

MOLAR HEAT CAPACITIES AND ENTHALPIES OF FUSION FOR THE SYSTEM ZINC CHLORIDE-DIMETHYL SULPHOXIDE

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Molar heat capacities and molar enthalpies of phase transitions in the system ZnCl_2 -DMSO have been investigated over the temperature range 240 to 405 K and the concentration range 11.1 to 40 mole % ZnCl_2 . The temperatures of fusion and of phase transitions were determined and compared with literature data. Equations were proposed for the description of the temperature dependence of the molar heat capacity in the liquid state. The concentration dependence of the molar heat capacity in the molten state was found to exhibit positive deviations from additivity.

It has been established recently that a number of salt-dimethyl sulphoxide (DMSO) solutions form glasses within a certain concentration ranges¹. A particularly wide concentration range of glass forming ability has been found for the system ZnCl_2 -DMSO (14 to 28 mole % ZnCl_2). Anomalous properties of concentrated salt solutions have been reviewed lately by Kodejš and Pacák² and by Sláma.³ They concluded that the glass forming ability of concentrated salt solutions is connected with anomalous temperature and concentration dependences of some physicochemical properties and probably results from specific interactions of ions with dipolar solvent molecules. In this context, the knowledge of the basic properties of glass forming systems is required before connections between the effects of the solution composition on various physicochemical properties and on the glass forming ability can be assessed. For the system ZnCl_2 -DMSO, only the density and viscosity⁴ and the liquidus temperatures⁵ have so far been investigated. The aim of the present work was to determine enthalpies of phase transitions and molar heat capacities of concentrated solutions of zinc chloride in dimethyl sulphoxide by differential scanning calorimetry.

EXPERIMENTAL

Samples were prepared by mixing weighed amounts of zinc chloride and dimethyl sulphoxide. The salt was an analytical grade product which had been dried in a vacuum oven, fused, and bubbled with gaseous HCl for 15 min. The solvent was Merck's analytical grade with a maximum water content of 0.03%. The metal content of the solutions was checked by complexometric

titration using xylene orange as indicator. Because of hygroscopicity of the samples, the water content was checked by Fischer's method. The samples prepared for the study were of the following concentrations: $R = 1.38, 1.98, 2.94, 4.00, 5.03, 6.02,$ and 8.00 , where R is the number of moles of DMSO *per* mole of $ZnCl_2$. The samples were kept in a desiccator over P_4O_{10} .

The measurements were made on a DSM-2M differential scanning calorimeter at a scan rate of 8 K min^{-1} in an atmosphere of nitrogen. Cooling down to about 230 K was achieved by using a mixture of solid CO_2 and ethanol.

Samples for measurements (20 to 50 mg) were sealed in air-tight aluminium containers of about 48-mg mass.

The temperature scale of the calorimeter was calibrated at two points by using the melting points of mercury (234.49 K) and indium (429.6 K). Linearity of the temperature scale was checked at three points within the temperature range of interest with the use of cyclohexane (279.9 K), *o*-terphenyl (329.4 K), and KNO_3 (400.8 K). The maximum deviation within the calibration range was $+0.8\text{ K}$. The temperature was read to 0.1 K .

The power calibration was made by classical method, using indium as the standard, and checked at the low-temperature end of the range with the use of mercury. At a scan rate of 8 K min^{-1} , a recorder's sensitivity of 10 mV , and a chart speed of $3\ 600\text{ mm h}^{-1}$, the instrument constants for individual ranges were $D1 = 33.98\text{ mJ cm}^{-2}$, $D2 = 18.41\text{ mJ cm}^{-2}$, and $D3 = 9.37\text{ mJ cm}^{-2}$. The integration of the peak areas was performed by the clip-and-weigh method.

Heat capacities were calculated by comparing the amplitude of the record for the sample investigated with that for the standard. Both records were corrected by subtracting the baseline for the empty calorimeter. A 116.617-mg sapphire disc was used as the standard.

RESULTS AND DISCUSSION

The temperature dependences of the molar heat capacity C_p (*per* mole of $ZnCl_2 \cdot R$ DMSO) are represented graphically in Figs 1 and 2. The samples with $R = 1.38, 1.98,$ and 2.94 exhibit one whereas the other samples two endothermic peaks.

To facilitate the handling of the data, we searched for a suitable equation to represent the temperature dependence of C_p . The most adequate equation was of the form

$$C_p = A + BT, \quad (1)$$

with different sets of constants A and B for the solid and liquid phases. Introduction of a further parameter proved to be statistically insignificant. The constants A and B for the solid and liquid phases are listed in Table I, along with standard deviations and the temperature ranges for which the constants were evaluated by the method of least squares. All the statistical computations were performed using a significance level of 0.05 .

