CALCULATION OF THE PHASE DIAGRAM FOR THE SYSTEM WATER–DIMETHYL SULPHOXIDE

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Liquidus curves of the phase diagram for the system water–dimethyl sulphoxide (DMSO) have been calculated in such a way as to give a good fit to experimental data for the phase diagram. The calculation is based on the assumption of an equilibrium chemical reaction yielding DMSO. 3 H_2O, and on the relation for the excess Gibbs energy in a ternary system composed of the two starting components and their compound. The data for the temperature dependence of the difference in the heat capacities of the liquid and solid phases of the pure components in the supercooling region have been obtained by extrapolation of experimental data in the case of DMSO, and for water by adopting published data measured down to $-40°C$ and by estimating their further trend.

The use of dimethyl sulphoxide (DMSO) in biology and medicine[1] has, *inter alia*, stimulated interest in the system water–DMSO. A part of the information about the system is the phase diagram of the solid–liquid type. The first study[2] in this direction presented only parts of the phase diagram outside the range 13 to 48 mol% DMSO where a great tendency for the system to supercooling had been observed.

A subsequent study[3] provided more detailed data and discovered the existence of a congruently melting hydrate, DMSO. 3 H_2O, which is formed within the above composition range. However, the authors presented their results only in graphical form; numerical values of the experimental points on the phase diagram used in the present work have been read off from the graph.

The usual procedure in the construction of liquidus curves is to fit a curve to experimental points either in a graphical way or numerically, using a least-squares polynomial fitting routine. It is well known, however, that neither a polynomial nor any other simple equation is adequate to describe a liquidus curve. Frequently, the relationships describing liquidus curves cannot even be expressed in an explicit form though the rules that are followed are well known. The stumbling block is the complexity of the calculations involved, necessitating the application of computerized optimization methods. The present work is an attempt at treating experimental data of a phase diagram in a consistent manner based on rigorous theoretical relations, and with the use of computerized techniques.

THEORETICAL

Phase Equilibrium

A solid–liquid equilibrium is generally described by the Le Chatelier–Schreder equation[4] of the differential form

$$\text{d} \ln a_i = \Delta H_{fi}/RT^2 \, \text{d}T \,, \tag{1}$$

where a_i is the activity of component i in the liquid phase in equilibrium with the pure solid component, ΔH_{fi} is the change of enthalpy of component i associated with its melting, and R is the gas constant. Assuming that ΔH_f is independent of temperature yields the simplest integrated form of Eq. (1),

$$\ln a_i = \frac{\Delta H_{fi}}{R} \left(\frac{1}{T_{fi}} - \frac{1}{T} \right), \tag{2}$$

where T_{fi} is the melting point of pure component i and ΔH_{fi} refers to this temperature. Considering that ΔH_f varies with temperature, at constant ΔC_p, according to Kirchhoff's equation $\left(\text{d}(\Delta H_f) = \Delta C_p \, \text{d}T \right)$, we obtain a more rigorous form of the Le Chatelier–Schreder equation,

$$\ln a_i = \frac{\Delta H_{fi}}{R} \left(\frac{1}{T_{fi}} - \frac{1}{T} \right) + \frac{\Delta C_p}{R} \left(\frac{T_{fi}}{T} - 1 - \ln \frac{T_{fi}}{T} \right). \tag{3}$$

There are cases, such as ours, where the assumption of temperature-independent ΔC_p proves to be unrealistic. If we assume a general temperature dependence of ΔC_p, specified by tabular data or by a functional relationship (linear or nonlinear) such as

$$\Delta C_p = (\Delta C_p)_{T_f} + b(T_f - T)^n \,, \tag{4}$$

we must use the general form of the Le Chatelier–Schreder equation

$$\ln a_i = \frac{\Delta H_{fi}}{R} \left(\frac{1}{T_{fi}} - \frac{1}{T} \right) + \frac{1}{R} \left\{ \frac{1}{T} \int_{T}^{T_{fi}} \Delta C_p \, \text{d}T - \int_{T}^{T_{fi}} \frac{\Delta C_p}{T} \, \text{d}T \right\}. \tag{5}$$

Analytical solution of the above integral equation allowing for temperature dependence of ΔC_p has been the subject of a previous publication[5]. In most cases, unfortunately, we can determine ΔC_p experimentally at a single temperature, T_{fi}, where the solid and liquid phases coexist in equilibrium. In order to determine the temperature dependence of ΔC_p below the melting point, we need

to know how C_p of supercooled liquid varies with temperature. However, most pure components show little tendency to supercooling, so that the only possibility s to extrapolate C_p data for the liquid phase below T_f.

