THE LIQUIDUS TEMPERATURE AND SUPERCOOLING ABILITY OF THE CALCIUM NITRATE–DIMETHYL SULPHOXIDE–WATER SYSTEM

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The liquidus temperatures have been measured for the system $Ca(NO_3)_2$–dimethyl sulphoxide–H_2O over a concentration range of 0—28 mol% $Ca(NO_3)_2$ and 0—100 mol% dimethyl sulphoxide. Comparison is made between the aqueous and the nonaqueous system, and the supercooling ability of both systems is discussed.

Dimethyl sulphoxide (DMSO) is well-known for its cryoprotective action in salt-rich aqueous solutions which resides in diminishing the ability of the system to crystallize. Cryoprotective substances, of which glycerine and saccharose may be named as further examples, maintain a system in the amorphous state by preventing the formation of the ice-salt eutectic. This effect is used in protecting living cells in tissues cooled to temperatures in the range 193 to 83 K. The mechanism of the protective action has not yet been satisfactorily elucidated. Some physicochemical properties of the DMSO–H_2O mixture (viscosity, refractive index, density, heats of mixing) have been studied, and their correlations with the structure of the liquid have been investigated[1–4]. Rasmunssen and MacKenzie[5] have measured the phase diagram and glass transition temperatures over the whole concentration range of the DMSO–H_2O mixture, and detected the existence of a congruently melting DMSO trihydrate (DMSO.3 H_2O). The system DMSO–salt has been studied by Sare[6], using calcium nitrate as the salt, from the aspect of the concentration dependence of glass transition temperature.

The present work deals with the study of liquidus temperatures and supercooling ability of the $Ca(NO_3)_2$–DMSO–H_2O system.

EXPERIMENTAL

The liquidus temperature, as well as the supercooling or the crystallization induction period, were measured by the methods described earlier[7]. Dimethyl sulphoxide (Merck) and calcium nitrate tetrahydrate (Merck) were used without further purification. The tetrahydrate was converted to anhydrous salt by drying *in vacuo* at 393 K. Calcium content of the samples was determined complexometrically. The required $DMSO/H_2O$ proportion was realized by mixing precisely weighed amounts of the pure components. The proportion is designated as y_{DMSO} (y_{DMSO} = mol DMSO/mol (DMSO + H_2O)). The calcium content is expressed in mol% Ca (mol Ca . 100/mol (Ca + DMSO + H_2O)).

RESULTS AND DISCUSSION

$Ca(NO_3)_2$–DMSO *System*

The measured liquidus temperatures, T_L, for the binary system are shown in Table I and in Fig. 1. Comparison with the data on the analogous $Ca(NO_3)_2$–H_2O system[8] reveals many similarities, but also some features of principal difference.

The local maximum in liquidus temperatures at 20 mol% $Ca(NO_3)_2$ points to the formation of a congruently melting tetrasolvate, $Ca(NO_3)_2.4\,DMSO$, by analogy with the hydrated $Ca(NO_3)_2.4\,H_2O$ system. The tetrasolvate was isolated, and 19·9 mol% $Ca(NO_3)_2$ was determined by analysis. The melting point of the tetrasolvate (approx. 332 K) is, however, by 17 K higher than that of the tetrahydrate. This is in keeping with the fact that the melting point of DMSO is by approx. 19 K higher than that of water.

For both systems the freezing point depression on addition of a small amount of calcium nitrate corresponds to that following from the modified van't Hoff equation

$$\mathrm{d}T/\mathrm{d}x = -vRT_L^2/\Delta H_L\,,$$

where x is the mole fraction of calcium nitrate in the solution, v is the number of ions into which the electrolyte is dissociated, T_L is the liquidus temperature and ΔH_L is the enthalpy of melting of the pure solvent (ΔH_{H_2O} = 6012 J/mol and ΔH_{DMSO} =