Evaluation of the concentration dependence of C_p at 375 K , *i.e.* above the liquidus temperature, see Fig. 3, has shown that the molar heat capacities (*per* mole of the mixture) exhibit positive deviations from additivity.

The temperatures characterizing the endothermic peaks are summarized in Table II, along with the corresponding confidence intervals. Phase-transition temperatures

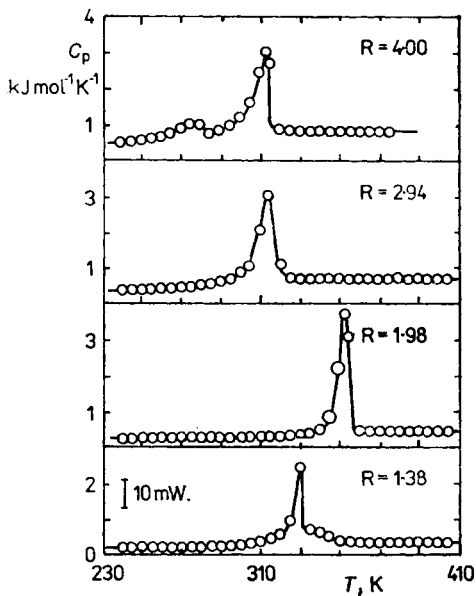


FIG. 1
The temperature dependence of C_p for $\text{ZnCl}_2 \cdot R \text{ DMSO}$

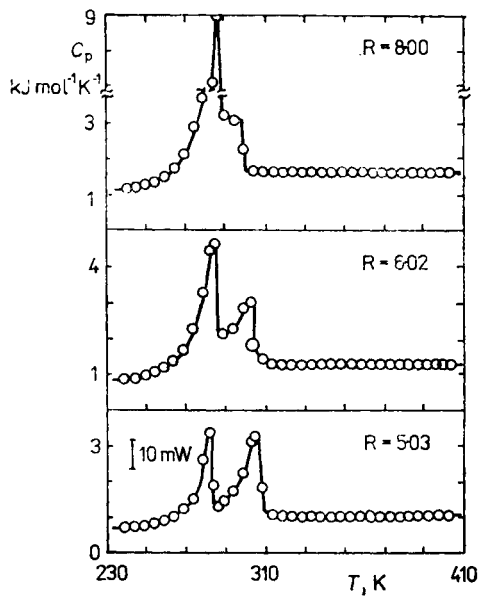


FIG. 2
The temperature dependence of C_p for $\text{ZnCl}_2 \cdot R \text{ DMSO}$

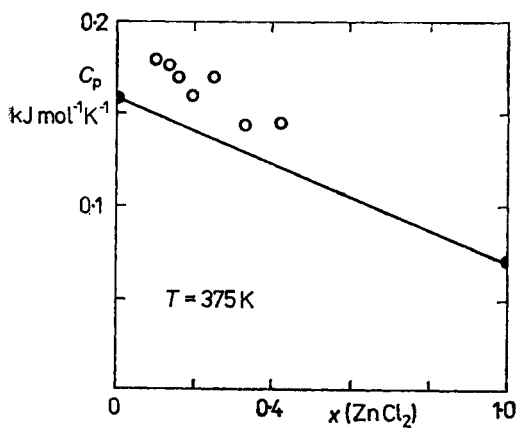


FIG. 3
The dependence of C_p on the mole fraction x at 375 K for the system ZnCl_2 -DMSO; \circ , C_p of DMSO (ref.⁶); \bullet , C_p of ZnCl_2 (ref.⁷)

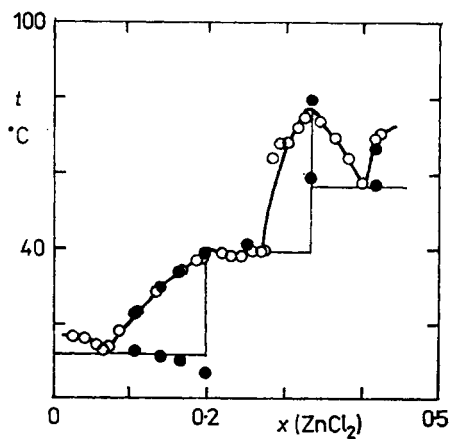


FIG. 4
Phase diagram for the system ZnCl_2 -DMSO

were obtained from the values of T_{\max} by correcting for the heating rate, the chart speed, and the rate of heat transfer within the calorimeter. The corrected values and the corresponding confidence intervals for all observed peaks are listed in Table III.

