# HEAT CAPACITIES AND ENTHALPIES OF FUSION AND TRANSFORMATION FOR SOLVATES OF SOME SALTS WITH DIMETHYL SULFOXIDE AND DIMETHYLFORMAMIDE

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Molar heat capacities and molar enthalpies of fusion of the solvates $Zn(NO_3)_2 . 2\cdot24$ DMSO, $Zn(NO_3)_2 . 8\cdot11$ DMSO, $Zn(NO_3)_2 . 6$ DMSO, $NaNO_3 . 2\cdot85$ DMSO, and $AgNO_3 . DMF$, where DMSO is dimethyl sulfoxide and DMF is dimethylformamide, have been determined over the temperature range 240 to 400 K. Endothermic peaks found for the zinc nitrate solvates below the liquidus temperature have been ascribed to solid phase transformations. The molar enthalpies of the solid phase transformations are close to 5 kJ $mol^{-1}$ for all zinc nitrate solvates investigated. The dependence of the molar heat capacity on the temperature outside the phase transformation region can be described by a linear equation for both the solid and liquid phases.

The recently discovered glass-forming ability of nonaqueous electrolyte solutions[1] is an interesting phenomenon. It has been found that concentrated solutions of calcium nitrate in a variety of solvents form glasses within limited concentration ranges when small samples of them are quenched rapidly in liquid nitrogen. Further studies have established that solutions of other salts in nonaqueous solvents can also be changed into glasses by this method[2,3]. Anomalous properties of concentrated salt solutions have recently been reviewed by Kodejš and Pacák[4] and by Sláma[5]. An appreciable tendency to glass formation has been observed for solutions of some salts in dimethyl sulfoxide[2] and dimethylformamide[5]. The glass-forming ability of salt solutions has been interpreted in terms of the formation of inhomogeneous clusters in the region of liquidus temperatures. This intepretation assumes that entities which do not form crystals are incorporated into clusters of crystal-forming particles to such an extent that no crystal nucleus can arise. The possibility of the generation of inhomogeneous clusters in salt solutions has been linked to the existence of congruently or incongruently melting solvates. Therefore, attention has been focused on the study of the properties of salts in nonaqueous solvents[6−8]. The aim of the present work was to determine molar heat capacities and molar enthalpies of fusion for solvates of some salts with dimethyl sulfoxide and dimethylformamide by the method of differential scanning calorimetry.

## EXPERIMENTAL

All the solvates studied were prepared from chemicals of analytical grade. The salts were dried in a vacuum and mixed with weighed stoichiometric amounts of solvents. So prepared mixtures were melted and subjected to crystallization. The chemical composition of samples was checked by standard analytical methods. The heat effects were measured by means of a DSM-2M differential scanning calorimeter, with a scanning rate of 8 K min$^{-1}$ in an atmosphere of nitrogen. A mixture of solid carbon dioxide and ethanol used as the cooling medium allowed a minimum temperature of 230 K to be attained. Sample weights of 30 to 50 mg were sealed in ~48 mg aluminium capsules. Calibration of the instrument and evaluation of the measurements were performed by standard methods[6].

## RESULTS AND DISCUSSION

The system $Zn(NO_3)_2$–DMSO shows some anomalies as regards the behaviour of supercooled liquids, and therefore has received special attention[7].

## $Zn(NO_3)_2$.2·24 DMSO

A plot of the molar heat capacity $C_p$ as a function of temperature is shown in Fig. 1$a$. In addition to the heat effect of fusion, the record exhibits two prominent peaks, due apparently to solid phase transformations. The ill-pronounced peak at
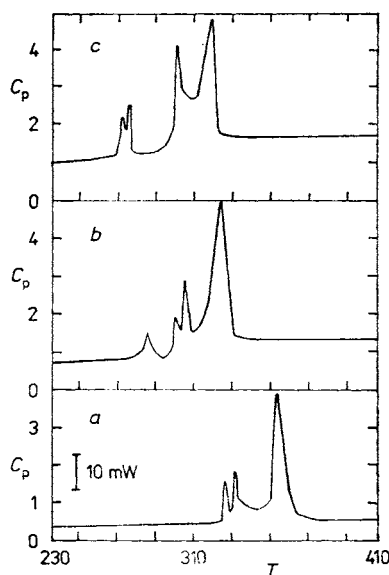


