
EVALUATION OF PHASE DIAGRAMS OF SOLVATE-FORMING BINARY SYSTEMS: THE SYSTEMS DIMETHYL SULPHOXIDE-LITHIUM NITRATE AND DIMETHYL SULPHOXIDE-CALCIUM NITRATE

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Phase diagrams of the solidus-liquidus type for two dimethylsulphoxide-nitrate systems have been evaluated using a rigorous method proposed previously. As both the systems involve the formation of solvates, the problem solved is one of simultaneous phase and chemical equilibria. The evaluation was performed by optimization of chosen adjustable parameters, namely the equilibrium constant of solvation, interaction parameters in expression for excess free energy, and the temperature and heat of fusion of pure crystalline solvate. In addition, a suitable model had to be found for the activities of ideal mixture components for the given type of system. The paper presents the first experimental data for the phase diagram of the system dimethyl sulphoxide-lithium nitrate.

Phase diagrams of the solidus-liquidus type for the systems ionic salt-polar solvent (water or dimethyl sulphoxide) are characterized by immiscibility in the solid phase and by frequent occurrence of solvates. When obtained by the polythermal method, experimental data on a phase diagram consist, in general, of pairs of temperatures corresponding to given concentrations of a liquid mixture. The higher temperatures indicate the points at which the solid phase begins to settle out, and make up the so-called liquidus curve. The lower temperatures represent the points at which the residual mixture of eutectic composition solidifies; in a phase diagram, these points are usually connected by a horizontal line. The eutectic points are represented by the points of intersection of the liquidus curves, their temperature coordinates being, in addition, indicated by the position of the horizontal lines.

There is an opinion that phase diagrams should be measured so as to obtain such density of points that the fitting of a curve is redundant. Some authors have published phase diagrams containing only points, without attempting to draw any lines through them. There is, however, an evident need for phase diagrams in the form of continuous curves, and this not only for the purposes of interpolation. As any other measurements, experimental points of phase diagrams are subject to experimental errors, and the objective of evaluation is to eliminate these errors. To perform the evaluation by an empirical method, whether graphical or numerical, is the best way how to impair a phase diagram by subjective or systematic errors.

In a previous paper¹ we proposed a method for evaluating phase diagrams of systems with compound formation, and tested the method on systems of anhydrous

salts. In another paper² we used the method to evaluate the phase diagram for the system water–dimethylsulphoxide (DMSO). The same aim, *i.e.* evaluation of phase diagrams for the systems polar solvent–salt, has been pursued independently by Tenu and Counioux³, who have proposed a semiempirical method of evaluating phase diagrams for some systems containing water. However, their method does not treat the problem as one of equilibrium chemical reaction.

Model of Ideal Mixture

The systems of DMSO and a nitrate may generally be treated as the system solvent–salt, A–B ($B = M_pX_q$), with the salt completely dissociated into ions. According to Haase's model⁴, the number of possible configurations in such a system may be defined as the number of configurations of all particles regardless of their charges, thus as

$$W_H = \frac{(N_A + vN_B)!}{(N_A)! (vN_B)!}, \quad (1)$$

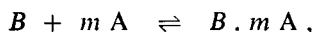
where $v = p + q$. According to Temkin's model⁵, the number of configurations in the system can be determined by assuming that the solvent molecules are distributed between the cation and anion sublattices in the ratio p/q :

$$W_T = \frac{(pN_A/v + pN_B)! (qN_A/v + qN_B)!}{(pN_A/v)! (pN_B)! (qN_A/v)! (qN_B)!}. \quad (2)$$

It can be proved that $W_H = W_T$.

Taking account of solvate formation, we may modify the concepts which lead to identifying the number of configurations in the system: configurations will now be formed both by solvated ions and by unsolvated ions and solvent molecules, the number of the last-mentioned components being reduced by those solvent molecules which take part in the solvation. For these purposes, the concepts of Haase's model may be used to good advantage, because by doing so one avoids consideration of preferential solvation of cations or anions.

