GLASS TRANSITION TEMPERATURES AND GLASS-FORMING REGION OF THE SYSTEM LITHIUM CHLORIDE– –DIMETHYL SULPHOXIDE–WATER

Jarmila MALÁ and Ivo SLÁMA

Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 160 00 Prague 6

Glass transition temperatures (Tg) of the system LiCl–DMSO–H$_2$O have been measured. A small addition of DMSO to the binary aqueous system removes its unusual variation of Tg with salt concentration. The concentration dependence of Tg of the ternary system at a constant composition of the mixed solvent can be described by a linear equation. The variation in Tg with the mixed solvent composition at constant LiCl concentration follows a complicated pattern which cannot be described by commonly used relations. The boundaries of glass-forming region are discussed in terms of the effect of a change in solution composition on the induction period of equilibrium solid phase nucleation.

Angell and Sare[1,2] have examined the glass-forming ability of aqueous solutions of a number of inorganic salts. They found that within certain concentration ranges many common inorganic salts can form glasses if the solutions are cooled by a standard method, *i.e.* by immersing a small sample in liquid nitrogen. Glass-forming regions of these systems differ in extent, covering concentration ranges from a few to tens mole per cent. Angell and Sare have also determined glass transition temperatures (Tg) of the systems and their dependence on salt concentration by means of low-temperature differential thermal analysis. With the exception of the system lithium chloride–water, they found Tg to show a steady increase with increasing salt concentration. In another study[3], similar behaviour was observed for calcium nitrate in other, non-aqueous solvents.

Supercooling ability, glass-forming ability and glass transition temperatures have also been reported for other types of liquid, such as polymers of organic liquids and melts of metal as well as non-metal compounds[4-7]. New data on the limits of glass-forming ability and on concentration dependences of glass transition temperatures of salt solutions are useful information for interpreting the structure of ionic liquids.

The aim of this work was to determine the glass-forming region and the concentration dependence of glass transition temperature for the system lithium chloride–dimethyl sulphoxide–water. Previous results for the system lithium chloride–di-

methyl sulphoxide[8] showed that the glass-forming concentration range of this system was different from that for lithium chloride in water and that there was a fundamental difference in the concentration dependence of Tg for the two systems. As ternary systems salt–DMSO–water had been found to exhibit some interesting features in both the glass-forming region and the concentration dependence of Tg[9-11], it was of interest to investigate how these properties would vary with gradual replacement of water by DMSO in the mixed solvent.

EXPERIMENTAL

Chemicals

Lithium chloride of analytical grade (Merck) was dehydrated by heating in a vacuum oven. Dimethyl sulphoxide of analytical grade (Merck) was used without any further purification or drying, because it had been established that neither traces of moisture nor trace elements had any observable effect on the properties studied.

Procedure

Lithium chloride content of the samples was checked by argentometric titration. Sample preparation and the method of determining Tg have been described previously[12].

RESULTS AND DISCUSSION

Results from determination of Tg as a function of lithium chloride concentration in solution $(x = $ mole fraction of LiCl$)$ for various compositions of the mixed solvent $(y_{DMSO} = n_{DMSO}/(n_{DMSO} + n_{H2O}))$ are presented in Table I. The figures under $y_{DMSO} = 0.00$ give selected Tg values[1] for the system LiCl–H_2O with mole fractions of LiCl identical or close to those used at $y_{DMSO} = 0.05$. Regression analysis has established that the data for the glass transition temperature as a function of the salt concentration for all solutions containing DMSO may be represented by the linear equation

$$Tg = A + Bx, \qquad (1)$$

whose parameters A and B remain constant for a constant composition of the mixed solvent. The values of the parameters for various y_{DMSO} values are listed in Table II.

