# GLASS TRANSITION TEMPERATURES IN THE SYSTEM CALCIUM CHLORIDE–WATER–DIMETHYLSULPHOXIDE

Jarmila MALÁ and Ivo SLÁMA

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

The glass-forming composition region of the $CaCl_2$–$H_2O$–DMSO system has been established, and the glass transition temperatures of the mixtures have been determined as a function of the $CaCl_2$ content at a constant DMSO mole fraction in the mixed solvent. The dependence of the glass transition temperature on the $CaCl_2$ mole fraction at a constant mole fraction of DMSO in the mixed solvent can be described by a linear relationship.

In the framework of a systematic study on glass transition temperatures of inorganic salt solutions, binary and ternary systems of various salts or their mixtures in water and in DMSO have been studied with the aim to assess the influence of the system composition on the concentration range of glass-forming ability and on the glass transition temperature[1–3]. One of the results of this study is the finding that the concentration ranges of the glass-forming regions of inorganic salt solutions in water and in DMSO differ for most of the systems studied[3]. Aqueous solution of calcium chloride, for instance, is able to form glass in the region from about 5 to 9 mol% of the salt, while the system $CaCl_2$–DMSO from about 5 to 18 mol% $CaCl_2$. The salt-rich limit of glass-forming ability is thus considerably higher in DMSO than in water. It was therefore of interest to study how the glass-forming composition region would change on gradual replacement of water by dimethylsulphoxide in aqueous solutions of calcium chloride.

Since the mixed solvent water + DMSO has itself the ability to form glass over a concentration range from 13 to 48 mol% DMSO (ref.[4]), we could also follow the effect of calcium chloride addition on the glass-forming ability of the solvent.

## EXPERIMENTAL

### Chemicals Used

DMSO was Merck analytical grade. Anhydrous $CaCl_2$ was prepared from a commercial product by recrystallization and dehydration of crystalline calcium chloride dihydrate through distillation with xylene[5].

Samples for the determination of glass transition temperatures were prepared by weighing required amounts of the salt and pipetting calculated amounts of the mixed solvent.

The content of $Ca^{2+}$ was checked chelatometrically. The DMSO content was expressed in terms of the mole fraction of DMSO in the mixed solvent: $y_{DMSO} = n_{DMSO}/(n_{DMSO} + n_{H_2O})$.

The glass transition temperature was determined by the low-temperature differential thermal analysis; the method and the instrument used have been described elsewhere[6].

## RESULTS AND DISCUSSION

### Glass-forming Composition Region

The experimentally determined glass transition temperatures, $Tg\,(K)$, for various compositions of the mixed solvent, and calcium chloride concentrations, $x$ (mol% $CaCl_2$), are given in Table I. The solvent-rich ($C$, mol% $CaCl_2$) and salt-rich ($D$, mol% $CaCl_2$) limits of the glass-forming ability at various compositions of the mixed solvent, $y_{DMSO}$, are as follows.

TABLE I

Dependence of the glass transition temperature, $Tg$ (K), on the calcium chloride concentration, $x$ (mol %), in the system $CaCl_2$–$H_2O$–DMSO at various DMSO mole fractions in the mixed solvent

| $x$ | $Tg$ | $x$ | $Tg$ | $x$ | $Tg$ | $x$ | $Tg$ |
|---|---|---|---|---|---|---|---|
| $y_{DMSO} = 0.05$ | | $y_{DMSO} = 0.2$ | | $y_{DMSO} = 0.4$ | | $y_{DMSO} = 0.8$ | |
| 4.1 | 145.4 | 0.0 | 137.9 | 0.0 | 142.3 | 4.9 | 165.8 |
| 5.1 | 150.1 | 1.8 | 146.4 | 1.1 | 145.5 | 6.8 | 179.3 |
| 6.7 | 157.2 | 2.6 | 151.4 | 2.1 | 150.1 | 10.0 | 191.3 |
| 8.9 | 166.2 | 3.0 | 154.1 | 3.4 | 157.6 | 13.2 | 220.1 |
| 9.9 | 169.4 | 3.7 | 158.0 | 4.0 | 160.6 | 16.4 | 232.9 |
| | | 4.9 | 163.9 | 4.7 | 163.6 | 16.3 | 238.6 |
| | | 4.9 | 164.8 | 6.5 | 173.8 | 18.6 | 247.5 |
| | | 5.9 | 170.9 | 9.4 | 195.1 | | |
| | | 5.3 | 162.8 | 12.2 | 212.8 | | |
| | | 6.8 | 172.3 | 15.7 | 231.0 | $y_{DMSO} = 0.9$ | |
| | | 9.6 | 180.6 | | | 6.9 | 176.9 |
| $y_{DMSO} = 0.1$ | | 11.4 | 199.3 | $y_{DMSO} = 0.6$ | | 6.9 | 178.4 |
| 2.9 | 144.7 | 12.5 | 205.7 | 4.9 | 166.0 | 9.9 | 193.3 |
| 4.8 | 151.2 | 13.1 | 207.8 | 6.8 | 177.7 | 13.1 | 214.3 |
| 7.1 | 160.8 | 13.1 | 209.8 | 9.6 | 193.6 | 15.8 | 229.0 |
| 10.2 | 176.5 | 14.9 | 212.4 | 12.6 | 216.3 | 16.1 | 232.9 |
| 12.8 | 191.0 | 15.3 | 217.2 | 19.4 | 251.6 | 18.6 | 239.0 |
| 15.3 | 200.2 | | | | | | |

