

SOLID-LIQUID AND LIQUID-LIQUID EQUILIBRIUM IN THE FORMAMIDE-ACETOPHENONE SYSTEM

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Solid-liquid (s-l) and liquid-liquid (l-l) equilibrium was determined in the binary system formamide-acetophenone. The s-l equilibrium was measured by recording time-temperature cooling and warming curves. The l-l equilibrium was obtained in a wide range of temperatures by the turbidity method. A considerable supercooling preceding solidification made it possible to examine metastable l-l equilibrium yet at temperatures lower than the solidus ones. Activity coefficients evaluated from the stable region of l-l equilibrium were correlated by Novák's modification of the Wilson equation. Calculation of the s-l equilibrium was performed with the obtained parameters. Heat capacity of solid and liquid acetophenone was measured and its dependence on temperature is given. The transition enthalpy between two solid modifications of acetophenone is also given.

Keywords: Acetophenone; Formamide; Solid-liquid equilibria; Liquid-liquid equilibria; Metastable; Heat capacity; Transition enthalpy; Thermodynamics.

Since the Bronze Age mankind knows that mixing of two or more substances can lead to surprising results. Phase diagrams which are measured and studied also in our laboratory provide fundamental information on the equilibrium relations among different compounds. Our interest was especially focused on systems of strongly associating compounds. Binary phase equilibria provide information on the intermolecular forces between solvent and solute and s-l equilibria, eventually, on the formation and nature of intermolecular compounds in the solid phase. We found an addition compound in the solid phase in the systems propanoic acid-trifluoroacetic acid¹, acetic acid-trichloroacetic acid² and acetic acid-formamide³. Although acetophenone is known to associate with acetic acid⁴, a simple sagged curve was obtained in the acetic acid-acetophenone system³ with small positive deviations from Raoult's law in the liquid phase.

The system formamide–acetophenone considered in this work behaves quite differently. The solid–liquid equilibrium involves two compounds that are immiscible in the solid phase and not only do not form a stoichiometric compound, but are partially miscible in the liquid phase.

EXPERIMENTAL

Chemicals

The best Aldrich and Fluka chemicals were used. Acetophenone was 99% Aldrich product, formamide >99.5% Fluka product. Purity of these substances was tested by determination of their melting points. The melting point of acetophenone was 292.69 K and that of formamide 275.54 K. These values were in a good agreement with values 292.77 and 275.70 K tabulated by Riddick et al.⁵ Both substances were used without further purification.

Methods and Measurements

Solid–liquid, liquid–liquid and calorimetric data were measured and are presented here. The s–l equilibrium was obtained from time–temperature cooling and melting curves. Nineteen solutions of acetophenone and formamide ranging in mole fraction from 0 to 1 were prepared by mass, so that composition could be calculated with an accuracy of ± 0.0001 in mole fraction. The freezing and melting point apparatus consisted of a double-wall equilibrium cylindrical vessel (capacity 180 cm³), Pt-thermometer, multimeter Agilent 34401A, a motor-driven Teflon stirrer, thermostat and a computer and was described in detail¹. The gold-plated resistance thermometer immersed directly into the solution had an ITS-90 certificate of calibration.

Liquid mixtures were first cooled and temperature changes were observed on a PC monitor. When the first solid phase occurred the temperature was held constant for half an hour and then the mixture was heated. The rates of temperature changes were 4 K/h both to cool and warm the mixture. More than 100 000 values of temperature (resistance) were often collected in one run. Liquidus temperatures were easier to read from warming curves because of a considerable supercooling attending formation of first crystals. Temperature was generally reproducible within 0.1 K in consecutive experiments.

At about 287 K and atmospheric pressure one solid and two liquid phases coexist in the system. Liquid–liquid equilibrium data were obtained by the turbidity method. A two-phase mixture of known composition was placed into a cell with platinum resistance thermometer Pt-100 introduced into the cell through a tight hole in a center of a stopper. The cell was immersed into a programmable clear-view thermostat and the mixture of acetophenone and formamide was agitated with a submerged magnetic stirrer. The rate of temperature change was this time 0.5 K/min. Turbidity appearance and disappearance were observed visually. The latter was found to be better detectable, as an appearance of two liquid phases occurred in a wider temperature range. The temperature reproducibility was better than 0.2 K when a binary liquid mixture was heated to transparency.