FIG. 1

Dependence of $C_p$ (kJ mol$^{-1}$ K$^{-1}$) of $Zn(NO_3)_2$.$R$ DMSO solvates on temperature $T$ (K). $R$: $a$ 2·24, $b$ 6, $c$ 8·11

about 300 K probably corresponds to the fusion of free DMSO. The values of $C_p$ for temperatures in the range 240 to 400 K are listed in Table I. The characteristic temperatures for the peak due to solvate fusion are $T_{on} = 348.4$ K, $T_{max} = 358.3$ K, and $T_{off} = 364.6$ K. The values (in K) for the other endotherms are as follows.

TABLE I

Dependences of molar heat capacities $C_p$ (J mol$^{-1}$ K$^{-1}$) on temperature $T$ (K)

| $T$ | Zn–2DMSO | Zn–6DMSO | Zn–8DMSO | Na–3DMSO | Ag–DMF |
|-----|----------|----------|----------|----------|--------|
| 240 | 347·6 | 711·6 | 1 011·4 | 396·2 | 211·1 |
| 245 | 356·3 | 732·6 | 1 044·0 | 410·8 | 218·6 |
| 250 | 362·7 | 747·9 | 1 078·0 | 423·9 | 225·2 |
| 255 | 369·6 | 766·3 | 1 100·9 | 437·7 | 230·4 |
| 260 | 375·1 | 783·6 | 1 119·7 | 446·5 | 232·2 |
| 265 | 381·3 | 798·0 | 1 143·2 | 459·8 | 246·4 |
| 270 | 387·0 | 816·1 | 1 192·7 | 477·5 | 252·8 |
| 275 | 390·4 | 846·2 | 1 897·0 | 494·7 | 260·6 |
| 280 | 396·6 | 909·8 | 1 250·6 | 511·4 | 268·5 |
| 285 | 402·5 | 1 123·4 | 1 255·9 | 539·1 | 274·4 |
| 290 | 407·9 | 1 097·3 | 1 289·2 | 597·1 | 283·0 |
| 295 | 416·8 | 872·9 | 1 430·3 | 696·7 | 299·7 |
| 300 | 418·4 | 1 170·7 | 2 026·1 | — | 336·8 |
| 305 | 420·3 | 1 566·5 | 3 007·5 | — | 424·7 |
| 310 | 419·1 | 1 560·7 | 2 761·4 | — | 571·3 |
| 315 | 440·0 | 1 797·1 | — | 690·8 | — |
| 320 | 466·6 | 3 215·0 | — | 596·0 | — |
| 325 | 550·1 | — | 1 839·7 | 589·1 | 328·4 |
| 330 | 805·7 | — | 1 696·7 | 585·7 | 320·2 |
| 335 | 1 093·3 | 1 382·7 | 1 695·5 | 580·4 | 321·1 |
| 340 | 991·9 | 1 369·4 | 1 690·9 | 574·8 | 322·9 |
| 345 | 864·8 | 1 361·9 | 1 689·0 | 572·1 | 325·5 |
| 350 | 1 031·2 | 1 360·5 | 1 687·7 | 572·9 | 328·8 |
| 355 | — | 1 358·9 | 1 686·1 | 569·3 | 331·2 |
| 360 | — | 1 357·2 | 1 692·1 | 569·1 | 331·7 |
| 365 | 765·0 | 1 359·3 | 1 686·5 | 572·1 | 329·8 |
| 370 | 655·6 | 1 349·0 | 1 681·5 | 572·6 | 333·3 |
| 375 | 566·4 | 1 346·7 | 1 670·1 | 572·8 | 334·5 |
| 380 | 572·7 | 1 344·2 | 1 690·2 | 576·9 | 337·3 |
| 385 | 573·5 | 1 341·6 | 1 691·3 | 577·7 | 336·4 |
| 390 | 577·6 | 1 338·8 | 1 694·1 | 580·4 | 335·5 |
| 395 | 581·2 | 1 335·8 | 1 700·8 | 587·3 | 330·9 |
| 400 | 584·6 | 1 328·7 | 1 703·0 | 595·0 | 322·7 |

