Glass-forming ability and glass transition temperatures of some salt—dimethylacetamide systems

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Glass transition temperatures of the solutions of ammonium nitrate, silver nitrate, lithium nitrate, lithium chloride, and zinc chloride in dimethylacetamide were determined as a function of salt concentration. All solutions were glass-forming in limited composition regions. Glass-forming composition limits of the solutions of these salts in dimethylacetamide have been compared with those in water, dimethyl sulfoxide, and dimethylformamide. The glass-forming ability has been interpreted in terms of the inhomogeneous cluster formation hypothesis.

Определены температуры застеклевания растворов нитрата аммония, нитрата серебра, нитрата лития, хлорида лития и хлорида цинка в диметилацетамиде в зависимости от концентрации соли. Все растворы застеклевывались в ограниченном интервале по составу. Границы по составу застеклевания растворов этих солей в диметилацетамиде были сопоставлены с соответствующими показателями для растворов в воде, диметилсульфоксиде и диметилформамиде. Способность к застеклеванию обсуждается с точки зрения гипотезы образования негомогенного кластера.

Our previous works investigated the glass-forming ability of some salt—nonaqueous solvent systems. Their number included, on the one hand, the salt—dimethyl sulfoxide systems [1], on the other hand the salt—dimethylformamide systems [2]. The solutions of some salts in these solvents in certain composition regions were not only supercoolable, but also glass-forming. The glass-forming composition region, however, was mostly diverse not only in the comparisons of the glass-forming ability of the individual salts in dimethyl sulfoxide and dimethylformamide solutions, but also in comparison with the glass-forming composition region of aqueous solutions of these salts [3—6].

In our study of the glass-forming ability of the salt—dimethylformamide systems [2] a hypothesis was proposed which could explain generally the glass-forming ability of concentrated electrolyte solutions. The hypothesis is based on the assumption of origin of inhomogeneous clusters in the liquidus range. In contradistinction to homogeneous clusters of crystal-forming particles, which form the nucleus of a crystal at the equilibrium temperature of the liquidus, these inhomogeneous clusters of crystal-forming and non-crystal-forming particles cannot become nuclei of an equilibrium crystal. If we add salt to a non-glass-forming solution, and only inhomogeneous clusters originate in the solution, the crystals cannot originate even below the liquidus temperature and the system appears as supercoolable and glass-forming. However, further increase of the mole fraction of salt may result in the origin of also a homogeneous equilibrium crystal cluster in the solution, *e.g.* of a crystalline solvate. In this way the process of normal nucleation can originate and the solution with a higher x value ceases to be glass-forming. In this way it is possible to explain logically the occurrence of the limit of high and low mole fraction values of glass-forming ability in electrolyte solutions. Unfortunately, however, the prediction of the limits of glass-forming composition is not possible, as so far we have little experimental information about the glass-forming ability of nonaqueous electrolyte solutions. For this reason, it is necessary to obtain further data on the glass-forming ability of salt—nonaqueous solvent systems in order that the hypothesis of the origin of inhomogeneous clusters may be further specified.

For this study we have selected the salt—dimethylacetamide system. Similarly as dimethyl sulfoxide and dimethylformamide, dimethylacetamide is an aprotic dipolar solvent. Its melting point (253 K), however, lies between the melting point of dimethyl sulfoxide (292 K) and that of dimethylformamide (212 K).

The purpose of this study was the determination of the composition limits of the glass-forming ability of the solutions of the previously investigated salts in dimethylacetamide and the determination of the glass transition temperatures of these glass-forming solutions.

Experimental

Chemicals

Dimethylacetamide (DMA) of anal. grade was the preparation of Merck. All other chemicals and the sample preparation were analogous with those used in the work [2].

Procedure

The glass transition temperature was determined by the low-temperature differential thermal analysis. The description of the method and of experimental equipment is given in paper [7].

Orientation experiments proving the existence of crystalline solvates as an equilibrium solid phase in glass-forming solutions were made by the separation of the solid phase from long-term supercooled solutions and microscopic comparisons of these crystals with the crystals of anhydrous salt.

Results and discussion

Glass transition temperatures

The results of the dependence of the glass transition temperature T_g on the mole fraction of the salt (x = mole fraction of salt in the solution) are shown in Figs. 1—5. Some differences of the individual salts are obvious at first sight. Some relations can be considered approximately linear (NH_4NO_3, $AgNO_3$, $ZnCl_2$), while a distinct curvature convex to the axis x can be observed in others ($LiNO_3$, LiCl).

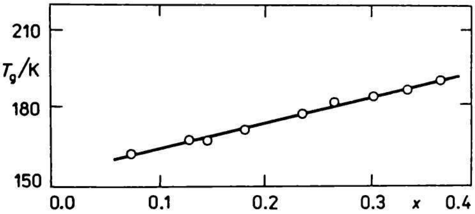

Fig. 1. The dependence of the glass transition temperature (T_g) on the mole fraction of the salt (x) in the NH_4NO_3—DMA system.

