

Glass transition temperatures of the system zinc chloride—dimethyl sulfoxide—water

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Glass transition temperatures of the mixture zinc chloride—dimethyl sulfoxide—water have been determined as a function of zinc chloride concentration at various mole fractions of dimethyl sulfoxide in the mixed solvent. Plots of these data are of a convex character. The calculated dependence of the glass transition temperature on the mixed solvent composition is also nonlinear. The glass-forming composition range has been determined and its boundaries are discussed.

Были определены температуры стеклования смесей хлористого цинка, диметилсульфоксида и воды в зависимости от концентрации хлористого цинка при постоянной мольной доле диметилсульфоксида в смешанном растворителе. Было показано, что у кривых этой зависимости конвексный характер. Вычисленную зависимость температуры стеклянного перехода от состава растворителя тоже нельзя описать линейным отношением. Была определена концентрационная область стеклообразования и были обсуждены ее границы.

The research into the glass-forming ability of concentrated solutions of inorganic salts in organic solvents is currently at the stage of data accumulation. The glass-forming composition range and the influence of chemical composition on the glass transition temperature have so far been investigated for only a few systems salt—dimethyl sulfoxide (DMSO) [1] and salt—water [2]. It has been established that the glass-forming composition ranges for binary aqueous solutions are different from those for the same salts in DMSO. It is therefore of interest to examine changes in the glass-forming ability and glass transition temperature of salt solutions in DMSO on gradual replacement of the organic solvent by water. Investigation of ternary systems has proved rewarding from one other aspect: the glass-forming ability of these systems allows the effect of composition on the glass transition temperature to be studied over wider composition ranges [3—7] than in the case of binary systems.

The aim of the present work was to investigate the effect of composition on the glass-forming ability and glass transition temperature of the system zinc chloride—DMSO—water.

Experimental

Anhydrous zinc chloride and DMSO (Merck) were used in the "as-received" condition.

Solutions were prepared by quickly weighing the salt in air, pipetting in the mixed solvent and heating gently until dissolution was complete. Turbidity of samples due to hydrolysis was removed by adding a drop of concentrated hydrochloric acid.

The glass transition temperature was determined by the DTA method, using the same procedure and experimental apparatus as described previously [8]. The experimental error did not exceed $\pm 1\%$.

The glass-forming composition range was determined partly by preliminary experiments in which samples in the same test tubes and in the same amounts as used in DTA measurements were quenched by immersion in liquid nitrogen to establish whether they crystallized or formed glass or a mixture of glass and crystals.

However, most points shown in Fig. 3 have been obtained by measurements of glass transition temperatures. The open circles in the figure indicate compositions for which ΔT (ind. — ref. sample) records showed large jumps and the samples immediately afterwards remained liquid without apparent crystals. The full circles denote compositions for which no jump appeared in the ΔT record and the samples were crystalline on removing from the measuring block. The circles ● denote compositions for which the ΔT records showed much smaller jumps and the samples exhibited two phases, glass and crystals. Finally, the circles ○ denote compositions for which glass transition temperatures could not be determined because no homogeneity was achieved by heating.

The zinc chloride content of solutions was expressed as the mole fraction of zinc chloride, $x = n(\text{ZnCl}_2) / (n(\text{ZnCl}_2) + n(\text{solvent}))$, and was checked by chelatometric titration. The mixed solvent composition was expressed in terms of the mole fraction of DMSO, $y(\text{DMSO}) = n(\text{DMSO}) / (n(\text{DMSO}) + n(\text{H}_2\text{O}))$.

Results and discussion

Results for the variation in the glass transition temperature with zinc chloride concentration in the mixed solvent water—DMSO at various water : DMSO ratios are given in Table 1. Data for $y(\text{DMSO}) = 0$ have been published by Sare [2] and those for $y(\text{DMSO}) = 1$ in our previous paper [1]. For each mixed solvent composition (expressed in terms of the mole fraction of DMSO in the solvent), the experimental points were fitted to a curve by the use of a regression method. The lines of best fit for all mixed solvent compositions were obtained by using a second-order polynomial. A typical plot, for $y(\text{DMSO}) = 0.5$, is shown in Fig. 1. Here, the curve for the glass transition temperature as a function of zinc chloride concentration is seen to be convex with respect to the x axis. This behaviour differentiates the system zinc chloride—DMSO—water from all hitherto studied systems of inorganic salts in the mixture DMSO—water [3—7], as well as from most binary systems salt—water [2] and salt—DMSO [1], for which the same

