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**LIQUIDUS TEMPERATURES OF SOME SYSTEMS  
SALT-DIMETHYL SULPHOXIDE AND SOLVATE FORMATION.  
PREFERENTIAL SOLVATION BY DIMETHYL SULPHOXIDE**

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Received June 29th, 1984

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Liquidus temperatures were measured for concentrated solutions of LiCl, CaCl<sub>2</sub>, ZnCl<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, NaNO<sub>3</sub> and Mg(NO<sub>3</sub>)<sub>2</sub> in dimethyl sulphoxide. Crystalline solvates of salts with dimethyl sulphoxide which separated from these solutions were isolated and subjected to chemical and infrared spectroscopic analyses. It has been proved that in concentrated solutions in the mixed solvent water-dimethyl sulphoxide, the salts are preferentially solvated by dimethyl sulphoxide.

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A study of physicochemical properties of concentrated solutions of salts in dimethyl sulphoxide (DMSO) requires a knowledge of the variation in the equilibrium solubility with salt concentration. Solubilities of some inorganic salts in DMSO at 25°C have been published by Janz<sup>1</sup> and by Butler<sup>2</sup>. Recently, liquidus temperatures have been measured for solutions of calcium nitrate<sup>3</sup>, lithium nitrate<sup>4</sup>, ammonium nitrate<sup>5</sup>, and silver nitrate<sup>6</sup> in DMSO. The present paper summarizes results for solubilities of lithium chloride, calcium chloride, zinc chloride, sodium nitrate, zinc nitrate, and magnesium nitrate in DMSO.

#### EXPERIMENTAL

Calcium chloride, sodium nitrate (both of analytical grade, Lachema, Czechoslovakia) and lithium chloride (suprapur, Merck) were dehydrated by drying in a vacuum oven at 110°C for 24 h. Zinc chloride (anhydrous, Merck) and dimethyl sulphoxide (analytical grade, 0.03% water, Merck) were used without any further treatment. Samples were prepared by dissolving appropriate amounts of salts in DMSO. Anhydrous solutions of zinc nitrate and magnesium nitrate in DMSO were obtained by a method based on preferential solvation of the salts by dimethyl sulphoxide. The method consists of adding DMSO to a salt hexahydrate in such an amount that the ratio salt : DMSO is 1 : 2 and heating the mixture in a rotating vacuum evaporator at 80°C. By 4 h all water will have evaporated, leaving a fused disolvate which crystallizes slowly on cooling. More dilute solutions were prepared by dissolving disolvates obtained in this way in appropriate amounts of DMSO. The calcium, zinc, and magnesium contents of samples were determined by complexometric titration. Lithium chloride solutions were analyzed for their chloride ion contents argentometrically. Sodium nitrate solutions were made up from precisely weighed components.

As all the solvates are highly hygroscopic, they were stored in a desiccator over  $P_2O_5$ . Most salt-DMSO solutions are easy to supercool and hence reluctant to crystallize. In such a case, crystallization was induced by a seed crystal of the respective solvate. No crystallization occurred when the solution was seeded with a crystal of a composition other than that of the solid phase to be separated. The liquidus temperatures were measured by the last-crystal-dissolution method, whose accuracy is  $\pm 1^\circ C$ . All measurements were made by visual observation, some of the samples being observed under a microscope with a thermostatted brass stage to ensure more precise detection of the phase transitions. Solubility measurements at temperatures above  $120^\circ C$  could not be made because of partial decomposition of DMSO. The conventional DTA method was impracticable, because high viscosity of the solutions, particularly at higher concentrations, caused the growth or dissolution of crystals to be a very slow process, giving a weak or no DTA signal at all.

In some cases, the crystals were separated by filtering the sample quickly through an S3 sintered glass, washed with acetone, dried on a filter paper, and stored in a vacuum desiccator over  $P_2O_5$ . After 48 hours, analyses were made for the salt and DMSO contents. The DMSO content was determined by titration with potassium permanganate with a relative accuracy of 1%.