Fig. 1 contains a comparison between the concentration dependences of Tg at $y_{DMSO} = 0.00$ and $y_{DMSO} = 0.05$. While the glass transition temperature of DMSO--containing solutions increases linearly with lithium chloride content, the variation for the aqueous solutions is as follows. Up to 15 mol % LiCl, the glass transition temperature remains virtually constant, showing no difference from Tg of water[1]. Only above 15 mol % does the addition of LiCl start producing an increase in the

Glass transition temperature Tg (K) as a function of lithium chloride concentration x at various y_{DMSO}

x	Tg	x	Tg	x	Tg	x	Tg
$y_{DMSO} = 0.00$		$y_{DMSO} = 0.05$		$y_{DMSO} = 0.1$		$y_{DMSO} = 0.2$	
0·0909	138·5	0·0957	138·7	0·0596	140·8	0·0000	138·9
0·1176	139·0	0·1169	144·3	0·0884	144·0	0·0307	141·4
0·1429	140·0	0·1493	148·6	0·1160	145·8	0·0599	146·6
0·1724	142·5	0·1761	151·8	0·1460	150·7	0·0880	151·4
0·1754	143·0	0·2062	153·7	0·1747	155·7	0·1163	158·3
0·2041	148·0	0·2330	156·9	0·2298	166·0	0·1449	163·7
0·2083	150·0	0·2626	162·1	0·2599	171·1	0·1700	167·9
0·2353	160·0	0·2926	166·5	0·2901	179·1	0·1963	172·3
0·2326	157·5			0·2916	162·2	0·2265	178·7
0·2596	164·0	$y_{DMSO} = 0.4$		0·2920	179·3	0·2519	181·5
0·2667	165·0			0·2920	180·0	0·3496	195·3
		0·0000	142·1				
$y_{DMSO} = 0.3$		0·0311	148·1				
		0·0590	157·4	$y_{DMSO} = 0.5$		$y_{DMSO} = 0.6$	
0·0000	140·6	0·0882	165·2	0·0000	143·0	0·0632	157·5
0·0297	145·3	0·1173	176·1	0·0309	149·0	0·0901	165·5
0·0631	154·1	0·1479	185·2	0·0592	157·2	0·1176	174·1
0·0937	163·6	0·1748	190·7	0·0809	165·5	0·1485	184·8
0·1146	168·5	0·1757	191·4	0·1174	170·7	0·1765	193·9
0·1451	178·1	0·2032	202·2	0·1457	182·2	0·2062	207·2
0·1744	188·9	0·2050	204·8	0·1797	197·4	0·2391	213·2
0·2023	194·6	0·2335	211·2	0·2093	207·6	0·2720	226·8
0·2309	201·9	0·2660	220·3	0·2344	209·0		
		0·3045	228·2	0·2640	215·3		
$y_{DMSO} = 0.7$		$y_{DMSO} = 0.8$		$y_{DMSO} = 0.9$			
0·0885	162·2						
0·1202	175·0	0·0929	168·2	0·1210	176·7		
0·1503	191·2	0·1193	178·6	0·1525	189·8		
0·1708	197·0	0·1499	185·2	0·1829	197·5		
0·2082	206·8	0·1816	196·0	0·2106	204·4		
0·2439	218·9	0·2111	205·4	0·2398	213·7		
		0·2378	213·1				
		0·2601	219·2				

glass transition temperature. Consequently, the greatest difference between glass transition temperaturss of aqueous and DMSO-containing solutions is observed at 15 mol %. At present, we have no explanation for these differences. Comparison with other systems shows the variation in Tg of LiCl–H_2O solutions to be completely atypical[1−3].