A considerable supercooling preceding solidification enabled us to examine the liquid–liquid equilibrium from 298.85 to 264.15 K although the liquidus temperature was 286.95 K and the solidus one 271.85 K. Thus all experimental points of liquid–liquid equilibrium at temperatures lower than 286.95 K are metastable.

Acetophenone for calorimetric measurements was purified by a multiple fractional crystallization. Differential scanning calorimeter TA Q1000 was used to measure both, specific heat capacity under atmospheric pressure and enthalpy of crystal transformation. The heat capacity of solid acetophenone was measured by the continuous heating method in the temperature range 183.15–283.15 K and that of liquid acetophenone in the temperature range 273.15–363.15 K. The scanning rate was 10 K/min and Al_2O_3 was used as a reference sample. During the measurement of enthalpy of acetophenone crystal transformation temperature was changed from 233.15 to 303.15 K with the scanning rate 5 K/min.

RESULTS AND DISCUSSION

Solid–liquid and liquid–liquid equilibrium for the binary system formamide (1) and acetophenone (2) was measured. Experimental data obtained for the binary system are given in Tables I and II and plotted in Fig. 1. The components which are partially miscible in the liquid phase are considered to be completely insoluble in the solid phase. Liquid–liquid binodal has an upper critical point at $T_c = 298.85$ K and $x_1 = 0.557$.

The behavior of liquid was described by Novák's modification of the Wilson equation⁶

$$Q = G^E/(RT) = Q_W + bx_1x_2 \quad (1)$$

TABLE I
Solid–liquid equilibrium

Acetophenone branch of liquid				Formamide branch of liquid		Solid	
Two-phase region		Three-phase region					
x_1	T, K	x_1	T, K	x_1	T, K	x_1	T, K
0	292.69	0.4172	287.02	0.9402	272.64	0.8085	271.89
0.1095	289.67	0.5037	287.15	0.9455	272.79	0.9265	271.81
0.2100	288.33	0.5974	287.15	0.9684	273.53	0.9455	271.74
0.3281	287.40	0.7739	286.95	0.9904	274.63		
0.3622	287.20	0.7888	286.97	1.0000	275.54		
0.8085	286.92						
0.8239	286.77						
0.8889	284.15						

TABLE II
Liquid–liquid equilibrium

Stable equilibrium		Metastable equilibrium	
x_1	T, K	x_1	T, K
0.4014	287.88	0.2948	265.31
0.4067	288.68	0.3000	266.91
0.4142	289.36	0.3075	269.58
0.4219	290.32	0.3151	271.76
0.4289	291.05	0.3215	273.25
0.4438	292.69	0.3272	274.58
0.4505	293.20	0.3341	276.24
0.4597	294.13	0.3405	277.82
0.4783	295.39	0.3432	278.50
0.4946	296.23	0.3502	279.78
0.5058	296.78	0.3573	281.16
0.5151	297.26	0.3648	282.42
0.5279	297.77	0.3734	284.23
0.5538	298.37	0.3811	285.49
0.5742	298.57	0.3910	286.80
0.6065	298.55	0.7975	286.22
0.6279	298.32	0.8027	284.45
0.6584	298.04	0.8072	283.25
0.6906	297.64	0.8125	281.26
0.7103	297.11	0.8195	279.18
0.7238	296.55	0.8241	276.72
0.7372	295.77	0.8293	273.98
0.7510	294.51	0.8341	270.66
0.7579	293.68	0.8378	268.31
0.7652	292.69	0.8422	265.98
0.7713	291.76		
0.7828	290.02		
0.7914	288.10		

were

$$Q_W = -x_1 \ln S_1 - x_2 \ln S_2 \quad (2)$$

$$S_1 = x_1 + A_{12} x_2, \quad S_2 = x_2 + A_{21} x_1 \quad (3)$$

$$A_{12} = V_{m2}/V_{m1} \exp(-a_{12}/T), \quad A_{21} = V_{m1}/V_{m2} \exp(-a_{21}/T) \quad (4)$$

with parameters $a_{12} = 113.451 \text{ K}^{-1}$, $a_{21} = 387.00 \text{ K}^{-1}$, $b = 0.37054 + 415.8/T$ and liquid molar volumes $V_{m1} = 39.888 \text{ cm}^3/\text{mol}$, $V_{m2} = 117.357 \text{ cm}^3/\text{mol}$. The fit of parameters was performed only for the stable range of liquid-liquid equilibrium ($i = 1, 2$).