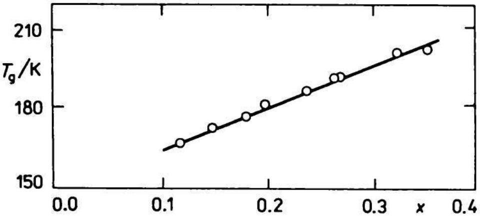

Fig. 2. The dependence of the glass transition temperature (T_g) on the mole fraction of the salt (x) in the $AgNO_3$—DMA system.

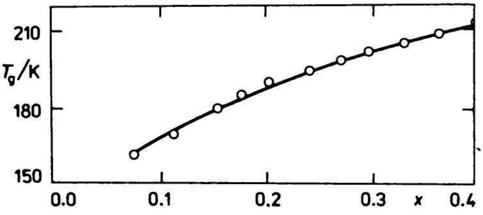

Fig. 3. The dependence of the glass transition temperature (T_g) on the mole fraction of the salt (x) in the $LiNO_3$—DMA system.

In the case of the linear dependence of the glass transition temperature on the mole fraction of the salt the values of the glass transition temperature extrapolated beyond the zero value of the salt mole fraction are within the limits of 143—154 K. This is in good agreement with the glass transition temperature of the dimethylacetamide solution equal to 150 K [5].

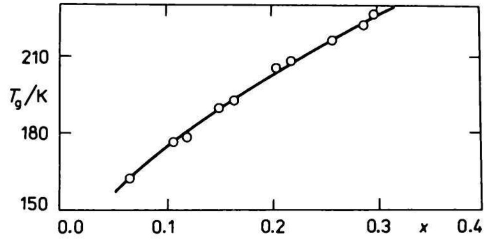

Fig. 4. The dependence of the glass transition temperature (T_g) on the mole fraction of the salt (x) in the LiCl—DMA system.

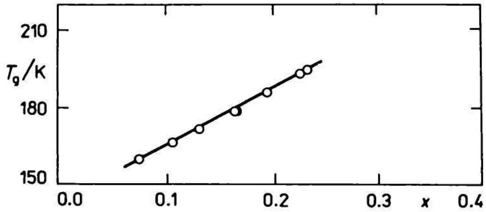

Fig. 5. The dependence of the glass transition temperature (T_g) on the mole fraction of the salt (x) in the $ZnCl_2$—DMA system.

Glass-forming regions

The solvent-rich and salt-rich glass-forming composition limits of the solutions of some salts are given in Table 1. For comparison the table includes also the glass-forming limits of the solutions of the studied salts in water, dimethyl sulfoxide, and dimethylformamide, taken over from earlier studies [1, 2, 4].

The table shows that NH_4NO_3 and $AgNO_3$ do not form glass-forming solutions in water. Both systems form only one eutectic and no congruently or incongruently melting hydrates have been ascertained in either system. In these systems of lower mole fractions of salt than those corresponding with eutectic composition the salt cannot prevent ice nucleation. On the other hand, in the case of higher mole fractions of salt than those corresponding with eutectic composition the water molecules cannot incorporate into the salt clusters to such an extent that could prevent the formation of the crystalline nucleus of salt.

Table 1

Glass-forming composition region of some salt solutions in water, DMSO, DMF, and DMA

Salt	x(salt)/%			
	Water[a]	DMSO[b]	DMF[c]	DMA
NH_4NO_3	no glass	20—49	6—42	8—40
$AgNO_3$	no glass	20—40	2—35	12—36
$LiNO_3$	10—13	25—31	17—40	8—40
LiCl	9—27	12—22	1—10	7—31
	—	—	14—30	—
$ZnCl_2$	6—40	14—28	7—32	7—23

a) Values from Ref. [4]; *b*) values from [1]; *c*) values from [2].

In dimethyl sulfoxide, dimethylformamide, and dimethylacetamide, on the other hand, both the ammonium nitrate and the silver nitrate form glass-forming solutions even in a rather wide range of solution compositions.

The study of phase equilibria in the NH_4NO_3—DMSO and $AgNO_3$—DMSO systems determined the formation of incongruently melting solvates of a composition of $NH_4NO_3 \cdot n$DMSO with $n = 1, 2$ for $x(NH_4NO_3) = 45\ \%$ [8], and of the congruently melting solvate $AgNO_3 \cdot$ DMSO for $x(AgNO_3) = 50\ \%$ [9].

With reference to the hypothesis of the formation of inhomogeneous clusters it would mean that the solvate originated within the limits of $x(NH_4NO_3) = 20—29\ \%$ and of $x(AgNO_3) = 20—25\ \%$ can form a part of the dimethyl sulfoxide cluster to such an extent that the originating inhomogeneous cluster cannot become the nucleus of a dimethyl sulfoxide crystal. For higher mole fractions of salts it is possible to assume that the dimethyl sulfoxide molecules are contained in the solvates of salts and thus prevent the nucleation of the solvate. Only a richer salt content in the solution than the upper glass-forming limit increases the probability of the formation of at least one homogeneous cluster of the given solvate which can become a nucleus of the solvate crystal.