The obtained phase-transition temperatures were used as a basis for constructing a phase diagram for the system ZnCl_2 -DMSO. The diagram is shown in Fig. 4, where full circles represent our experimental results, which can be compared with published data for the liquidus curves⁵ indicated by empty circles. Our data are seen to be in very good agreement with literature values. What remains unclear are changes in the solid phase over the range of mole fractions from $x = 0.111$ to 0.200 , where the deviations of measured from expected values clearly exceed the uncertainty of the measurement. This inconsistency is most probably due to some as yet unidentified endothermic process which shows up as an apparent increase in the molar heat capacity of the solid phase for samples with $R \geq 4$ over the temperature range 240 to 270 K. In line with this hypothesis are negative changes in the molar heat capacity on melting calculated for $R \geq 4$. Another indication for the correctness of this explanation is a small low-temperature peak at $R = 4$ which appears at 277 K, *i.e.* at a temperature much lower than the eutectic temperature (286 K). This would mean that the molar heat capacities of the solid phase for samples with $R \geq 4$ are

TABLE I

Constants ($\cdot 10^3$) of Eq. (1) for the temperature dependence of the molar heat capacity C_p ($\cdot 10^3$) and their standard deviations s ($\cdot 10^3$)

R	Temperature range	Phase	A	$s(A)$	B	$s(B)$
1.38	240—280	<i>s</i>	132.0	7.0	0.42	0.02
	355—405	<i>l</i>	267.6	14.2	0.21	0.04
1.98	240—315	<i>s</i>	10.5	4.0	1.04	0.01
	365—405	<i>l</i>	390.0	13.6	0.10	0.04
2.94	240—275	<i>s</i>	-319.1	36.7	3.01	0.14
	325—425	<i>l</i>	801.4	11.1	-0.33	0.03
4.00	240—255	<i>s</i>	-932.1	75.5	6.14	0.30
	355—375	<i>l</i>	1 020.4	14.9	-0.70	0.04
5.03	240—255	<i>s</i>	-1 225.6	227.0	7.92	0.92
	320—405	<i>l</i>	1 098.7	20.4	-0.20	0.06
6.02	240—255	<i>s</i>	-2 477.4	296.0	13.80	1.20
	315—405	<i>l</i>	1 336.3	5.3	-0.26	0.01
8.00	240—255	<i>s</i>	-2 228.2	270.5	13.97	1.09
	310—405	<i>l</i>	1 562.8	8.3	0.11	0.02

much too low, and data measured over this range cannot be used as $C_p(s)$ values. This would also explain the seemingly lower eutectic temperatures for samples with $R \geq 4$. On the basis of these considerations, only data for $R = 1.98$ can be used to calculate the enthalpy change on melting. This value has been calculated as $27.97 \pm 0.78 \text{ kJ mol}^{-1} \text{ K}^{-1}$ and can be considered as an approximate enthalpy change on melting of $\text{ZnCl}_2 \cdot 2 \text{ DMSO}$ disolvate.

TABLE II
Characteristic temperatures (K) of the observed peaks

R	T_{on}	T_{max}	T_{off}
1.38	321.2 ± 1.5	330.1 ± 1.3	336.2 ± 2.2
	—	340.4 ± 0.9	348.0 ± 1.6
1.98	347.8 ± 2.6	353.2 ± 1.0	357.1 ± 1.1
2.94	306.2 ± 2.0	315.4 ± 1.7	320.1 ± 1.8
4.00	265.0 ± 6.3	277.2 ± 3.6	281.1 ± 3.4
	304.5 ± 0.7	313.5 ± 0.4	317.5 ± 0.3
5.03	275.9 ± 4.0	283.2 ± 2.8	287.1 ± 2.3
	294.9 ± 0.9	307.5 ± 1.1	310.6 ± 1.2
6.02	273.9 ± 3.9	284.5 ± 4.4	287.9 ± 3.8
	287.9 ± 3.9	303.0 ± 1.9	306.8 ± 1.9
8.00	277.3 ± 4.7	286.5 ± 2.4	291.1 ± 1.9
	291.3 ± 1.3	296.1 ± 0.7	301.3 ± 1.1

TABLE III
Corrected temperatures (K) of phase transitions

R	T	R	T
1.38	329.5 ± 1.3	5.03	280.9 ± 1.2
	340.2 ± 0.7		306.4 ± 1.2
1.98	352.4 ± 0.9	6.02	283.4 ± 4.5
2.94	314.8 ± 1.0		302.1 ± 2.5
4.00	274.9 ± 0.6	8.00	285.9 ± 2.2
	312.9 ± 0.4		295.0 ± 0.1

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