The concentration dependence of glass transition temperature for mixtures of some polymers, for inorganic oxides and for isomeric alcohol + water mixtures can be

TABLE II

Best-fit parameters A and B of Eq. (*1*), number of experimental points (m), mean relative deviation of Tg in % (δ), and glass transition temperature of the mixed solvent (Tg_m)

y_{DMSO}	A	B	m	δ	Tg_m
0·05	127·3	131·1	8	0·69	
0·1	127·3	174·0	11	1·01	
0·2	135·9	185·9	9	0·38	139·9
0·3	136·7	285·0	9	0·36	140·6
0·4	139·8	301·3	13	0·70	142·1
0·5	139·0	302·6	9	1·15	143·0
0·6	135·7	332·8	8	0·52	
0·7	132·5	359·2	6	0·85	
0·8	140·9	302·8	7	0·37	
0·9	142·0	300·0	5	0·57	
1·0	149·3	273·3	13	0·30	
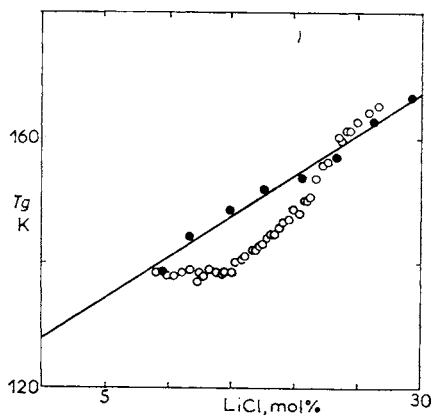
FIG. 1

Comparison of the variations in Tg with LiCl concentration (mol %) at $y_{DMSO} = 0{\cdot}00$ (○) and $y_{DMSO} = 0{\cdot}05$ (●)

described by the relation

$$Tg = Tg_1(1 - x) + Tg_2 x + kx(1 - x), \qquad (2)$$

where Tg_1 and Tg_2 are the glass transition temperatures of the components, and k is an adjustable parameter. Another relation that has been successfully applied to describe the concentration dependence of Tg for mixtures is of the form

$$Tg = [xTg_1 + C(1 - x) Tg_2]/[x + C(1 - x)], \qquad (3)$$

where C usually represents an adjustable parameter[5].

Glass transition temperatures of solvent–salt systems exhibit, however, certain specific features that preclude the use of the above relations. One might think of converting Eq. (2) to the form

$$Tg = Tg_1 + Bx - kx^2, \qquad (4)$$

where $B = k + Tg_2 - Tg_1$, which for $k = 0$ would predict a linear dependence of Tg on the mole fraction of salt. In solvent–salt systems it is, however, usually impossible to determine experimentally the glass transition temperature of solvent, and so the above proposal cannot be verified.

Another difficulty is in determining experimentally glass transition temperatures of anhydrous salts, for these substances usually do not form glasses. The third specific feature of salt solutions is that the glass-forming ability is found only within limited concentration ranges. Therefore, it is not justifiable to use large extrapolations to verify the above relations.

The variation in the glass transition temperature with the mole fraction of DMSO in the mixed solvent at various LiCl concentrations is shown in Fig. 2. At lithium chloride concentrations above 3 mol %, the curves are characterized by a steep increase in Tg over the range $y_{DMSO} = 0-0.4$, and a reasonably constant Tg over the range $y_{DMSO} = 0.5-1$.

It is of interest to compare the observed variation in Tg with mole fraction of DMSO with those for other salt–DMSO–water systems so far investigated[9−11]. The systems silver nitrate–DMSO–water[11] and ammonium nitrate–DMSO–water[9] have been found to show a linear dependence of Tg on y_{DMSO}. A characteristic feature in both cases is the absence of glass-forming ability for the binary systems salt–water. The system calcium chloride–DMSO–water, in contrast, exhibits much the same variation in Tg with y_{DMSO} as does the system studied in this work. Thus, the reason for the different behaviour of glass transition temperature may be either that the simple pattern of variation in Tg with y_{DMSO} is peculiar to systems whose binary aqueous counterparts are not glass-forming or that the more complicated pattern is due to the presence of chloride ions. Measurements on further salt–DMSO–water systems are needed to verify these hypotheses.