$$T_{1,\text{on}} = 297 \cdot 2 \qquad T_{1,\text{max}} = 300 \cdot 7 \qquad T_{1,\text{off}} = 304 \cdot 6$$
$$T_{2,\text{on}} = 321 \cdot 4 \qquad T_{2,\text{max}} = 327 \cdot 9 \qquad T_{2,\text{off}} = 330 \cdot 6$$
$$T_{3,\text{on}} = 324 \cdot 2 \qquad T_{3,\text{max}} = 331 \cdot 4 \qquad T_{3,\text{off}} = 340 \cdot 0$$

The molar enthalpy of fusion was found to be $33 \cdot 4 \, \text{kJ mol}^{-1}$. The changes in the molar enthalpies corresponding to peaks 2 and 3 could not be determined because the two features overlapped. The total change in the molar enthalpy corresponding to both peaks, $\Delta H_{2,3}$, was found to be $8 \cdot 1 \, \text{kJ mol}^{-1}$. For the first, ill-pronounced peak at 300 K, preliminary determination yielded $\Delta H_1 = 0 \cdot 6 \, \text{kJ mol}^{-1}$. If it is assumed that the signal originated from the fusion of free DMSO, it follows that the sample contained 2·5 to 3·5 mass % of unbound DMSO. This would imply that, although the analysis indicated a molar solvent-to-salt ratio of 2·24, the crystals consisted of disolvate contaminated with free DMSO, either occluded on the surface or enclosed in the crystal cavities.

## $Zn(NO_3)_2.6 \, DMSO$

The temperature dependence of $C_p$ is represented in Fig. 1b. As for the disolvate, the record shows four endothermic peaks, but that at the lowest temperature is much more pronounced than its counterpart in Fig. 1a. The values of $C_p$ for various temperatures are given in Table I. The characteristic temperatures for the peak due to fusion are $T_{\text{on}} = 318 \cdot 7 \, \text{K}$, $T_{\text{max}} = 325 \cdot 6 \, \text{K}$, and $T_{\text{off}} = 330 \cdot 6 \, \text{K}$. The values (in K) for the other peaks are as follows.

$$T_{1,\text{on}} = 280 \cdot 0 \qquad T_{1,\text{max}} = 287 \cdot 9 \qquad T_{1,\text{off}} = 293 \cdot 5$$
$$T_{2,\text{on}} = 298 \cdot 5 \qquad T_{2,\text{max}} = 300 \cdot 8 \qquad T_{2,\text{off}} = 306 \cdot 4$$
$$T_{3,\text{on}} = 303 \cdot 7 \qquad T_{3,\text{max}} = 306 \cdot 0 \qquad T_{3,\text{off}} = 309 \cdot 0$$

The values found for enthalpy changes are $\Delta H_{\text{fus}} = 64 \cdot 5 \, \text{kJ mol}^{-1}$ and $\Delta H_{2,3} = 7 \cdot 2 \, \text{kJ mol}^{-1}$. The size of the first peak was not reproducible, and therefore the corresponding $\Delta H$ was not determined. The results of the measurements and their confidence intervals are summarized in Tables II and III.

## $Zn(NO_3)_2.8 \cdot 11 \, DMSO$

A plot of $C_p$ as a function of temperature is shown in Fig. 1c. As for the hexasolvate, there are four endothermic peaks, the first of which has characteristic values corresponding very well to the fusion of water, and the third is close to the third peak of the hexasolvate. The numerical calues of $C_p$ are listed in Table I. The characteristic temperatures of the peaks are summarized in Table II, and the calculated enthalpy values are given in Table III. Since the crystals were highly hygroscopic, we decided to determine, at least approximately, the value of $\Delta H_1$ and to describe this peak to

the fusion of water. On this assumption, the water content of the sample was found to be $0.8-1\%$. Thus, the prepared compound was octasolvate which had become slightly wetted during handling.