Viscosities of fused solvates were measured by an Ubbelohde capillary viscometer, and densities by a DMA 40 digital vibration densimeter (Paar, Austria). Densities of solid samples were determined pycnometrically. Infrared spectra were taken on an IR-20 spectrometer (Beckman) in the range  $4\ 000-600\text{ cm}^{-1}$  from a capillary layer of fused solvate between NaCl plates. AgCl plates were used for silver nitrate monosolvate.

The solution compositions are expressed in terms of the mole fraction of salt,  $x$ , or the molar solvent-to-salt ratio,  $R$ .

## RESULTS

Results for the liquidus temperature as a function of composition for the various systems salt-DMSO are shown in Figs 1-3, along with phase diagrams of the corresponding aqueous solutions<sup>6,7</sup>. Numerical values of the liquidus temperatures in tabular form are available as Supplementary Material (to be sent by the authors upon request).

Zinc chloride (Fig. 1a): The liquidus temperature-salt content curve shows two distinct maxima at  $x = 0.20$  and  $x = 0.33$ . From sample of  $x = 0.169$  crystalline phase with  $x = 0.205$ , corresponding to the tetrasolvate  $ZnCl_2 \cdot 4\text{ DMSO}$ , was isolated. Samples with  $x = 0.28$  and  $0.305$  yielded the disolvate  $ZnCl_2 \cdot 2\text{ DMSO}$ . The two solvates melt congruently at  $39$  and  $74^\circ C$ , respectively. Both compounds were submitted to thermogravimetric analysis. The tetrasolvate started losing mass at  $40^\circ C$ , and at  $100^\circ C$  the mass loss was 2 mol DMSO per 1 mol  $ZnCl_2$ . Further loss occurred at  $120^\circ C$ , reaching 4 mol DMSO per 1 mol  $ZnCl_2$  on increasing the temperature up to  $180^\circ C$ . Gavlas and Ribar<sup>8</sup> have reported the existence of a trisolvate, but Fig. 1a is more in line with an eutectic at  $x = 0.25$  (*i.e.*  $R = 3$ ).

Calcium chloride (Fig. 1b): A single distinct maximum around  $x = 0.20$  was observed. The crystalline phase isolated from a solution with  $x = 0.18$  contained 4 mol DMSO per 1 mol  $CaCl_2$ , indicating the presence of  $CaCl_2 \cdot 4\text{ DMSO}$ . The

tetrasolvate melts congruently at 95°C. The liquidus curve shows another break near  $x = 0.13$ . The solid phase separated from solution with  $x = 0.108$  was, however, found to have  $x = 0.185$ . It is likely that an incongruently melting compound is formed so that the crystalline phase contains a mixture of tetrasolvate and hexa- or octasolvate. The viscosity of fused calcium chloride tetrasolvate is rather high compared to the solvates of other salts (Table I).

Lithium chloride (Fig. 2), like calcium chloride, shows low solubility in DMSO. At 100°C, it dissolves up to a content of  $x = 0.22$ , but the monosolvate LiCl.DMSO

