol is not available so that the system cannot be discussed any further.



*Fig. 1.* Dependence of the glass transition temperature  $(T_g/K)$  on the mole fraction of salt x in the system: *1.* LiNO<sub>3</sub>—CH<sub>3</sub>OH; *2.* CaCl<sub>2</sub>—CH<sub>3</sub>OH; *3.* LiCl—CH<sub>3</sub>OH.



Fig. 2. Dependence of the glass transition temperature  $(T_g/K)$  on the mole fraction of salt x in the system  $ZnCl_2$ —CH<sub>3</sub>OH.

No solvates are known to exist in aqueous solutions and hence, if glass formation is critically dependent on the existence of solvates, then ammonium nitrate in aqueous solutions cannot prevent ice nucleation.

The glass-forming ability observed for ammonium nitrate in nonaqueous solvents (DMSO, DMF, and DMA) seems very likely to be associated with solvate formation [2, 3].

#### Table 2

Salt	Water [4]	DMSO [1]	DMF [2]	DMA [3]	CH <sub>3</sub> OH
NH <sub>4</sub> NO <sub>3</sub>	non-glass-forming	20-49	6—42	8—40	non-glass-forming
AgNO <sub>3</sub>	non-glass-forming	20-40	2—35	1236	less soluble
LiNO <sub>3</sub>	10-13	25-31	1740	840	4—27
LiCl	9—27	12-22	1—10, 14—30	7—31	5—14, 21—24
ZnCl <sub>2</sub>	640	14—28	7—32	7—23	2—49

Glass-forming composition range of some salt solutions in water, DMSO, DMF, DMA, and  $CH_3OH$  in mole % of the salts

Both water and methanol belong to the same class of protonic solvents. If there is some similarity within the class as regards the phase equilibria, it is possible that no methanolates are formed in the system ammonium nitrate— —methanol [7].

The solubility of silver nitrate in methanol is very low — about 0.6 mole % at 50 °C. A homogeneous solution obtained at this temperature did not form glass when immersed in liquid nitrogen. The phase diagram of the system exhibits no congruently or incongruently melting crystallosolvates [8]. No glass formation has been observed in water, either. The system water—silver nitrate has a simple phase diagram with a single eutectic, thus no hydrates are involved [8]. All the other silver nitrate—nonaqueous solvent systems studied form glasses, and for all of them the existence of solvates has been demonstrated [2, 3, 9]. Thus ammonium nitrate and silver nitrate behave similarly in solutions with water and methanol.

Lithium nitrate in methanol has a fairly wide glass-forming range from 4 to 27 mole % LiNO<sub>3</sub>, whereas in water the range is very narrow, from 10 to 13 mole % LiNO<sub>3</sub>. The substantially lower limit at the methanol-rich end of the range is probably associated with the lower melting point of the solvent  $(-97.5 \,^{\circ}\text{C} \text{ compared with } 0 \,^{\circ}\text{C} \text{ for water})$ . The phase diagram for the system LiNO<sub>3</sub>—CH<sub>3</sub>OH is not available.

Lithium chloride in methanol solutions has two glass-forming composition ranges: at 8—14 mole % LiCl and 21—24 mole % LiCl. A study of phase equilibria in the system LiCl—CH<sub>3</sub>OH established the existence of a single solvate with three methanol molecules at 25 mole % LiCl [8]. In terms of the hypothesis of inhomogeneous cluster formation, the glass-forming ability of this system may be explained by assuming that a non-crystal-forming solvated particle formed on addition of the salt to the solvent disrupts a homogeneous cluster of the solvent, thus preventing the crystallization. At mole fraction of lithium chloride higher than 24%, the equilibrium solid phase consists of lithium chloride. In this region, there is a higher probability that only homogeneous clusters will be formed, and the ability of the solutions to form glass vanishes.

No explanation has yet been found for the existence of two glass-forming composition ranges. It is interesting to note that the same phenomenon has been observed for solutions of lithium chloride in dimethylformamide. In aqueous solution, even a wide variety of lithium chloride crystallohydrates have been shown to exist. In this case, there is but one glass-forming composition range, but it is wider than that for methanolic solutions. Lithium chloride also forms glasses in DMSO, DMF, and DMA, where monosolvates, plus a hexasolvate for DMSO, have been shown to exist. At low LiCl mole fractions, the glassforming composition limit in aqueous solutions as well as in nonaqueous solvents is higher than that for methanolic solutions, this being again in accord with the magnitudes of the melting points of the solvents.

Calcium chloride in methanol solutions has a glass-forming composition range from 1 to 11 mole %  $CaCl_2$ . This range is wider than that found for aqueous and dimethylformamide solutions. A study of the solubility of calcium chloride in methanol revealed the existence of two types of solvate,  $CaCl_2$ · 4CH<sub>3</sub>OH up to 12.24 mole %  $CaCl_2$ , and  $CaCl_2$  3CH<sub>3</sub>OH above 12.24 mole %  $CaCl_2$ . At 12.24 mole %  $CaCl_2$ , both the solvates can occur together [8]. Thus the glass formation in this system may again be explained in terms of inhomogeneous cluster formation.

The glass-forming composition limit at the methanol-rich end of the range is the lowest of all the calcium chloride—solvent systems studied, once again in accord with the low melting point of methanol.

The glass-forming composition range for zinc chloride in methanol extends from 2 to 49 mole %  $ZnCl_2$ . This is the widest range we have so far found for a binary system. Second to it is the glass-forming composition range for aqueous solutions of zinc chloride. Apart from DMSO, the glass-forming composition limits at low mole fractions of  $ZnCl_2$  for all the solvents studied are comparable (CH<sub>3</sub>OH — 2 mole %, H<sub>2</sub>O — 6 mole %, DMF — 7 mole %, DMA — 7 mole % ZnCl<sub>2</sub>), but it is interesting to note that the highest glass-forming composition limits for the salt-rich end of the range have been found for solutions in methanol (49 mole % ZnCl<sub>2</sub>) and water (40 mole % ZnCl<sub>2</sub>).

The phase diagram for the system  $ZnCl_2$ — $CH_3OH$  is not available, but our study of phase equilibria has indicated that there are at least two types of solvate, probably an incongruently melting trimethanolate and a congruently melting monosolvate, with a methanol—trimethanolate eutectic at about 10 mole %  $ZnCl_2$ . Thus, as with most systems studied so far, the glass-forming composition range occurs near the eutectic point. The eutectic is found at a relatively high salt content, but the glass-forming composition limit for the methanol-rich end of the range is low (2 mole %), as could be expected on the basis of the low melting point of the solvent. Within the context of the hypothesis of inhomogeneous cluster formation, this would imply that inhomogeneities caused by the zinc chloride trimethanolate in the range  $x(\text{ZnCl}_2) = 0.02-0.1$  hinder the nucleation of methanol. In the range 10-49 mole %, the glass-forming ability is more likely due to inhomogeneous clusters of zinc chloride monomethanolate. Above this region, pure zinc chloride probably crystallizes. The phase diagram of the system  $\text{ZnCl}_2-\text{H}_2\text{O}$  shows the formation of three hydrates. If there is a similarity in the behaviour of aqueous and methanolic solutions, then the existence of the above solvates in methanol seems to be quite probable. Crystalline solvates have been found in other nonaqueous solutions of zinc chloride [2, 3].

It may be concluded from this discussion that even for methanolic solutions of salts there is evidence to support the hypothesis of inhomogeneous cluster formation as an interpretation of the glass-forming ability of solutions of inorganic compounds in molecular solvents.

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