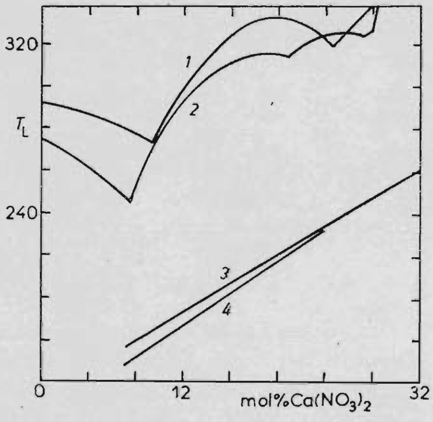

FIG. 1

Liquidus temperature, T_L (K), as a function of composition for the $Ca(NO_3)_2$–DMSO *1* and $Ca(NO_3)_2$–H_2O *2* systems. Glass transition temperature, T_g, as a function of composition for the same systems: DMSO *3*, H_2O *4*

TABLE I

Liquidus temperatures for the system $Ca(NO_3)_2$-DMSO-H_2O

y_{DMSO}	mol % Ca	T_L K^a	y_{DMSO}	mol % Ca	T_L K^a
0·1	18·6	308	0·7	20·0	—
	13·7	—		13·9	291
	12·1	—		11·8	287
	10·9	220		9·5	273
	10·1	223		7·9	257
	9·6	228		7·0	250
	8·9	231		6·9	251
	7·8	237		5·1	253
	7·0	242		0·0	273^b
	5·2	246			
	0·0	259^b	0·8	19·2	308
				14·0	307
0·2	20·0	—		9·9	281
	16·5	—		7·5	259
	14·3	—		4·1	275
	10·0	218		0·0	281^b
	3·1	213			
	0·0	222^b	0·9	18·0	325
				13·9	313
0·3	18·6	—		10·9	288
	12·2	—		7·5	269
	0·0	208^b		5·1	275
				2·2	282
0·4	15·5	—		0·0	286^b
	8·8	—			
	2·2	217	1·0	28·5	339
	0·0	221^b		25·5	323·5
				24·0	323
0·5	14·3	—		22·7	325
	9·8	—		20·5	332·5
	3·0	229		18·6	331
	0·0	243^b		16·5	326
				14·9	314
0·6	18·9	—		12·7	303
	13·9	277		11·2	289
	9·4	268		9·9	279
	7·8	242		9·4	273
	6·1	—		9·0	275
	5·1	233		8·1	278
	0·0	261^b		5·5	282

[a] The dash signifies that the sample of the given composition would not crystallize even after having been seeded with crystal nuclei — the system has great tendency to supercooling. [b] Values taken from ref.[5].

= 12683 J/mol). This implies that calcium nitrate dissociation occurs in a similar manner in both cases.

The activity coefficients of both the solvent and the salt in the two systems somewhat differ, as reflected by eutectic compositions of 9·4 and 7·7 mol% $Ca(NO_3)_2$ for the $Ca(NO_3)_2$–DMSO and the hydrated system, respectively. The eutectic temperature is by about 28 K lower with the hydrated system, which is consistent with the lower melting point of water as compared with that of DMSO.

A principal difference has been found in the variation of the liquidus temperature at concentrations above 29 mol% $Ca(NO_3)_2$. With the hydrated system, the liquidus temperature increases to a local maximum of 325 K corresponding to the formation of a congruently melting trihydrate. With the $Ca(NO_3)_2$–DMSO system, on the other hand, the liquidus temperature decreases, showing a local minimum at concentrations corresponding to the trisolvate composition. This fact indicates that the trisolvate has no stable existence in non-aqueous systems.

The concentration ranges of the glass-forming region are similar for both compared systems. Fig. 1 shows the variation of the glass transition temperature, T_g, as a function of concentration. The solvent-rich limit of the glass-forming ability is about 5 mol% $Ca(NO_3)_2$. The salt-rich limit, however, is somewhat higher for DMSO[6], lying at 30 mol% as compared with 24 mol% $Ca(NO_3)_2$ for the aqueous system. Here, formation of a second eutectic in the trisolvate region with the $Ca(NO_3)_2$––DMSO system may be of importance.