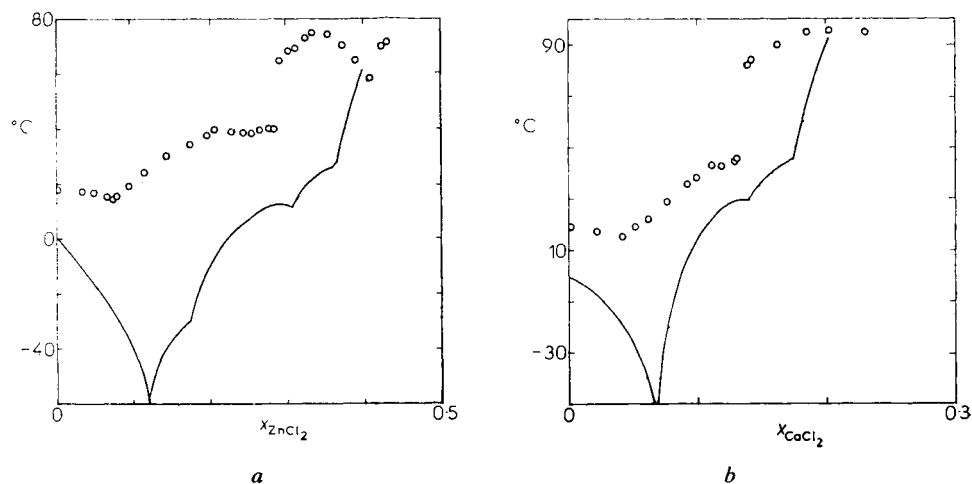


FIG. 1

Liquidus temperature as a function of salt content. The systems *a*) ZnCl<sub>2</sub>-DMSO (○) and ZnCl<sub>2</sub>-H<sub>2</sub>O (—) (ref.<sup>7</sup>); *b*) CaCl<sub>2</sub>-DMSO (○) and CaCl<sub>2</sub>-H<sub>2</sub>O (—) (ref.<sup>7</sup>)

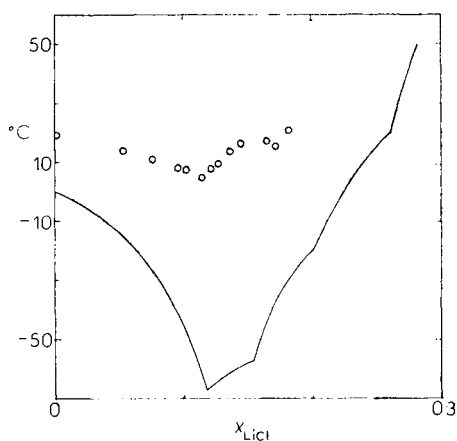


FIG. 2

Liquidus temperature as a function of salt content. The systems LiCl-DMSO (○) and LiCl-H<sub>2</sub>O (—) (ref.<sup>7</sup>)

TABLE I

Melting points ( $t_L$ ), densities ( $d$ ) and viscosities ( $\eta$ ) of fused solvates at the melting points, and densities and molar volumes ( $V_m$ ) of solid solvates

Solvate	$t_L$ °C	fused		solid	
		$d$ g cm <sup>-3</sup>	$\eta$ Pa s	$d$ g cm <sup>-3</sup>	$V_m$ cm <sup>3</sup> mol <sup>-1</sup>
LiNO <sub>3</sub> ·3 DMSO	19	1.2553	0.133	—	—
LiCl·DMSO	100	—	—	1.26	95.65
NH <sub>4</sub> NO <sub>3</sub> ·1.2 DMSO	-2	1.2870	0.163	—	—
AgNO <sub>3</sub> ·DMSO	53	2.3002	0.118	2.38	104.1
NaNO <sub>3</sub> ·2.7 DMSO	38	1.2905	0.0577	1.34	220.7
Ca(NO <sub>3</sub> ) <sub>2</sub> ·4 DMSO	59	1.3471	0.174	1.35	353
CaCl <sub>2</sub> ·4 DM SO	95	1.296	0.2812	1.34	314.3
ZnCl <sub>2</sub> ·4 DM SO	39	1.4060	0.055	1.42	315.7
ZnCl <sub>2</sub> ·2 DMSO	74	1.5243	0.0961	1.62	180.5
Zn(NO <sub>3</sub> ) <sub>2</sub> ·2 DMSO	81	1.551	0.0364	1.67	207
Zn(NO <sub>3</sub> ) <sub>2</sub> ·3 DMSO	57	1.5201	0.1741	1.569	270
Zn(NO <sub>3</sub> ) <sub>2</sub> ·6 DMSO	49	1.3651	0.0379	1.40	468
Zn(NO <sub>3</sub> ) <sub>2</sub> ·8 DMSO	46	1.3072	0.0181	1.34	607
Mg(NO <sub>3</sub> ) <sub>2</sub> ·2 DMSO	53	1.4384	2.1734	1.454	209.5