## NaNO$_3$.2·85 DMSO

A study of the glass-forming ability of the systems salt–dimethyl sulfoxide has shown that solutions of sodium nitrate in DMSO do not form glasses. By investigating the liquidus temperatures, Pacák and Sláma[7] found that the system forms a congruently melting solvate with an analytical composition of NaNO$_3$.2·7 DMSO. Since the glass-forming ability of concentrated electrolyte solutions is considered to be associated with significant salt solvation[3], the properties of the solvate have received special attention. The temperature dependence of $C_p$ for this congruently melting substance is represented in Fig. 2$a$. There is only one endothermic peak, with the following characteristic temperatures: $T_{on} = 303.2$ K, $T_{max} = 309.9$ K, and $T_{off} = 313.0$ K. The molar enthalpy of fusion has a value of 17·7 kJ mol$^{-1}$. The numerical results are summarized in Tables I, II and III.

TABLE II

Temperatures of fusion and transformation (K)

| Temperature | Solvate | | | | |
|---|---|---|---|---|---|
| | Zn–2DMSO | Zn–6DMSO | Zn–8DMSO | Na–3DMSO | Ag–DMF |
| | | | Fusion | | |
| $T_{on}$ | 348·4 ± 2·0 | 318·7 ± 0·7 | 311·5 ± 1·4 | 303·2 ± 0·3 | 315·0 ± 0·3 |
| $T_{max}$ | 358·3 ± 7·5 | 325·6 ± 0·4 | 319·5 ± 0·8 | 309·9 ± 0·7 | 319·4 ± 0·4 |
| $T_{off}$ | 364·6 ± 4·1 | 330·6 ± 0·5 | 324·1 ± 0·8 | 313·9 ± 0·7 | 325·3 ± 0·2 |
| | | | Solid-phase transformations | | |
| $T_{on}$ | 324·2 ± 3·6 | 303·7 ± 0·4 | 300·6 ± 0·9 | — | — |
| $T_{max}$ | 331·4 ± 4·0 | 306·0 ± 0·4 | 304·1 ± 1·4 | — | — |
| $T_{off}$ | 340·0 ± 2·8 | 309·0 ± 0·5 | 308·2 ± 1·5 | — | — |
| $T_{on}$ | 321·4 ± 3·1 | 298·5 ± 0·5 | 276·1 ± 0·2 | — | — |
| $T_{max}$ | 327·9 ± 1·2 | 300·8 ± 0·3 | 277·6 ± 0·2 | — | — |
| $T_{off}$ | 330·6 ± 6·7 | 306·4 ± 1·7 | 279·6 ± 0·4 | — | — |
| $T_{on}$ | 297·2 ± 0·5 | 280·0 ± 0·2 | 272·5 ± 0·2 | — | — |
| $T_{max}$ | 300·7 ± 1·4 | 287·9 ± 1·8 | 272·5 ± 0·2 | — | — |
| $T_{off}$ | 304·6 ± 2·7 | 293·5 ± 3·4 | 275·8 ± 0·5 | — | — |

## AgNO₃.DMF

Silver nitrate solutions show anomalous behaviour as regards glass formation. While aqueous solutions do not form glasses, the system $AgNO_3$–DMSO is glass-forming over a wide concentration range from 20 to 40 mol % $AgNO_3$. Glass formation has also been observed for solutions of $AgNO_3$ in dimethylformamide[3], over an even wider range from 2 to 35 mol % $AgNO_3$. The difference in the behaviour of silver nitrate in aqueous and nonaqueous solutions has been interpreted in terms of

TABLE III

Temperatures (K, upper line) and molar enthalpies (kJ mol$^{-1}$, lower line) of fusion and solid--phase transformation

| Solvate | Fusion | Solid-phase transformation |
|---------|--------|----------------------------|
| Zn–2DMSO | 348·4 | 321·1; 324·2 |
|  | 33·4 ± 2·6 | 8·1 ± 1·3 |
| Zn–6DMSO | 318·7 | 298·5; 303·7 |
|  | 64·5 ± 3·2 | 7·2 ± 3·7 |
| Zn–8DMSO | 311·5 | 300·6[a] |
|  | 61·4 ± 3·5 | 8·8 ± 6·1 |
| Na–3DMSO | 303·2 | — |
|  | 17·7 ± 0·9 | — |
| Ag–DMF | 315·0 | — |
| Ag–DMF | 13·7 ± 1·1 | — |