The supercooling ability may be expressed in terms of the resistance of a system to crystallization. Fig. 2 and 3 show the regions of composition and supercooling ($\Delta T = T_L - T$) in which the systems will crystallize within 60 min. It can be seen that there are regions, around 18 mol% $Ca(NO_3)_2$ and below 12 mol% ($Ca(NO_3)_2$ where the solution readily crystallizes (the system is relatively difficult to supercool); at the concentrations 13–14 mol% and above 23 mol% $Ca(NO_3)_2$, on the other hand, both systems can easily be supercooled, showing little tendency to crystallization. Apart from these similarities, it can also be seen from the figures that, in general, the calcium nitrate aqueous melt shows greater tendency to supercooling within the concentration range under study than does the DMSO system.

Another measure of the supercooling ability is the crystallization induction period, *i.e.*, the time in which the first crystal will appear in a solution of a given composition at a given supercooling. The dependence of the induction period on the supercooling is expressed by the so-called *T–T–T* curves (time–temperature–transformation) which are shown in Fig. 4 for the systems 16·4 mol% $Ca(NO_3)_2$–H_2O and 16·4 mol% $Ca(NO_3)_2$–DMSO. The solutions will crystallize within the supercooling region defined by the *T–T–T* curve. The shortest induction period for the aqueous system is $\tau_{min} = 10$ min at $\Delta T = 75$ K while for the DMSO system it is only 2 min at $\Delta T = 35$ K. These facts once again confirm that the DMSO system is more difficult to supercool than the $Ca(NO_3)_2$ aqueous solution.

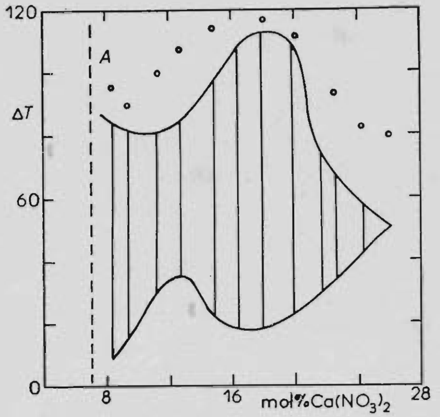

FIG. 2

The regions of composition and supercooling, ΔT, in which the $Ca(NO_3)_2$–DMSO system crystallizes spontaneously within 60 min; A the limit of glass-forming ability, ○ supercooling corresponding to the glass transition temperature ($\Delta T_g = T_L - T_g$)

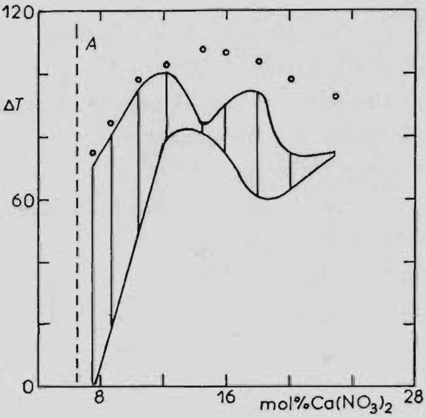

FIG. 3

The regions of composition and supercooling, T, in which the $Ca(NO_3)_2$–H_2O system crystallizes spontaneously within 60 min; A the limit of glass-forming ability, ○ supercooling corresponding to the glass transition temperature ($\Delta T_g = T_L - T_g$)

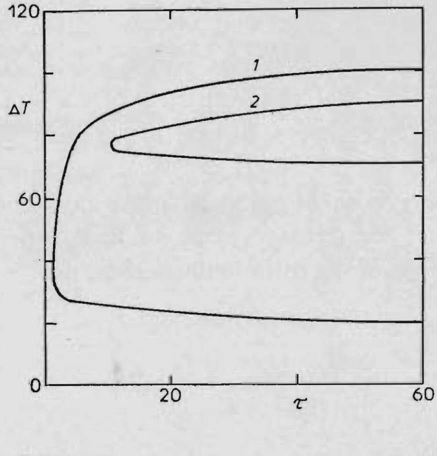

FIG. 4

T–T–T curves (induction period, τ (min), as a function of supercooling, ΔT) for the $Ca(NO_3)_2$–DMSO 1 and $Ca(NO_3)_2$–H_2O 2 systems at a composition of 16·4 mol% $Ca(NO_3)_2$