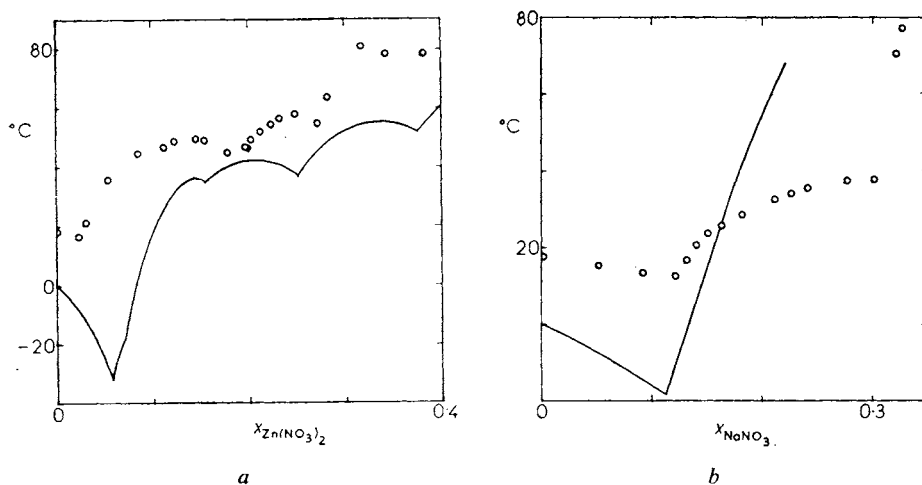


FIG. 3

Liquidus temperature as a function of salt content. The systems a) Zn(NO<sub>3</sub>)<sub>2</sub>-DMSO (○) and Zn(NO<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O (—) (ref.<sup>7</sup>); b) NaNO<sub>3</sub>-DMSO (○) and NaNO<sub>3</sub>-H<sub>2</sub>O (---) (ref.<sup>7</sup>)

(with  $x = 0.495$  as indicated by analysis) crystallizes out of this solution. The melting point of the monosolvate is above  $120^{\circ}\text{C}$ . Thermogravimetric analysis showed that DMSO began to liberate already at this temperature and that the total mass loss at  $160^{\circ}\text{C}$  corresponded to 1 mol DMSO per 1 mol LiCl. The liquidus curve shows a maximum around  $x = 0.15$ . This would suggest the existence of a congruently melting hexasolvate, but crystals isolated from a solution of  $x = 0.135$  were found to have  $x = 0.185$ , so that we cannot rule out the formation of tetrasolvate which escaped our detection. The crystalline phase could then be a mixture of the two solvates.

Zinc nitrate (Fig. 3a): The liquidus curve shows three distinct maxima at  $x = 0.143$ ,  $0.25$  and  $0.33$ , and two faint maxima at  $x = 0.111$  and  $0.20$ . Analyses of crystalline phases isolated from solutions of  $x = 0.08$ ,  $0.12$ ,  $0.20$ ,  $0.24$ , and  $0.31$  established the existence of the solvates  $\text{Zn}(\text{NO}_3)_2 \cdot R \text{ DMSO}$  ( $R = 8, 6, 4, 3$  and  $2$ , respectively). The tetrasolvate, unlike the other solvates, is unstable and becomes runny at room temperature although its melting point is  $50^{\circ}\text{C}$ . All DMSO-solvates of zinc nitrate melt congruently. The temperatures of liquidus (melting) are listed in Table I. An interesting result is the higher viscosity of fused trisolvate compared to the other zinc nitrate solvates (Table I).

Sodium nitrate (Fig. 3b) forms a DMSO solvate incongruently melting at  $40^{\circ}\text{C}$ . The solids separated from solutions of  $x = 0.18$ ,  $0.21$ ,  $0.24$ , and  $0.275$  all contained  $2.7$  mol DMSO per 1 mol  $\text{NaNO}_3$ . This crystalline phase melted at  $40^{\circ}\text{C}$  with simultaneous formation of crystallites of another kind which persisted in the newly formed solution even at  $65^{\circ}\text{C}$  (observed under a microscope).