Glass-Forming Region

Results for the system lithium chloride–DMSO–water are shown in Fig. 3 in the form of a ternary diagram with the glass-forming region *PSEKLMNP*. The lines *PSEK* and *NML* represent, respectively, the solvent-rich and salt-rich composition limits. The boundaries of the glass-forming region separate solution compositions for which different products are obtained on rapid cooling. For compositions outside the glass-forming region, cooling of solution produces crystals. On changing slightly the solution composition rapid cooling no longer results in equilibrium crystalliza-tion, but the supercooled liquid passes into the metastable region, transforming at the glass transition temperature into an amorphous solid substance, the glass. The composition change may be effected by decreasing or increasing the salt con-centration, or by changing the relative proportion of solvent components.

On the most general level, the effect of solution composition on the glass-forming ability might be understood by assuming that a small change in the relative propor-tion of the components produces a structural change that causes an abrupt increase in the induction period of equilibrium solid phase nucleation. Thus, one might expect substantial structural reorganization to occur in the boundary region, pre-venting the nucleation of equilibrium solid phase.
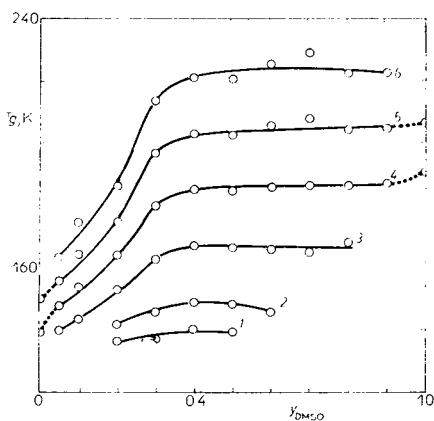

FIG. 2

Glass transition temperature Tg (K) as a function of mole fraction of dimethylsul-phoxide y_{DMSO} in the mixed solvent at var-ious lithium chloride concentrations. *1* sol-vent alone; *2* 3 mol %; *3* 9 mol %; *4* 15 mol %; *5* 21 mol %; *6* 27 mol % LiCl
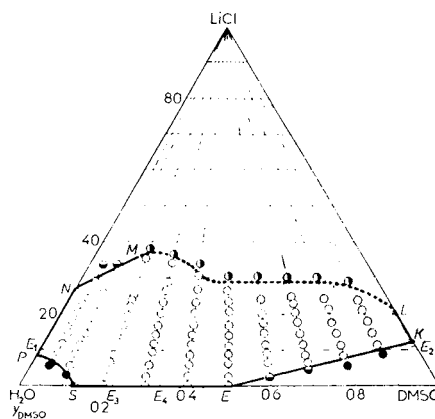
FIG. 3

Glass-forming region of the system lithium chloride–DMSO–water. ○ solutions which yielded glass on cooling; ◑ solution which yielded both glass and crystals on cooling; ● crystal-producing solutions; ◐ solutions which would not dissolve

It may be assumed that in the *PS* region the equilibrium solid phase is crystalline ice. The addition of lithium chloride and/or DMSO results in an increase of the induction period of ice crystal nucleation. In the SE region, conditions in the binary system water–DMSO are unfavourable for rapid nucleation of any equilibrium phase. At point *E*, a small change in the ratio $DMSO/H_2O$ favours the crystallization of solid DMSO. At point *K*, an increase in lithium chloride concentration hampers nucleation presumably of a lithium chloride solvate. The phase diagram of the system lithium chloride–DMSO has not been published, so that nothing more specific can be said about the composition of the equilibrium solid phase.

The salt-rich concentration limit of glass-forming ability (*LN* line) probably lies above 30 mol% LiCl. The equilibrium solid phase might therefore be expected to be lithium chloride disolvate or monosolvate, or crystalline lithium chloride. The maximum observed at $y_{DMSO} = 0.2 - 0.3$ suggests, however, that the disolvate can probably be ruled out as the equilibrium phase. At this composition, glass is produced over the widest range of lithium chloride concentrations $(0 - 36$ mol %$)$.

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