According to Table 1 all other studied systems are glass-forming in a narrower or wider solution composition region.

The phase diagram of the lithium nitrate in aqueous solution points to the formation of a congruently melting hydrate of $LiNO_3 \cdot 3H_2O$ and an eutectic at $x(LiNO_3) = 7.8\ \%$. The glass-forming ability, consequently, could be interpreted in terms of the significant content of water molecules in $LiNO_3 \cdot 3H_2O$ clusters. These inhomogeneous clusters could not become crystalline nuclei of the crystallohydrate of $NiNO_3 \cdot 3H_2O$. An increase of the mole ratio of $LiNO_3 \cdot 3H_2O$ for $x(LiNO_3) = 13\ \%$ could explain the higher probability of formation of merely the homogeneous cluster of $LiNO_3 \cdot 3H_2O$ particles, which could become a nucleus of the $LiNO_3 \cdot 3H_2O$ crystals.

In the $LiNO_3$—DMSO systems the study of phase equilibria has revealed the formation of the congruently melting $LiNO_3 \cdot 3DMSO$ [10]. This case is interesting, as the glass-forming region lies within the range of higher values of x of salts than those corresponding with the composition of a crystalline solvate. In the salt—water systems the glass-forming ability begins to manifest itself as a rule in the region of the solvent—solvate eutectic [3, 4]. The $LiNO_3$—DMSO system has this eutectic composition at $x(LiNO_3) = 14.5\,\%$ [10]. In this range, however, the glass-forming ability has not been ascertained. With reference to the hypothesis of inhomogeneous cluster formation, consequently, the $LiNO_3 \cdot 3DMSO$ particles cannot prevent the DMSO nucleation and the DMSO molecules have no significant influence on the nucleation of crystalline $LiNO_3 \cdot 3DMSO$. In the composition region of $x(LiNO_3) = 25\,\%$ the existence of crystalline $LiNO_3$ as an equilibrium solid phase is assumed. In spite of that, however, the solutions within the ranges of $x(LiNO_3) = 25$—$31\,\%$ are glass-forming. Therefore, it is necessary to assume that the $LiNO_3 \cdot 3DMSO$ particles are contained in a significant extent in the $LiNO_3$ cluster, so that the $LiNO_3$ cluster cannot become a nucleus of the $LiNO_3$ crystal.

The phase diagram of the LiCl—water system points to the origin of a whole number of incongruently melting hydrates of the $LiCl \cdot nH_2O$ type, where $n = 1, 3, 4, 5$. The study of the equilibrium of the LiCl—DMSO system has shown that in the solutions of a higher value of x the equilibrium solid phase consists in the crystalline monosolvate of $LiCl \cdot DMSO$ [11]; apart from that also the possibility of formation of the congruently melting hexasolvate of $LiCl \cdot 6DMSO$ was ascertained [11].

The lithium chloride has the peculiar quality of forming two glass-forming regions in the DMSO solution.

The phase diagram of the $ZnCl_2$—water system points to the formation of incongruently melting hydrates of $ZnCl_2 \cdot nH_2O$, where $n = 4$, 3, 2.5, 1.5, and 1. It is interesting that the eutectic of H_2O—$ZnCl_2 \cdot 4H_2O$ is situated near the rather high values of the mole fraction $x(ZnCl_2) = 12\,\%$. With reference to the hypothesis of inhomogeneous cluster formation it would mean that within the range of $x(ZnCl_2) = 6$—$12\,\%$ the inhomogeneities caused by the $ZnCl_2$ hydrates prevent the nucleation of crystalline ice. Within the range of $x(ZnCl_2) = 12$—$40\,\%$ the glass-forming ability can be explained by the inhomogeneous clusters of water and various hydrates.

The study of phase equilibria in the $ZnCl_2$—DMSO system proved the existence of the $ZnCl_2 \cdot 2DMSO$ solvate [11]. The existence of the glass-forming region, consequently, can be explained by the possibility of formation of inhomogeneous clusters of various solvates.

The phase diagrams of the solutions of NH_4NO_3, $AgNO_3$, $LiNO_3$, LiCl, and $ZnCl_2$ in dimethylformamide and/or dimethylacetamide have not been published yet. Informative experiments have revealed, however, that these systems form solvates.

The afore mentioned data, consequently, are in agreement with the assumption that only those salt-molecular solvent systems are glass-forming in which congruently or incongruently melting solvates originate. The mutual relation between the glass-forming ability and solvation of the salt in the given solvent, therefore, seems highly probable.

In conclusion it is possible to state that the hypothesis of the inhomogeneous cluster formation and prevention of formation of homogeneous nuclei of the crystalline phase has proved well so far for all the studied glass-forming systems. It has been ascertained that the existence of the solvate in the glass-forming systems exerts a probable influence on the possibility of the glass-forming ability. As for the possibility of formation of inhomogeneous clusters, the existence of various solvates is favourable for this formation. These facts, consequently, support the adequacy of application of the proposed hypothesis for a more general explanation of the glass-forming ability of electrolyte solutions.

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