Magnesium nitrate forms a disolvate which in the fused state has a high viscosity (Table I) and is extremely reluctant to crystallize. Its melting point is  $53^{\circ}\text{C}$ . The disolvate was prepared by the method described in Experimental. No solid phase crystallized from solutions of  $x = 0.25$ ,  $0.20$ ,  $0.14$  and  $0.11$ , even after seeding with a crystal of the disolvate at  $22$ ,  $-3$  and  $-15^{\circ}\text{C}$ , and therefore no liquidus temperatures could be determined.

Molar volumes, viscosities and densities have been measured for all hitherto prepared crystalline DMSO-solvates of salts in the fused state at the melting points. The data are summarized in Table I.

## DISCUSSION

All salts studied previously and in the present work, even those which give no hydrates, form one or more crystalline solvates with DMSO. This is due to a higher donor number of DMSO (29.8) compared with that of water (18) and hence a stronger cation-DMSO bonding. Most of these systems can be partially supercooled and form glasses in the range between the DMSO-solvate eutectic and the lowest solvate. In the solvate-forming region, the liquidus temperatures are mostly higher than those

of aqueous solutions. Exceptions occur with silver, sodium and ammonium nitrates which do not form crystalline hydrates<sup>7</sup>; here, the liquidus temperatures of DMSO-solvates are lower than those of unhydrated salts in water at the same concentrations. This implies that these salts are more readily soluble in DMSO than in water. Salts with bivalent cations are less soluble in DMSO than in water, and all of them form several solvates, including those higher than tetrasolvate. Salts with univalent cations, on the other hand, tend rather to form solvates with a low number of DMSO molecules.

The infrared spectra show a shift of the S—O stretching frequency from 1 050  $\text{cm}^{-1}$  (for pure DMSO) to 1 010  $\text{cm}^{-1}$ , indicating that the cations are bound to DMSO through the oxygen atom in all the solvates under study. As the vibration frequencies of the nitrate ion and DMSO overlap in the region 1 300–1 500  $\text{cm}^{-1}$ , it is not possible to tell whether or not ion pairs are formed in fused solvates. An exception is the system  $\text{Zn}(\text{NO}_3)_2$ -DMSO of  $x > 0.20$  for which an increase in the intensity of the band at 740  $\text{cm}^{-1}$  was observed as the DMSO content was reduced, apparently as a result of the splitting of the  $\nu_4(E')$  vibration frequency of  $\text{NO}_3^-$  at 719  $\text{cm}^{-1}$ . This could be an indication of increasing strength of inner-sphere interactions and hence of the formation of the ion pair  $\text{ZnNO}_3^+$ .

*Preferential Solvation of Salt by Dimethyl Sulphoxide  
in Concentrated Solutions Salt-DMSO-Water*

Preferential solvation by DMSO has only been dealt with in the literature for dilute solutions. In a previous work<sup>6</sup> on liquidus temperatures in the system  $\text{AgNO}_3$ -DMSO- $\text{H}_2\text{O}$ , we found that DMSO solvated preferentially silver nitrate in concentrated solutions, even in those with a molar ratio  $\text{DMSO} : \text{H}_2\text{O} = 1 : 5$  from which the monosolvate  $\text{AgNO}_3 \cdot \text{DMSO}$  crystallized. As silver nitrate forms no crystalline hydrate, the preferential solvation and crystalline monosolvate formation in the mixed solvent DMSO- $\text{H}_2\text{O}$  might seem to be peculiar to this type of salt. It was therefore of interest to see if salt-DMSO-water systems with salts that form crystalline hydrates involve preferential solvation by DMSO or mixed (DMSO +  $\text{H}_2\text{O}$ )-solvate formation.