Chemical Equilibrium

Since the water–DMSO phase diagram exhibits a single maximum (at 25 mol% DMSO), we assume that the system involves a single equilibrium reaction

$$DMSO + 3\, H_2O \;\rightleftharpoons\; DMSO.3\, H_2O$$

The equilibrium composition in the system is given by the expression

$$K = a_C/(a_{DMSO} a_{H_2O}^3) \,, \tag{6}$$

where K is the true equilibrium constant, and a_C, a_{DMSO} and a_{H_2O} are the activities of the compound, DMSO and H_2O, respectively. The relationship $a_i = x_i \gamma_i$ is assumed to hold for the activities of the components, with γ_i indicating the activity coefficient, and x_i the mole fraction. Denoting by x the mole fraction of DMSO in the initial binary mixture, and by y the amount of compound C per one mol of the binary mixture, we can write for the mole fractions of the three components present at equilibrium

$$x_{H_2O} = (1 - x - 3y)/(1 - 3y) \,; \quad x_{DMSO} = (x - y)/(1 - 3y) \,; \quad x_C = y/(1 - 3y) \tag{7}$$

or

$$x_{H_2O} = 1 - x - 3xx_C \,; \quad x_{DMSO} = x - x_C + 3xx_C \,. \tag{8}$$

As in a previous paper[6] where the method of phase diagram calculation was proposed, we consider the system described above as a ternary one. It goes without saying that the concentration of DMSO trihydrate is not an independent variable, being determined by the equilibrium constant.

Nonideality of the System

We assume that the excess Gibbs energy of the ternary system can be expressed as

$$\Delta G^E/RT = \alpha x_1 x_2 + \beta x_1 x_3 + \delta x_2 x_3 \tag{9}$$

where α, β, and δ are the interaction parameters. Using the well-known relationship between ΔG^E and activity coefficients of components,

$$\Delta G^{E}/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 + x_3 \ln \gamma_3 , \qquad (10)$$

we can express the activity coefficients in terms of the interaction parameters:

$$\ln \gamma_1 = \alpha(1 - x_1) x_2 + \beta(1 - x_1) x_3 - \delta x_2 x_3 \qquad (11a)$$

$$\ln \gamma_2 = \alpha x_1(1 - x_2) - \beta x_1 x_3 + \delta(1 - x_2) x_3 \qquad (11b)$$

$$\ln \gamma_3 = -\alpha x_1 x_2 + \beta x_1(1 - x_3) + \delta x_2(1 - x_3) \qquad (11c)$$

Method of Phase Diagram Evaluation

The method requires an estimation of the values of the equilibrium constant K and the interaction parameters α, β, and δ. Knowing α, β, and δ, we can calculate from Eq. *(11)* the activity coefficients of the components. From these and the equilibrium constant we then calculate the equilibrium composition or the concentrations of all the components in the system for such compositions of the initial binary system as found in the experimental phase diagram. Using the Le Chatelier–Schreder equation in the form *(2)*, *(3)* or *(5)*, we can calculate theoretical liquidus temperatures for the components and compare them with the experimental values.

The criterion adopted for goodness of fit was the sum of the squares of differences between theoretical and experimental liquidus temperatures for all experimental points of the phase diagram. In other words, the parameters K, α, β, and δ were adjusted so that the sum of the squares of differences in the temperatures was a minimum.