Table 1

Variation of the glass transition temperature, T_g (K), with zinc chloride concentration, x , at various mole fractions of DMSO, $y(\text{DMSO})$, in the mixed solvent

x	T_g/K	x	T_g/K	x	T_g/K
$y(\text{DMSO}) = 0.05$		$y(\text{DMSO}) = 0.1$		$y(\text{DMSO}) = 0.2$	
0.0863	161.8	0.0969	166.9	0.0993	171.8
0.1424	171.3	0.1397	179.2	0.1920	198.4
0.2201	189.1	0.1469	179.6	0.2994	215.3
0.2921	203.9	0.2439	199.8	0.3885	223.7
0.4507	221.8	0.3466	215.3	0.4014	226.1
		0.3960	219.3	0.4357	228.5
		0.4367	223.5	0.4870	230.6
$y(\text{DMSO}) = 0.3$		0.5205	228.5	0.5343	233.2
0.0966	169.1			0.5471	238.2
0.1005	173.1	$y(\text{DMSO}) = 0.4$		$y(\text{DMSO}) = 0.5$	
0.1926	197.9	0.0970	169.8	0.0975	167.1
0.2939	226.6	0.1975	202.9	0.1953	204.3
0.3884	226.3	0.2985	223.0	0.2482	218.7
0.4388	231.3	0.3898	227.9	0.2960	226.2
0.4548	233.8	0.4494	233.5	0.3972	232.3
0.4869	233.5	0.5085	236.3	0.4436	231.9
0.5433	234.8	0.5592	239.6	0.4871	236.4
0.5667	235.3	0.5886	242.9	0.5327	236.7
$y(\text{DMSO}) = 0.6$		$y(\text{DMSO}) = 0.7$		$y(\text{DMSO}) = 0.8$	
0.0472	153.1	0.0692	155.2	0.0823	158.7
0.0976	168.8	0.0998	163.3	0.0978	161.7
0.1101	169.3	0.1488	184.0	0.1407	175.2
0.1482	188.6	0.1950	203.0	0.1950	199.4
0.1978	206.0	0.2490	217.7	0.2575	219.3
0.1979	206.0	0.2993	225.4	0.3058	223.1
0.2522	220.3	0.3512	228.7	0.4040	230.4
0.3003	225.5	0.4395	230.6	0.4985	237.3
0.3550	229.1	0.4595	235.2		
0.4063	231.4				
0.4416	231.1	$y(\text{DMSO}) = 0.9$			
0.4774	232.6	0.1156	166.9		
		0.1461	175.7		
		0.1991	197.3		
		0.2457	216.8		
		0.2810	224.4		
		0.3585	226.9		
		0.4031	233.4		

dependence can be described, within the limits of experimental error, by a linear equation.

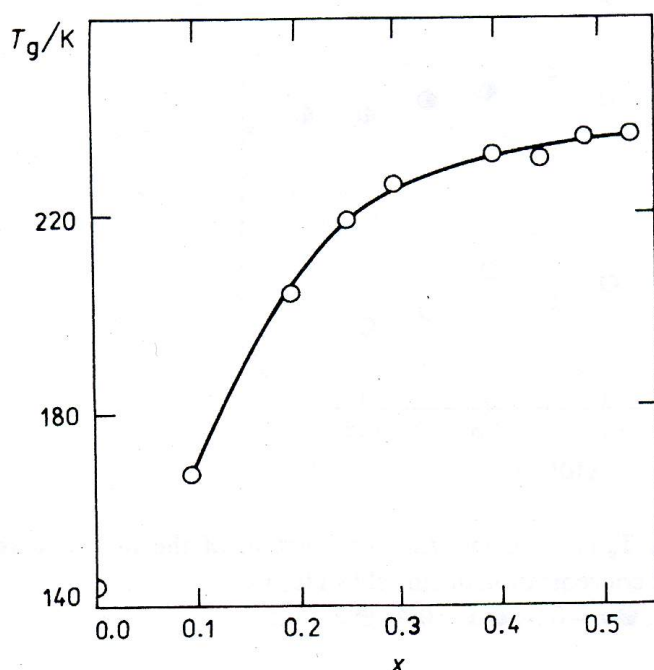


Fig. 1. Glass transition temperature, T_g (K), as a function of the mole fraction of zinc chloride, x , in the mixed solvent water—DMSO at a constant mole fraction of DMSO in the solvent, $y(\text{DMSO}) = 0.5$.

The linearity of the concentration dependence of glass transition temperature for most binary and ternary systems allowed at least a rough estimation of the unmeasurable glass transition temperatures of the components (*i.e.* the solvent and salt, or the mixed solvent and salt). Such estimation cannot be made for the system zinc chloride—DMSO—water because long extrapolation of a nonlinear plot is unjustifiable. Experimental data have shown that the concentration dependence of glass transition temperature for the system zinc chloride—DMSO—water cannot be represented by a linear equation even in the limited salt concentration range investigated.