If m solvent molecules take part in solvation,



the number of configurations is

$$W = \frac{(vN_B + N_A - mN_C)!}{(vN_B - vN_C)! (vN_C)! (N_A - mN_C)!}, \quad (3)$$

where the subscript C indicates the solvate. If we denote by N_A^0 and N_B^0 the numbers of particles introduced into the system, we may write for the numbers of particles present after establishment of equilibrium in the system: $N_A = N_A^0 - mN_C$; $N_B = N_B^0 - N_C$. The ideal Gibbs energy of mixing in dimensionless form, ψ , may be expressed in terms of the number of configurations, and hence as a function of $x = N_B^0/(N_A^0 + N_B^0)$ and $y = N_C/(N_A^0 + N_B^0)$:

$$\begin{aligned}\psi &= \Delta G^*/RT = \ln W/(N_A^0 + N_B^0) = \\ &= (vx - vy) \ln (vx - vy) + (1 - x - my) \ln (1 - x - my) + \\ &\quad + vy \ln (vy) - (vy + 1 - x - my) \ln (vx + 1 - x - my).\end{aligned}\quad (4)$$

Assuming that the Gibbs energy of mixing can be expressed as

$$\Delta G^*/RT = (1 - x - my) \ln a_A^* + (x - y) \ln a_B^* + y \ln a_C^*, \quad (5)$$

the activities of ideal mixture components are given by

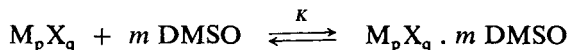
$$a_A^* = (1 - x - my)/(vx + 1 - x - my) \quad (6a)$$

$$a_B^* = [(vx - vy)/(vx + 1 - x - my)]^v \quad (6b)$$

$$a_C^* = [(vy)/(vx + 1 - x - my)]^v. \quad (6c)$$

Principle of the Method for Evaluating Phase Diagrams

We assume that the binary system DMSO-salt involves a solvate-producing equilibrium reaction,



or in simple notation,



where p and q are the stoichiometric coefficients of an ionic compound (*i.e.*, the numbers of cations and anions, respectively), and m is the number of solvent molecules. The true equilibrium constant of the reaction, K , may be expressed in terms of the activities of the components A, B and C as

$$K = a_C/a_B a_A^m. \quad (7)$$

Following Haase's concept, we assume that the activities may be expressed as products of activities of ideal mixture components and activity coefficients,

$$a_i = a_i^* \gamma_i, \quad (8)$$

both the activity of an ideal mixture component a_i^* and the activity coefficient γ -being, in general, functions of concentration (γ_i , in addition, a function of temperature). The concentration dependence of a_i^* has been dealt with in the preceding section.

To express the concentration dependence of $\ln \gamma_i$, we assume, as in a previous paper¹, that the binary system in question may be regarded as a ternary one with salt, DMSO and solvate as the components. If the equilibrium is shifted to favour the solvate, the term corresponding to the salt-DMSO interaction may be neglected, and the molar excess Gibbs energy may be expressed in terms of two interaction parameters α and β ,

$$\Delta G^E = \alpha x_A x_C + \beta x_B x_C. \quad (9)$$

If

$$\Delta G^E/RT = x_A \ln \gamma_A + x_B \ln \gamma_B + x_C \ln \gamma_C, \quad (10)$$

then by applying the Gibbs-Duhem relation we obtain for the concentration dependences of $\ln \gamma_i$

$$\ln \gamma_A = [\alpha x_C(1 - x_A) - \beta x_B x_C]/T \quad (11a)$$

$$\ln \gamma_B = [-\alpha x_A x_C + \beta x_C(1 - x_B)]/T \quad (11b)$$

$$\ln \gamma_C = [\alpha x_A(1 - x_C) + \beta x_B(1 - x_C)]/T. \quad (11c)$$

From mass balances, the concentrations of ternary system components x_A , x_B and x_C are related to the concentrations of binary system components x ($\equiv x_{\text{salt}}$) and y (solvate concentration) by

$$\begin{aligned} x_A &= (1 - x - my)/(1 - my) \\ x_B &= (x - y)/(1 - my) \\ x_C &= y/(1 - my) \end{aligned} \quad (12a)$$

or

$$x_A = 1 - x - mx x_C \quad x_B = x - (1 - mx) x_C. \quad (12b)$$

With known interaction parameters α and β and equilibrium constant K , we can calculate the equilibrium composition for each pair of (x, T) values by using Eqs (7), (8), (6), (11) and (12b) and solving iteratively for y .