$$\ln x_i + \ln(\gamma_{i,x_i}) = \ln(z_i) + \ln(\gamma_{i,z_i}) \quad (5)$$

Solid-liquid equilibrium at temperature T for compounds that are immiscible in the solid phase is given by the following equation ($i = 1, 2$)

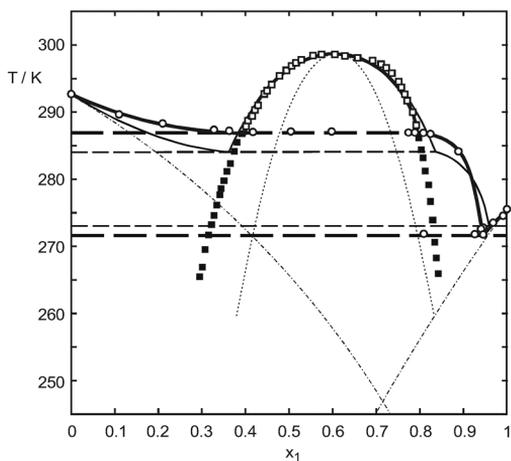


FIG. 1

Phase diagram for the formamide (1)-acetophenone (2) system: \circ , experimental data on solid-liquid equilibrium; \square , experimental data on liquid-liquid equilibrium in the stable region; \blacksquare , experimental data on liquid-liquid equilibrium in the metastable region; bold solid lines, graphically smoothed experimental data; bold dashed straight lines, experimental invariant temperatures; thin solid lines, calculated equilibrium curves; thin dashed straight lines, calculated invariant temperatures; dotted line, spinodal curve; dash-and-dotted lines, solid-liquid equilibrium for ideal behavior

$$\ln(\gamma_i x_i) = -\Delta_{\text{fus}} G_{m,i}^0(T)/(RT), \quad (6)$$

where

$$\Delta_{\text{fus}} G_{m,i}^0(T) = \Delta_{\text{fus}} H_{m,i}^0(T) - T\Delta_{\text{fus}} S_{m,i}^0(T) \quad (7)$$

and

$$\begin{aligned} \Delta_{\text{fus}} H_{m,i}^0(T) &= \\ &= \Delta_{\text{fus}} H_{m,i}^0(T_{\text{fus},i}) + \int_{T_{\text{fus},i}}^{T_{\text{tr},i}} \Delta C_{\text{pm},i} dT + \Delta_{\text{tr}} H_{m,i}^0(T_{\text{tr},i}) + \int_{T_{\text{tr},i}}^T \Delta C'_{\text{pm},i} dT, \end{aligned} \quad (8)$$

$$\begin{aligned} \Delta_{\text{fus}} S_{m,i}^0(T) &= \\ &= \Delta_{\text{fus}} S_{m,i}^0(T_{\text{fus},i}) + \int_{T_{\text{fus},i}}^{T_{\text{tr},i}} \frac{\Delta C_{\text{pm},i}}{T} dT + \Delta_{\text{tr}} S_{m,i}^0(T_{\text{tr},i}) + \int_{T_{\text{tr},i}}^T \frac{\Delta C'_{\text{pm},i}}{T} dT. \end{aligned} \quad (9)$$

In Eqs (8) and (9) is included one first-order transition in a solid phase at $T_{\text{tr},i}$ as we found a note about solid–solid transition of acetophenone crystals in literature⁷.

In the equations above,

$$\Delta C_{\text{pm},i} = C_{\text{pm},i}^{\text{l}} - C_{\text{pm},i}^{\text{s}} \quad (10)$$

and

$$\Delta C'_{\text{pm},i} = C_{\text{pm},i}^{\text{l}} - C_{\text{pm},i}^{\text{s}'}, \quad (11)$$

are differences in isobaric heat capacities, where superscript l denotes liquid phase, s a solid phase stable between the fusion temperature $T_{\text{fus},i}$ and the temperature of crystal transformation $T_{\text{tr},i}$ and s' denotes a solid phase stable at temperature lower than that of crystal transformation.