| $y_{DMSO}$ | 0·0 | 0·05 | 0·1 | 0·2 | 0·4 | 0·6 | 0·8 | 0·9 | 1·0 |
|------------|-----|------|-----|-----|-----|-----|-----|-----|-----|
| $C$ | 5·2 | 4·1 | 2·9 | 0·0 | 0·0 | 4·9 | 4·9 | 5·5 | 5·5 |
| $D$ | 8·7 | 9·9 | 15·3 | 15·3 | 15·7 | 19·4 | 18·6 | 18·6 | 18·7 |

Because of different mechanisms of supercooling and glass formation involved, it is preferable to discuss the solvent-rich and salt-rich limits of glass-forming ability separately. At the solvent-rich limit of glass-forming ability the supercooling is influenced primarily by the small value of the nucleation rate of the solid crystalline solvent. In an earlier paper[3] this was discussed in terms of a shortage of structural entities of unaffected solvent molecules in the solution, due to solvation of calcium chloride by an average of 18 solvent molecules. Addition of DMSO into the binary system calcium chloride–water gradually lowers the solvent-rich limit which is found to be zero at $y_{DMSO} = 0.2$. This value can be further refined by taking account of the work by Rasmussen and Mac Kenzie[4] who found that in the system water––DMSO glass formation occurs in the region 13·3–48 mol% DMSO. It has been assumed that this binary system involves strong association of the two liquids, manifesting itself in extreme values found in the concentration dependences of physico--chemical properties of mixtures[7]. It may therefore be expected that addition of DMSO to aqueous solution of calcium chloride would diminish, through association of DMSO with water, the content of unaffected water molecules in the system, resulting in gradual lowering of the solvent-rich limit of glass-forming ability. At 13·3 mol% DMSO the association with water is already sufficient to prevent virtually the nucleation of ice even in the absence of calcium chloride.

At DMSO concentrations above 48 mol% the system water–DMSO is no longer able to form glass. The phase diagram of this system[4] shows that starting from about 34 mol% DMSO the equilibrium solid phase in this region is crystalline dimethyl sulphoxide. In the region 34–48 mol% the association of DMSO with water should restrict the DMSO nucleation. At higher concentrations the number of DMSO entities available is large enough for the formation of nucleation centres. The solvent--rich limit in this region is governed by the calcium chloride solvation only and its value rapidly increases.

The salt-rich limit of glass-forming ability in aqueous solutions of calcium chloride lies in the region between the eutonic and calcium chloride hexahydrate, the latter being the equilibrium solid phase. The glass-forming and supercooling ability thus depends upon restricting the nucleation of the crystalline hexahydrate. Addition of DMSO to the calcium chloride solutions raises the salt-rich limit of glass-forming ability quite substantially. At $y_{DMSO} = 0.1$ the calcium chloride concentration at the salt-rich limit is higher than the composition of hexahydrate. This would imply that association of DMSO with water restricts the nucleation of the hexahydrate even at a calcium chloride concentration higher than the hexahydrate composition. The phase diagrams of the systems CaCl₂–DMSO and CaCl₂–DMSO–H₂O have not

yet been established, and it cannot be ruled out that even at lower DMSO concentrations the equilibrium solid phase in the ternary system is not the calcium chloride hexahydrate, but some mixed solvate. This could explain the rise in the salt-rich limit above the hexasolvate composition.

### Glass Transition Temperature

As in previous papers[1-3], it has been found that the concentration dependence of the glass transition temperature at a constant composition of the mixed solvent, $y_{DMSO}$, can be described, to a first approximation, by the relation

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

where $Tg$ is the glass transition temperature (K), $A$ and $B$ are empirical constants, and $x$ denotes the mole percent of $CaCl_2$. The calculated parameters are as follows.

| $y_{DMSO}$ | 0·05 | 0·1 | 0·2 | 0·4 | 0·6 | 0·8 | 0·9 |
|---|---|---|---|---|---|---|---|
| $A$ | 129 | 129 | 138 | 138 | 138 | 136 | 140 |
| $B$ | 4·16 | 4·67 | 5·28 | 6·00 | 5·95 | 6·09 | 5·56 |