A somewhat more complicated situation was encountered in the case of the third component, the compound DMSO.3 H_2O. Since the association reaction proceeds to an equilibrium which does not lie quite over to the right in favour of the product, the activity a_C at $x = 0.25$ is not equal to unity. For this reason, a hypothetical melting point, T_{fC}^{hyp}, must be considered, which would correspond to pure component C. Its value was estimated by allowing the calculated temperature of liquidus at $x = 0.25$ to match exactly the experimental value. Another unknown quantity, ΔH_{fC} of the hypothetical pure component C was obtained by optimization using the criterion of the minimum in the sum of squares of differences in temperatures for the liquidus curve corresponding to this component. Because of the considerable amount of computation involved, the parameters K, α, β, δ, and ΔH_{fC} had to be estimated using the computerized optimization technique.

Heat Capacities of Water and DMSO

Owing to the accuracy of the experimental data for the phase diagram, and to the relatively large temperature range involved (extending, for DMSO, from 18 to $-73°C$) it is necessary to allow for variation in ΔC_p as a function of temperature.

C_p data for DMSO (Fig. 1) have been taken from recent work of Clever and Westrum[7]. The temperature dependences of C_p for solid and liquid DMSO over the given temperature range are well represented by the equations $(t_f = 18.55°C)$

$$C_p(s)/R = 2.46 + 0.0407T \qquad (12a)$$

$$C_p(l)/R = 15.15 + 0.0110T \qquad (12b)$$

so that

$$\Delta C_p/R = 12.69 - 0.0297T \approx 4 + 0.03(T_f - T). \qquad (12c)$$

In fitting data for solid DMSO the sudden increase in C_p near the melting point has been disregarded. From the paper cited above we have also adopted the value for ΔH_f, $\Delta H_f = 3\ 434$ cal/mol (hence $\Delta H_f/R = 1\ 728$ K).
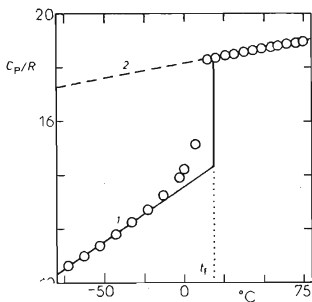

FIG. 1

Temperature dependence of C_p for DMSO (ref.[7]). *1* linear fit for DMSO(s) according to Eq. (*12a*); *2* linear fit for DMSO(l) according to Eq. (*12b*); broken line — extrapolation for $T < T_f$
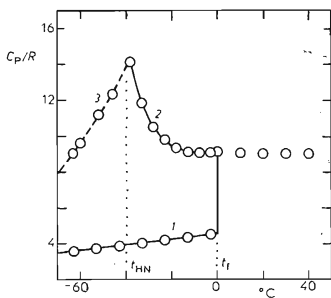
FIG. 2

Temperature dependence of C_p for water[8,9]. *1* linear fit for H_2O(s) according to Eq. (*13a*); *2* fit for H_2O(l) in the range 0 to $-40°C$ according to Eq. (*13b*); *3* extrapolation for H_2O(l) for $t < -40°C$, prediction based on ref.[9]

C_p data for ice (Fig. 2) have also been taken from the literature[8]. Over the given temperature range, they are very well fitted by the linear relationship

$$C_p(s)/R = 4\cdot559 - 0\cdot01586(T_f - T).\qquad(13a)$$

From the same source[8] we have taken the values $\Delta C_p = 8\cdot911$ cal K^{-1} mol^{-1} (hence $\Delta C_p/R = 4\cdot484$) and $\Delta H_f = 1\,436\cdot3$ cal/mol so that $\Delta H_f/R = 722\cdot8$ K.