The liquid behavior is well known from liquid–liquid measurements and literature data on molar enthalpies of fusion at normal fusion temperatures $\Delta_{\text{fus}} H_{m,1}^0(275.54 \text{ K}) = 6694 \text{ J/mol}$ for formamide⁵ and $\Delta_{\text{fus}} H_{m,2}^0(292.69 \text{ K}) = 16\,650.7 \text{ J/mol}$ for acetophenone⁸. To recalculate these enthalpies to an-

other temperature, the knowledge of $\Delta C_{pm,i} = C_{pm,i}^l - C_{pm,i}^s$ values was necessary.

Heat capacities of de Wit et al.⁹ for formamide in the temperature range 200–270 K for liquid phase and 217–231 K for solid phase were used to fit temperature dependence of $\Delta C_{pm,1}$. We obtained $\Delta C_{pm,1} = 83.71 - 0.2057T$.

Practically no experimental data on heat capacities were found in literature for acetophenone; this is why we decided to measure them. The obtained linear part of the data in the temperature range 193.15–268.15 K for solid and 283.15–353.15 K for liquid were fitted by the following equations: $C_{pm,2}^l = 126.26 + 0.2419T$ and $C_{pm,2}^s = 26.05 + 0.4472T$ which gave $\Delta C_{pm,2} = 100.21 - 0.2053T$. Our value of heat capacity in liquid phase $C_{pm,2}^l = 198.4$ J/(mol K) agreed within 3% with the only found data¹⁰ 204.6–205.5 J/(mol K) at 25.1 °C. Harrison's approximations¹¹ at $T = 298.15$ K were $C_{pm,2}^l = 194.24$ J/(mol K) and $C_{pm,2}^s = 161.02$ J/(mol K).

We also measured $\Delta_{tr}H_{m,2}^0$ of the solid–solid transition of acetophenone mentioned by Deffet⁷ in his seventy-years-old work where the influence of pressure on fusion temperature of some organic compounds was measured. The author wrote: “the difference between volumes of both solids is extremely small therefore the transition temperature 16.8 °C (289.95 K) is less precise than the other ones”. We found that this transition takes place at 289.65 K and $\Delta_{tr}H_{m,2}^0 = -1360 \pm 100$ J/mol when the high-temperature solid is transformed to the low-temperature one.

With all the measured and collected data we were able to calculate the phase diagram of the formamide (1)–acetophenone (2) system. The calculated and experimental data are given in Fig. 1. The thin solid line in Fig. 1 represents the back-calculated liquid–liquid and solid–liquid equilibrium with activity coefficients obtained from Eq. (1). The dotted line marks a calculated spinodal. There are two invariant temperatures within the system. At 286.95 K and atmospheric pressure one solid phase and two liquid phases coexist while at 271.85 K two solid phases and one liquid phase are in equilibrium. This invariant temperature is the eutectic temperature of the system at atmospheric pressure. The agreement between experimental and calculated solubility of formamide is excellent, that of acetophenone is somewhat worse. The attentive reader could argue that in Eqs (8) and (9) we knew only $\Delta C_{pm,2}^l$ not $\Delta C_{pm,2}$. Calculation of the solid–liquid equilibrium with constant $\Delta_{fus}H_{m,2}^0$ and $\Delta_{fus}S_{m,2}^0$ as well as $\Delta_{tr}H_{m,2}^0$ and $\Delta_{tr}S_{m,2}^0$, i.e. with both $\Delta C_{pm,2} = 0$ and $\Delta C_{pm,2}^l = 0$, gives equilibrium temperatures differing only in hundredths of K. The lower values of activity coefficients obtained from Eq. (1) in comparison with those obtained from Eq. (6) (highest deviation less than 8%) are the reason for the calculated lower

temperatures of solid–liquid equilibrium. The eutectic temperature calculated for the case of ideal solubility (dash-and-dotted line in Fig. 1) is in this case by nearly 25 K lower, $T_e^{\text{id}} = 247.3$ K.

SYMBOLS

A, a, b	parameters
C	heat capacity
G	Gibbs energy
H	enthalpy
R	gas constant
S	entropy
T	thermodynamic temperature
V	volume
x	mole fraction in a liquid phase
z	mole fraction in a coexisting liquid phase

Subscripts

c	critical
e	eutectic
fus	fusion
m	molar
p	isobaric
tr	transition

Superscripts

id	ideal
o	pure compound at T, p
l	liquid
s	solid
E	excess

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