Dependence of glass transition temperature on $y(\text{DMSO})$

In order to express this dependence it was necessary to calculate glass transition temperatures at constant x for $y(\text{DMSO})$ ranging from 0.05 to 0.9. These values were obtained from a fit of experimental data for the concentration dependence of glass transition temperature to a third-order polynomial. The values obtained at the mole fractions of zinc chloride $x = 0.1, 0.2, 0.3, 0.4$, and 0.5 are plotted in Fig. 2. The plot shows that the glass transition temperature is not a linear function of solvent composition, the curves being convex with respect to the y axis. The glass transition temperature increases with increasing mole fraction of zinc chloride, but follows roughly the same trend for all x 's investigated.

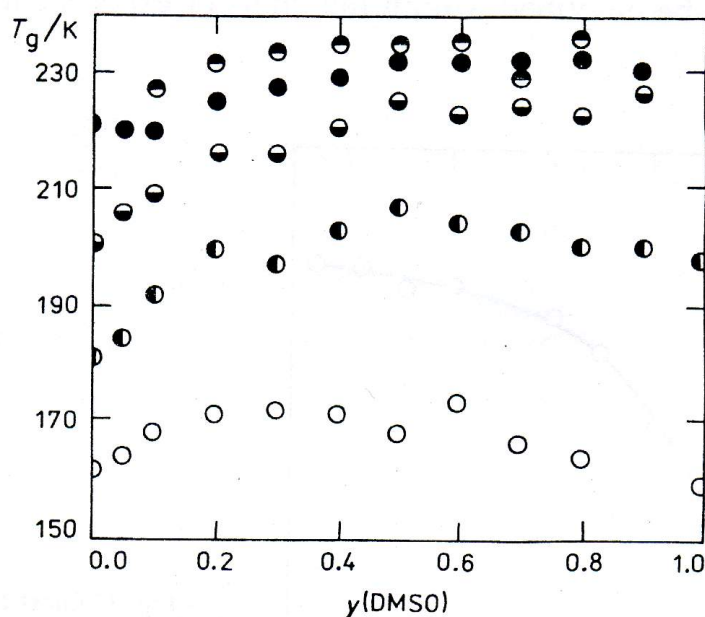


Fig. 2. Plot of glass transition temperature, T_g (K), against the composition of the mixed solvent, $y(\text{DMSO})$, at various concentration of zinc chloride, x .
 $\bigcirc x = 0.1$; $\bullet x = 0.2$; $\bullet x = 0.3$; $\bullet x = 0.4$; $\bullet x = 0.5$.

It is interesting to compare the dependences of the glass transition temperature on the mole fraction $y(\text{DMSO})$ for the present and previously studied systems salt—DMSO—water [3–6]. For the systems ammonium nitrate—DMSO—water [3] and silver nitrate—DMSO—water [4], the glass transition temperature is a linear function of $y(\text{DMSO})$. A characteristic feature in both the cases is that the corresponding binary systems salt—water are not glass-forming. The systems calcium chloride—DMSO—water [5] and lithium nitrate—DMSO—water [6], on the other hand, exhibit a dependence of glass transition temperature on $y(\text{DMSO})$ very similar to that found for zinc chloride—DMSO—water. Here, the corresponding binary systems salt—water are all glass-forming. Thus, a general conclusion which may be drawn from the experimental observations is that ternary systems that have no glass-forming binary aqueous counterparts are characterized by a simpler variation of glass transition temperature with $y(\text{DMSO})$.

Glass-forming region

The glass-forming composition range is delineated in the triangular diagram shown in Fig. 3. The lines PSJK and LMN represent the salt-poor and salt-rich composition limits, respectively. The boundary of the glass-forming region separates solution compositions for which different products are obtained on rapid cooling. For solutions of compositions close to the boundary of the glass-forming region (on the outside of it) rapid cooling produces crystals. When, however, the