Extrapolation of the C_p data for water from the range $0 - 100°C$ below the melting point suggests a steep increase in C_p as water is supercooled. This has recently been confirmed experimentally by Angell and coworkers[9] who used the DSC technique for measurements in the supercooled state, but only down to $-38°C$ because of homogeneous nucleation starting at $-40°C$. C_p data for supercooled water as measured by Angell and coworkers[9] (curve 2, Fig. 2) are well represented by

$$C_p(1)/R = 9\cdot043 + 2\cdot37 \cdot 10^{-6}(T_f - T)^4\qquad(13b)$$

Combining Eqs (13a) and (13b) yields the relation for the variation of ΔC_p of water over the temperature range from 0 to $-40°C$:

$$\Delta C_p/R = 4\cdot484 + 0\cdot01586(T_f - T) + 2\cdot37 \cdot 10^{-6}(T_f - T)^4\qquad(13c)$$

On the theoretical argument given by Angell and coworkers[9] it is expected that ΔC_p will decrease as water is still further supercooled. The prediction for the variation in ΔC_p in this region is represented by curve 3 in Fig. 2. Accordingly, the values of $\Delta C_p/R$ corresponding to the four points on the liquidus curve for water at $-46°$, $-52°$, $-60°$, and $-63°C$ have been estimated at 8·5, 7·5, 6, and 5·5, respectively.
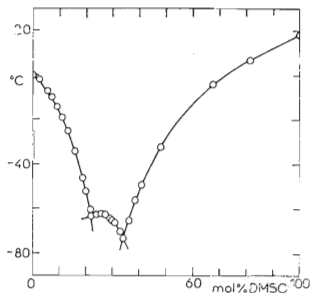
Fig. 3

Phase diagram for the system H_2O–DMSO. Circles — experimental points[3], curves — calculation by the proposed method

TABLE I
Experimental and calculated temperatures of liquidus of the system H_2O-DMSO

Solid phase: H_2O (s)

mass % DMSO	10	20	25	30	35	40	45	50	52	54·5	55[a]
t(exp), °C	− 2	− 7	− 10	− 14	− 19	− 25	− 34	− 46	− 52	− 60	− 63
t(calc), °C	− 2·93	− 7·46	− 10·61	− 14·50	− 19·58	− 25·82	− 34·10	− 45·57	− 51·53	− 60·07	− 62·70

Solid phase: DMSO . 3 H_2O (s)

mass % DMSO	55[a]	58	59·1	62	64	65	66	68	69[b]
t(exp), °C	− 63	− 62·5	− 62	− 62·5	− 64	− 65	− 66	− 70	− 73
t(calc), °C	− 63·21	− 62·20	− 62	− 62·46	− 64·17	− 65·25	− 66·47	− 70·12	− 72·56

Solid phase: DMSO (s)

mass % DMSO	69[b]	71	73	75	80	90	95
t(exp), °C	− 73	− 65	56	− 49	− 32	− 4	7
t(calc), °C	− 73·03	− 64·31	− 56·69	− 49·29	− 31·56	− 4·30	6·96

[a] H_2O-DMSO.3 H_2O eutectic, [b] DMSO.3 H_2O-DMSO eutectic.

RESULTS AND DISCUSSION

In optimization of all the adjustable parameters, the minimum in the sum of the squares of differences in the liquidus temperatures was found at 5·337, with contributions from the liquidus curves of water, DMSO and DMSO trihydrate of 3·332, 1·325 and 0·681, respectively. The respective standard deviations were 0·55, 0·435 and 0·275, with an overall standard deviation of 0·43 K.

The best fit values of the parameters were as follows:

$$\ln K = 0.77 \, ; \quad \alpha = -518 \, ; \quad \beta = -815 \, ; \quad \delta = -1\,365.$$

At $x = 0.25$ and $t = -62°C$ the concentration of the trihydrate $x_C = 0.17$, and its activity $a_C = 0.01$. The relatively low activity value is consistent with a high hypothetical melting point of undissociated trihydrate which has been calculated as 551 K (278°C); $\Delta H_{fC}/R$ has a value of 1 555 K.

The calculated values of liquidus temperatures are listed in Table I together with the experimental values, and plotted in Fig. 3. The liquidus curves are extended beyond the eutectic points into the metastable regions of the phase diagram.

This work was undertaken to support the view that besides providing ultimate information about phase equilibria in a system, the phase diagram can serve as a source of additional information about interactions between species making up the system. If allowance is made for all the factors that are involved, then an additional outcome of this approach is a smooth or even a theoretical phase diagram.

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