[a] Further transformations at 272·5 K and 276·1 K, $\Delta H = 5·4 \pm 1·6$ kJ mol$^{-1}$.
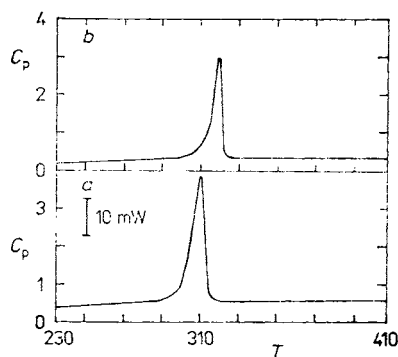


Fig. 2

Dependence of $C_p$ (kJ mol$^{-1}$ K$^{-1}$) of $NaNO_3 . 2·85$ DMSO (a) and $AgNO_3.DMF$ (b) on temperature $T$ (K)

different solvation of the salt. In water, $AgNO_3$ forms a simple eutectic system, without an indication of any congruently or incongruently melting hydrate. In DMSO, on the other hand, a congruently melting solvate of the composition $AgNO_3.DMSO$ has been identified[7].

A crystallosolvate of the composition $AgNO_3.DMF$ has been detected in the system $AgNO_3$–DMF, and its thermodynamic properties have been investigated in greater detail.

As seen from the plot of $C_p$ against temperature in Fig. 2b, the system gives a single endothermic peak, with the following characteristic temperatures: $T_{on} = 315\cdot0$ K, $T_{max} = 319\cdot4$ K, and $T_{off} = 325\cdot3$ K. The molar enthalpy of fusion is $13\cdot7$ kJ mol$^{-1}$. The numerical values are summarized in Tables I, II and III.

In calculating a phase diagram, it is important to know the temperature dependence of $C_p$ for both the solid and liquid phases. For our experimental $C_p - T$ data, the best least-squares fit was obtained for the linear dependence on the absolute temperature, $C_p = A + BT$. Introduction of a further term proved to be statistically insignificant. The constants $A$ and $B$ of this equation for both the solid and liquid phases are given in Table IV, along with the standard deviations. Also included in the table are the temperature ranges for which the constants were calculated. The confidence intervals were calculated for a significance level of $0\cdot05$. No statistically significant correlation

TABLE IV

Constants of the equation for $C_p$ (J mol$^{-1}$) as a function of temperature (K), and their standard deviations

| Solvate | Temperature interval | Phase | $A$ | $s(A)$ | $B$ | $s(B)$ |
|---|---|---|---|---|---|---|
| Zn–2DMSO | 240—290 | s | 70·410 | 7·599 | 1·1671 | 0·0286 |
|  | 375—400 | l | 308·752 | 20·550 | 0·6897 | 0·0530 |
| Zn–6DMSO | 240—270 | s | — 109·131 | 15·460 | 3·4286 | 0·0606 |
|  | 340—400 | l | 1 574·589 | 13·677 | —0·6066 | 0·0369 |
| Zn–8DMSO | 240—290 | s | — 278·624 | 28·735 | 5·3969 | 0·1099 |
|  | 335—375 | l | 1 840·907 | 41·468 | —0·4347 | 0·1195 |
| Na–3DMSO | 240—280 | s | — 276·623 | 22·395 | 2·8060 | 0·0860 |
|  | 320—355 | l | 832·601 | 26·163 | —0·7483 | 0·0774 |
| Ag–DMF | 240—285 | s | — 129·678 | 4·473 | 1·4187 | 0·0170 |
|  | 330—380 | l | 211·411 | 9·747 | 0·3305 | 0·0274 |

could be found for the molar enthalpies. The molar enthalpies of the solid phase transformations were close to a value of 5 kJ mol$^{-1}$.

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