Knowing the equilibrium composition, and hence activities of the components, we can calculate the theoretical liquidus temperature using the LeChatelier-Scherer equation⁶

$$\ln a_i = \frac{\Delta H_{fi}}{R} \left(\frac{1}{T_{fi}} - \frac{1}{T} \right) + \frac{\Delta C_{pj}}{R} \left(\frac{T_{fi}}{T} - 1 - \ln \frac{T_{fi}}{T} \right), \quad (13)$$

whence

$$T = \Delta H_{fi} / \left[\frac{\Delta H_{fi}}{T_{fi}} - R \ln a_i + \Delta C_{pi} \left(\frac{T_{fi}}{T} - 1 - \ln \frac{T_{fi}}{T} \right) \right]. \quad (14)$$

For non-zero ΔC_{pi} , T is calculated by an iterative technique¹¹, the first estimate being obtained from Eq. (14) for $\Delta C_{pi} = 0$.

Liquidus temperatures calculated in this way were compared with experimental values, either graphically or numerically in optimization of adjustable parameters (equilibrium constant and interaction parameters). The criterion used in the optimization was a minimum in the sum of the squares of the deviations of temperatures.

For liquidus temperatures corresponding to the solvate-solution equilibrium ($i = C$), additional two adjustable parameters entered in, namely the temperature and heat of fusion of hypothetical pure solvate. In optimization, the temperature of fusion was adjusted so that the calculated liquidus temperature at the concentration corresponding to the solvate stoichiometry matched the experimental value. The optimum value of ΔH_{fC} was then obtained by minimization of the sum of the squares of deviations, summing over liquidus temperatures of the solvate only.

When the proposed method is used, there may be a complication in that the method requires, in principle, values of T_{fB} and ΔH_{fB} of pure salt, but the liquidus curve corresponding to the separation of anhydrous salt, if measured at all, does not reach nearly as far. Then a small error for example in ΔH_{fB} gives rise to large errors in liquidus temperatures. Another case that may arise is a modification change occurring between the liquidus temperature and the temperature of fusion of pure salt. Finally, lack of knowledge on $(\Delta C_p)_B$ of pure salt may also lead to errors in calculated liquidus temperatures. Therefore, it has turned out expedient to modify the optimization program so as to search additionally for optimum values of T_{fB} and/or ΔH_{fB} or in addition $(\Delta C_p)_B$. So obtained values may be regarded as hypothetical (if the relevant phase is not capable of equilibrium fusion), as corrected (when the differences are small and/or when the reliability of one of the values is suspected) or ultimately, as parameters without any physical significance. In the last named case, one merely attempts to describe the measured region of liquidus curve by a formally adequate equation.

EXPERIMENTAL

The phase diagram of the system DMSO-LiNO₃ was measured by the last-crystal-dissolution method. As the system is easy to supercool and hence reluctant to crystallize, the crystallization in most cases had to be induced by introducing a seed crystal of the solid phase. As the temperature was increased, the crystals dissolved, and the temperature at which the last crystal disappeared was taken as the liquidus temperature. The method has been described in detail by Pacák⁷; the accuracy of measurement is 1K. Lithium nitrate (Merck) was dried in a vacuum at 90°C for 24 h and stored in a desiccator. DMSO (dry, Merck) was used without further treatment.