Eq. (1) is valid only within the glass-forming region. Angell and Sare[8] found that for binary aqueous systems of many salts linear extrapolations of the concentration dependences of glass transition temperature to zero salt concentration yield a value of about 139 K, and concluded that the 139 K is true, experimentally inaccessible temperature of glass transition of water. Applying this procedure to the concentration dependence of glass transition temperature for solutions of calcium chloride in the mixed solvent water + DMSO of a constant DMSO mole fraction, we should arrive at the glass transition temperature of the mixed solvent with the given $y_{DMSO}$. Experimentally determined glass transition temperatures for the water–DMSO system are 140 K at $y_{DMSO} = 0·2$ and 146 K at $y_{DMSO} = 0·4$. Comparison with the values of $A$ in the above table shows that the values of glass transition temperature obtained by extrapolation to zero salt concentration according to Eq. (1) are by 2 and 8 K, respectively, lower. This discrepancy may result from the long extrapolation of the linear concentration dependence of the glass transition temperature to the region of low calcium chloride concentrations.

The effect of the composition of the mixed solvent on the glass transition temperature of the system $CaCl_2$–$H_2O$–DMSO at various concentrations of the dissolved salt can be seen from Fig. 1. Curves 1 and 2 correspond to solutions of calcium chloride concentrations at which the system forms glass at any composition of the mixed solvent. In this region the dependence of the glass transition temperature of the ternary mixtures on the mole fraction of DMSO in the mixed solvent at constant calcium chloride concentration cannot be described by a linear relationship.

Deviations from linearity are found to be positive for all the calcium chloride concentrations $(5-9 \text{ mol%})$ at which glass formation occurs in both the boundary binary systems and in the ternary solutions of any composition of the mixed solvent. Maximum positive deviations of $14.5-19.1$ K are found at DMSO mole fraction in the mixed solvent approaching 0.4.

Curve *3* in Fig. 1 represents the dependence of the glass transition temperature on the composition of the mixed solvent at 12 mol% $CaCl_2$, thus in the region where the binary mixture $CaCl_2$—$H_2O$ cannot form glass, and where the ternary solutions exhibit glass-forming ability only when the DMSO concentration in the mixed solvent reaches a certain value, namely $y_{DMSO} = 0.1$. Thus, deviations from linearity cannot be evaluated, but as seen in Fig. 1, the shape of this curve resembles that of curves *1* and *2*, and the maximum value is likewise reached at $y_{DMSO}$ round 0.4. The same behaviour has been observed with all solutions of $CaCl_2$ concentration above 9 mol%. As seen in Fig. 2, the deviations of glass transition temperatures from linearity become larger as the calcium chloride concentration is increased.

Comparison with previously studied ternary systems[1] reveals differences in the concentration dependences of the glass transition temperature. For ternary systems
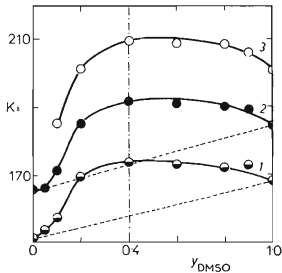


FIG. 1

Effect of composition of the mixed solvent on glass transition temperature in the system $CaCl_2$–$H_2O$–DMSO. *1* and *2*, experimentally found glass transition temperatures at 6 and 9 mol % $CaCl_2$, respectively. *3*, glass transition temperatures of the mixture at 12 mol % $CaCl_2$. $y_{DMSO}$ the mole fraction of DMSO in the mixed solvent, $T_g$ glass transition temperature in K
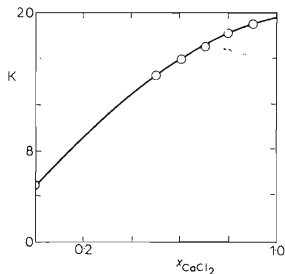
FIG. 2

Plot of maximum deviations from the linear dependence of the glass transition temperature *vs* calcium chloride concentration in the system $CaCl_2$–$H_2O$–DMSO. $x$ mole fraction of $CaCl_2$. The value at $x = 0$ has been taken from ref.[4]

of the type two salts + water, the glass transition temperature is an additive property of the components, so that it can be predicted on the basis of known properties of the binary systems. Such a prediction is impossible for the system under study, which involves a salt + two solvents.

REFERENCES

1. Malá J., Sláma I.: This Journal *44*, 1877 (1979).
2. Malá J., Sláma I.: This Journal *45*, 1896 (1981).
3  Malá J., Sláma I.: Chem. Zvesti *35*, 207 (1981).
4. Rasmussen D. H., Mac Kenzie A. P.: Nature (London) *220*, 1315 (1968).
5. *Gmelins Handbuch der Anorganischen Chemie*, Teil 28, Calcium B 2, p. 432.
6. Malá J., Novák J., Kodejš Z., Sláma I.: This Journal *43*, 183 (1978).
7. Werblan L., Lesiński J.: Polish J. Chem. *52*, 1211 (1978).
8. Angell C. A., Sare E. J.: J. Chem. Phys. *52*, 1058 (1970).