TABLE II

Theoretical and experimental values of calcium nitrate content at maxima in liquidus curves for various molar ratios  $\text{DMSO} : \text{H}_2\text{O}$

DMSO : $\text{H}_2\text{O}$		6 : 4	7 : 3	8 : 2	9 : 1
$x_{\text{Ca}(\text{NO}_3)_2}$	theor.	0.13	0.149	0.167	0.184
	exp.	0.13	0.148	0.165	0.180

The tests were made on the systems  $\text{Ca}(\text{NO}_3)_2\text{-DMSO-H}_2\text{O}$  with molar ratios  $\text{DMSO} : \text{H}_2\text{O}$  of 6 : 4, 7 : 3, 8 : 2 and 9 : 1, and  $\text{CaCl}_2\text{-DMSO-H}_2\text{O}$ , and  $\text{ZnCl}_2\text{-DMSO-H}_2\text{O}$  with  $\text{DMSO} : \text{H}_2\text{O} = 7 : 3$ .

The liquidus temperatures for the system  $\text{Ca}(\text{NO}_3)_2\text{-DMSO-H}_2\text{O}$  had been measured previously<sup>3</sup>, but experimental points were lacking for a number of mixed solvent compositions because the samples would not crystallize spontaneously. It was not until later that we found that only a DMSO-solvate crystallizes from a solution of the salt in the mixed solvent and that the crystallization can be induced by seeding with a crystal of calcium nitrate tetrasolvate. When the seeding technique was used, most solutions of the above mixed solvent compositions readily crystallized, which was indirect proof that the crystalline product from these solutions was the tetrasolvate  $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{ DMSO}$ . Next, additional liquidus temperatures were measured for various calcium nitrate contents in solutions of the above mixed solvent compositions.

The experiments were designed to locate maxima in liquidus temperature-salt content curves indicative of the existence of compounds. As the  $\text{DMSO} : \text{H}_2\text{O}$  ratio was decreased, the positions of the maxima shifted towards lower salt contents of solutions. Assuming the formation of tetrasolvate (*i.e.* the molar ratio salt : DMSO = 1 : 4) in a solution of a given mixed solvent composition (*e.g.*  $\text{DMSO} : \text{H}_2\text{O} = 7 : 3$ ), we can calculate the salt content at which a maximum should be observed ( $x = 7 : 4 : (3 + 7 + 7 : 4)$ ). Comparison of theoretical and experimental values of these salt contents is given in Table II. Analysis established that the crystalline phases separated from these solutions were DMSO-tetrasolvate of calcium nitrate.

The same procedure was followed in the cases of calcium chloride and zinc chloride. Calcium chloride forms a tetrasolvate with DMSO, so that the maximum in the liquidus temperature-salt content curve for  $\text{CaCl}_2\text{-DMSO-H}_2\text{O}$  solutions with  $\text{DMSO} : \text{H}_2\text{O} = 7 : 3$  should theoretically lie at  $x = 0.149$ . Experimentally, the maximum was found at  $x = 0.15$ . Zinc chloride forms both disolvate and tetrasolvate which, for  $\text{DMSO} : \text{H}_2\text{O} = 7 : 3$ , should give rise to maxima at  $x = 0.259$  and  $0.149$ , respectively; experimentally found maxima were at  $x = 0.26$  and  $0.15$ . This indicates that anhydrous solvates do indeed separate from the solutions, and this was also confirmed by chemical analysis of the crystals.

The experiments have shown that even salts which form crystalline hydrates are preferentially solvated by dimethyl sulphoxide and that DMSO-solvates crystallize from concentrated solutions of the salts in the mixed  $\text{DMSO} + \text{H}_2\text{O}$  solvent. Based on these findings, a simple method, described in Experimental, has been proposed and used for the preparation of anhydrous solvates of salts from their hydrates.

*The authors wish to thank Mrs H. Oesterreicherová for technical assistance with the liquidus temperature measurements, Dr H. Špalková for measuring the densities and viscosities of fused solvates, and Dr F. Hanousek for measuring the infrared spectra.*

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Translated by M. Škubalová.