The mole percentages of LiNO_3 and the liquidus temperatures measured for solid phase coexisting with solution were as follows:
for solid DMSO

4.76	9.09	11.1	13	14.3	mol%
13.5	8	5.5	4	1	°C

for solid solvate

14.3	15.5	16.6	20	20	23	25	mol%
3.5	9.5	12	16.5	17	18	18	°C

for solid LiNO_3

25	26	30	33	mol%
14.5	18.5	36	53.5	°C

The data indicate that the system involves the formation of a solvate with the stoichiometric ratio $\text{LiNO}_3 : \text{DMSO} = 1 : 3$, by analogy to the trihydrate formed with water used as solvent. The liquidus temperature at the concentration corresponding to the trisolvate composition was determined experimentally as 18°C, but a correction to 19°C provided a better fit of the theoretical curve to all the points. The data used for pure LiNO_3 were as follows:⁸ temperature of fusion, 254°C (527 K); $\Delta H_f/R = 3\,070$ K ($\Delta H_f = 6\,100$ cal/mol); and $\Delta C_p/R = 0.6$.

Experimental data for the phase diagram of the system $\text{DMSO}-\text{Ca}(\text{NO}_3)_2$ were taken from a previous paper⁹. Like the analogous aqueous system, this system forms a tetrasolvate. The temperature of fusion of the tetrasolvate was estimated from the experimental data as 60°C. The data used for pure $\text{Ca}(\text{NO}_3)_2$ were as follows:¹⁰ temperature of fusion, 561°C (834 K), and $\Delta H_f/R = 2\,818$ K ($\Delta H_f = 5\,600$ cal/mol).

Thermochemical data for pure DMSO were the same as used in a previous paper², namely, temperature of fusion, 18.55°C (291.7 K); $\Delta H_f/R = 1\,728$ K; $\Delta C_p/R = 4$ at T_f , the slope of the ΔC_p vs T plot¹¹ being 0.03 K^{-1} .

RESULTS AND DISCUSSION

Experimental data for each liquidus curve (DMSO, solvate, salt) were evaluated separately. The optimized parameters were varied either sequentially (gradient method) or simultaneously (Gauss-Newton method with Marquardt's modification). In computer optimization, we used experience presented in a recently published book¹². For each chosen combination of interaction parameters we first calculated equilibrium concentrations of components, and then evaluated liquidus temperatures and compared them with experimental values. The overall sum of the squares of the deviations of temperatures, whose minimum was the criterion of optimization, consisted of three contributions, in accordance with division of the data into groups. The contribution associated with the liquidus curve of solvate was, in addition, minimized by choosing an optimum value of ΔH_{fC} . Table I gives optimum values of equilibrium constant, interaction parameters and ΔH_{fC} , along with statistical characteristics, *i.e.* the overall sum of the square of the deviations of temperatures

and the standard deviations for the three contributions. Standard deviations of the interaction parameters were obtained using the Gauss–Newton method in the usual manner¹². The standard deviations s_A , s_B and s_C for both the systems studied are less than 1 K, consistent with the accuracy of measurements (± 1 K). Figs 1 and 2 provide a comparison between experimental points and theoretical liquidus curves based on the parameters given in Table I. Also shown are metastable regions of the

TABLE I
Optimized parameters and statistical characteristics for phase diagrams of DMSO–salt systems

Salt	$\ln K$	Interaction parameters				$\frac{\Delta H_{fC}}{R}$ K	T_{fC} K	S	s_A	s_B	s_C
		α	s_α	β	s_β						
LiNO_3	4.875	211	17	-1.518	46	2.342	383	9.27	0.47	0.55	0.99
$\text{Ca}(\text{NO}_3)_2$	10.03	515	15	-0.786	130	1.721	424	9.61	0.34	0	0.88

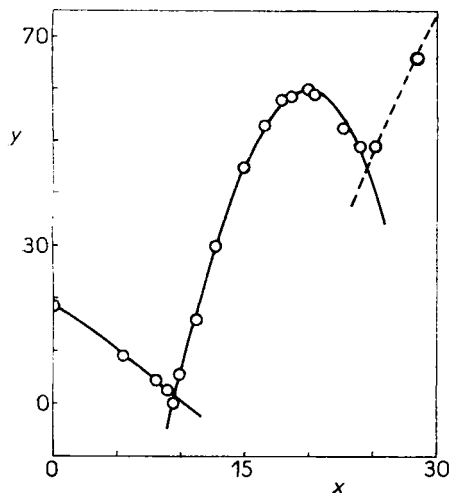


FIG. 1
Phase diagram of the system DMSO– LiNO_3 . Calculated liquidus curves are based on parameters given in Table I. (x mol% LiNO_3 , temperature y , °C)