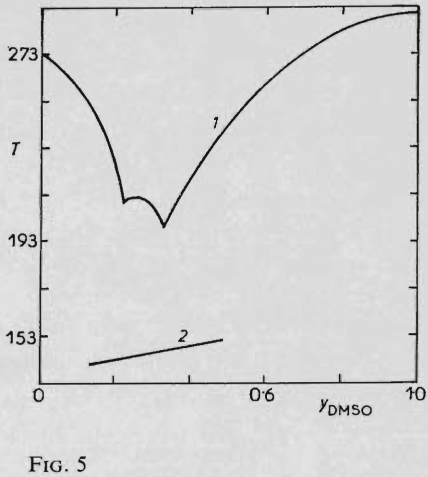

FIG. 5

Liquidus temperatures 1 and glass transition temperatures 2 for the DMSO–H_2O system — taken from ref.[5]

$Ca(NO_3)_2$-DMSO-H_2O *System*

The results of liquidus temperature measurements on the ternary system are given in Table I. The dash in the table signifies that at the given composition and temperature the solution could not be brought to crystallization, even after having been seeded with a defined solid phase, presumably because of the presence of metastable equilibria. Attempts to isolate and identify the solid phase also failed, as the washing with various solvents resulted in inconstancy of the solvate composition. On these grounds, it is only possible to discuss the results on a qualitative, or in the best case a semiquantitative, basis.

It can be seen from the DMSO–H_2O phase diagram[5] (Fig. 5) that on adding DMSO to water the liquidus temperatures of the mixed solvent decrease rapidly down to 203 K at 33 mol% DMSO, *i.e.*, at $y_{DMSO} = 0{\cdot}33$. Further additions of DMSO give rise to less steep increase of the liquidus temperature. If the pseudobinary cross-sections of the ternary phase diagram are similar in shape at low calcium nitrate concentrations, the eutectic temperature of the ternary diagram should also decrease. From the measured values of the liquidus temperature we have tried to assess the dependence of the eutectic temperature on the DMSO concentration in the mixed solvent. The eutectic temperature becomes minimum in the region of y_{DMSO} between 0·2 and 0·4, and the minimum rises gradually with further increase in DMSO concentration of the ternary system ($y_{DMSO} = 0{\cdot}4-1$). Hence, the eutectic compositions in the pseudobinary cross-sections of the ternary phase diagram may be estimated to lie between the eutectic concentrations of the two binary systems, $Ca(NO_3)_2$–H_2O and $Ca(NO_3)_2$–DMSO.

The maximum liquidus temperatures of the pseudobinary systems show a similar trend. It seems therefore reasonable to conclude that the formation of the solid tetrasolvate is a characteristic feature of the ternary system. In view of the existence of the congruently melting DMSO trihydrate[5] in the DMSO–H_2O system, moreover, the mixed solvate $Ca(NO_3)_2.DMSO.3\,H_2O$ may be envisaged to be formed as a new phase in the ternary system. The readiness of the ternary system to form supercooled solution is probably due to the complexity of the solvation equilibria.

REFERENCES

1. LeBel R. G., Goring D. A.: J. Chem. Eng. Data *7*, 100 (1962).
2. Cowie J. M. C., Toporowski P.: Can. J. Chem. *39*, 2240 (1961).
3. Schichman S. A., Amey R. L.: J. Phys. Chem. *75*. 98 (1971).
4. Werblan L., Leinski I.: Polish J. Chem. *52*, 1211 (1978).
5. Rasmunssen D. H., MacKenzie A. P.: Nature (London) *220*, 1315 (1968).
6. Sare E. J.: *Thesis*. Purdue University, 1971.
7. Pacák P., Sláma I.: J. Solution Chem. *8*, 529 (1979).
8. *Spravochnik po Rastvorimosti Solevykh Sistem*, Vol. IV., p. 2481. Goskhimizdat, Leningrad 1963.

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