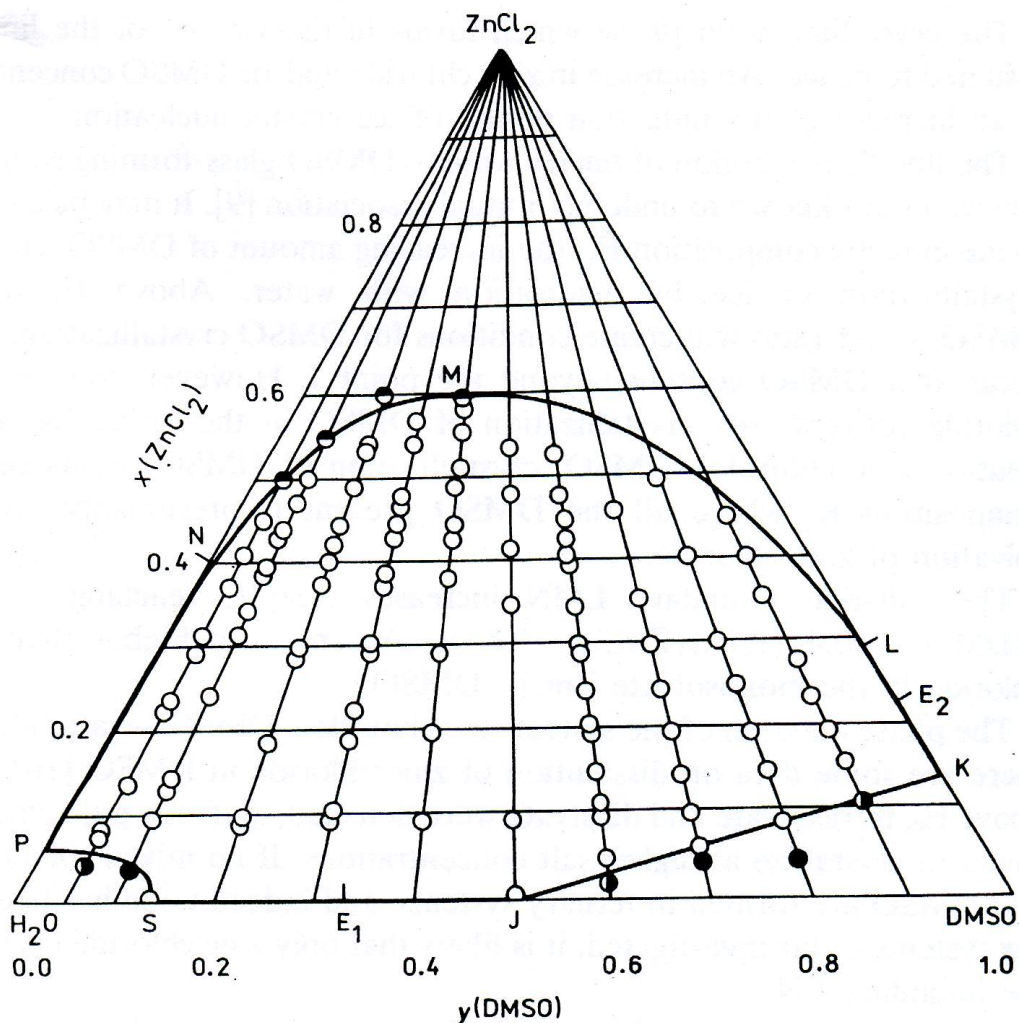


Fig. 3. Glass-forming region for the system zinc chloride—DMSO—water.

○ Glass-forming solutions; ● crystal-producing solutions; ◐ solutions which yielded both glass and crystals on cooling; ● solutions which would not dissolve on prolonged heating.

composition is changed slightly, no crystallization occurs and the solution passes as a supercooled liquid into a metastable region, transforming at a glass transition temperature into an amorphous solid phase, the glass. The composition change can be effected by changing either the zinc chloride concentration or the relative proportions of DMSO and water.

On the most general level, the influence of composition on the glass-forming ability may be explained in terms of a structural change which occurs on slightly changing the solution composition. In the limiting regions the glass formation may be due to a great increase of the induction period of equilibrium solid phase nucleation brought about by a small change in solution composition or alternatively, the above-mentioned structural change may prevent crystallization of the equilibrium solid phase.

The crystalline solid phase which forms in the vicinity of the line PS may be assumed to be ice. An increase in zinc chloride and/or DMSO concentration results in an increase of the induction period of ice crystal nucleation.

The line SJ is a region of binary water—DMSO glass-forming solutions. DMSO and water are known to undergo mutual association [9]. It may be assumed that up to the eutectic composition E_1 , the increasing amount of DMSO will act to hinder crystallization of ice by association with water. Above E_1 the increasing DMSO:water ratio will create conditions for DMSO crystallization, which should occur at a DMSO content beyond the point J. However, the presence of zinc chloride prevents the crystallization of DMSO in the range JK. In the binary solution zinc chloride—DMSO, crystallization of DMSO occurs only up to the composition K, where all the DMSO present is presumably involved in the solvation of zinc chloride.

The salt-rich boundary LMN increases steeply, reaching a maximum at $y(\text{DMSO})=0.4$ and $x(\text{ZnCl}_2)=0.6$, a concentration higher than that of zinc chloride in the monosolvate $\text{ZnCl}_2 \cdot \text{DMSO}$.

The phase diagram of the system zinc chloride—DMSO—water is unknown, but there are some data on dissolution of zinc chloride in DMSO [10]. In the range above E_2 , tetrasolvate and disolvate were detected, and only pure zinc chloride was found to crystallize at higher salt concentrations. If no mixed solvates with water and DMSO are formed in ternary systems, and indeed none has been detected in the systems so far investigated, it is likely that only zinc chloride crystallizes above the boundary LN.

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