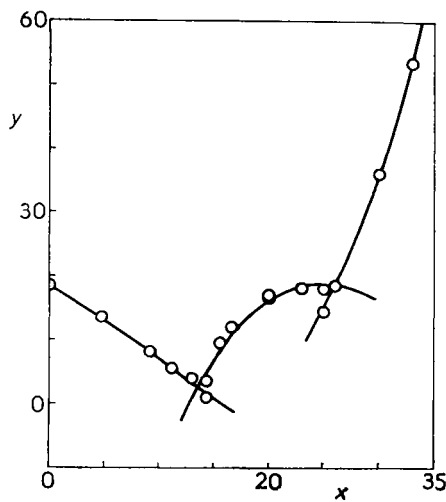


FIG. 2
Phase diagram of the system DMSO– $\text{Ca}(\text{NO}_3)_2$. Experimental points from ref.⁹, calculated liquidus curves based on parameters given in Table I. (x mol% $\text{Ca}(\text{NO}_3)_2$, temperature y , °C)

phase diagrams defined by extensions of the liquidus curves beyond their points of intersection (eutectic points).

For the system DMSO–LiNO₃, the above mentioned variant of evaluation with the temperature of fusion and/or ΔH_f of pure salt as additional adjustable parameters was also tested. This, however, did not lead to any appreciable reduction in the sum of the squares of the deviations.

The phase diagram of the system DMSO–Ca(NO₃)₂ was evaluated without considering the two points relating to the highest concentrations of the salt (Fig. 2). The initial assumption that these points belonged to the liquidus curve of anhydrous salt turned out to be erroneous; they very likely belong to the liquidus curve of a solvate poor in DMSO, probably the disolvate. The fact that the data treated include no points of the liquidus curve of anhydrous salt is reflected in a comparatively greater standard deviation of the second interaction parameter.

LIST OF SYMBOLS

a_i	activity of i -th component
a_A, a_B, a_C	activities of solvent, salt and solvate, respectively
a_A^*, a_B^*, a_C^*	activities of ideal mixture components
A	subscript indicating solvent
B	subscript indicating salt
C	subscript indicating compounds (solvate)
ΔC_p	difference in molar heat capacities of solid and liquid components
ΔG^E	excess Gibbs energy
ΔG^*	ideal Gibbs energy of mixing
H	subscript indicating Haase's model
ΔH_{fi}	enthalpy of fusion of i -th component
$\Delta H_{fB}, \Delta H_{fC}$	enthalpies of fusion of salt and solvate, respectively
K	equilibrium constant
m	number of solvent molecules in stoichiometric formula of solvate
M	cation
N	number of particles
N_A, N_B, N_C	numbers of particles of solvent, salt and compound, respectively
N_A^0, N_B^0	initial numbers of solvent and salt particles, respectively
p	number of cations in stoichiometric formula of salt
q	number of anions in stoichiometric formula of salt
R	gas constant
s_A, s_B, s_C	standard deviations for liquidus curves of individual components
T	subscript indicating Temkin's model
T	temperature in K
T_{fi}	temperature of fusion of i -th component
T_{fA}, T_{fB}, T_{fC}	temperatures of fusion of solvent, salt and solvate, respectively
W	number of configurations
X	anion
x	mole fraction of salt in binary system

x_A, x_B, x_C	mole fractions of solvent, salt and solvate, respectively, in ternary system
y	mole fraction of solvate in binary system
α	interaction parameter in expression for ΔG^E
β	interaction parameter in expression for ΔG^E
γ_i	activity coefficient of i -th component
$\gamma_A, \gamma_B, \gamma_C$	activity coefficients of solvent, salt and solvate, respectively
$v = p + q$	
$\psi := \Delta G^*/RT$	

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