

## SOLID-LIQUID EQUILIBRIUM IN THE SYSTEM PROPANOIC ACID-FORMAMIDE

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Solid-liquid equilibria in the system propanoic acid-formamide were determined from time-temperature cooling and warming curves. In the system, two solid adducts, stable and metastable, were found and their equilibrium dissociation constants were calculated.

**Keywords:** Formamide; Propanoic acid; Solid-liquid equilibrium; Phase diagrams; Binary mixtures; Thermodynamics.

Requirements of the contemporary life, automobilism on one end and qualified chemistry on the other, necessitate well tailored methods of separation. Phase diagrams provide fundamental information on the equilibrium relations among different compounds. The efficacy of phase diagram methods is limited by the requirement of a complete thermodynamic model for the phases of interest. Effort to expand data compilations have made substantial progress toward overcoming this limitation and activity coefficient models such as UNIFAC or modified UNIFAC (Dortmund) can be today used to take into account the real behavior of the liquid phase. While the models solved more or less problems connected with distillation, solubility data still need experimental knowledge, since it is possible for the liquid phase to be accompanied by various coexistent solid phases such as crystals of pure compounds, mixed crystals or stoichiometric compounds. In particular, formation of stoichiometric compounds by adductive crystallization requires experimental data since the formation of adducts in a mixture cannot be predicted with certainty. The statement confirms also our recent discovery that in two very similar systems acetic acid-formamide and propanoic acid-formamide adducts of a different kind form in the solid phase. In the present paper we report not only a solid-phase adduct forma-

tion as in the preceding papers<sup>1-3</sup> but also the observation of a metastable adduct.

## EXPERIMENTAL

### Chemicals

Formamide as well as propanoic acid was of the best (>99.5%) grade supplied by Fluka. Purity of these substances was tested by determination of their melting points. The melting point of formamide was 275.54 K and that of propanoic acid 252.54 K. These values were in a good agreement with those (275.70 and 252.45 K) tabulated by Riddick et al.<sup>4</sup> Both substances were used without further purification.

### Methods and Measurements

The used freezing and melting point apparatus consisting of equilibrium cell, thermometer, stirrer, thermostat and a computer is described in detail elsewhere<sup>1</sup>. The gold-plated resistance thermometer has a certificate of calibration on ITS-90. We recorded both the cooling and warming curves, although the latter were easier to read. The rate of temperature change was  $4 \text{ K h}^{-1}$ . Temperature changes were observed on a PC monitor. More than 50 000 values of temperature (resistance) were typically collected in one run. Generally, the determination of temperature was reproducible within 0.1 K in consecutive tests. The liquidus line was obtained by carrying out measurements on mixtures of varying composition.

A major experimental problem when measuring solid-liquid equilibria is supercooling. In the case of organic H-bonded systems, which we deal with, supercooling of 25 K is quite common and neither a change of cooling rate nor crystal seeding helps. The emergence of a new phase was determined from the change in slope of the recorded resistance  $R$  vs time dependence by the method of thermal analysis. To establish the phase boundaries analysis of cooling curves cannot be usually employed for our H-bonded systems (Fig. 1, supercooling ca. 10 K) but warming curves can be analyzed easily (Fig. 2).

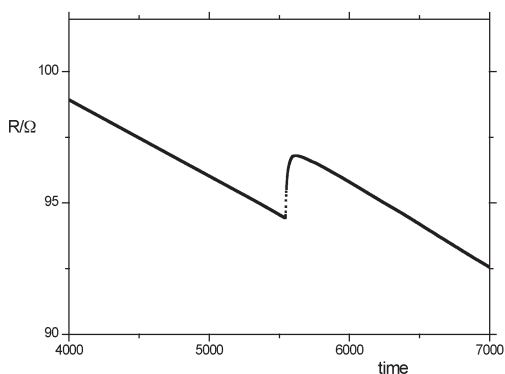


FIG. 1

A typical solidification curve for H-bonded systems

After filling, the measuring cell was always placed in a thermostat and cooled till a solid phase was formed. Due to supercooling, we were able to record not only the emergence of a new metastable solid but also its transformation to a stable one (Figs 3 and 4).

## RESULTS AND DISCUSSION

The measured data on solid-liquid equilibrium of the propanoic acid (1)-formamide (2) system obtained from the warming curves are given in Table I and plotted in Fig. 5. The components which are completely miscible in the liquid phase are considered to be completely insoluble in the solid phase. The solid-liquid equilibrium at temperature  $T$  for components that are immiscible in the solid phase is given by the following equation ( $i = 1, 2$ )

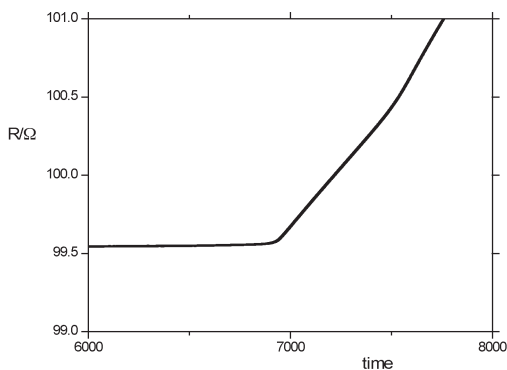


FIG. 2  
A typical melting curve for H-bonded systems

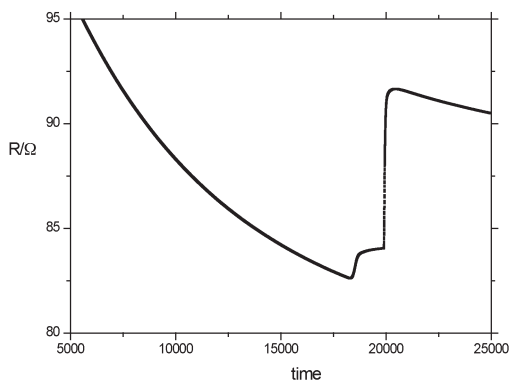


FIG. 3  
A leap during solidification

$$\ln(\gamma_i x_i) = -\Delta_{\text{fus}} G_{m,i}^{\circ}(T) / (RT) \quad (1)$$

where

$$\Delta_{\text{fus}} G_{m,i}^{\circ}(T) = \Delta_{\text{fus}} H_{m,i}^{\circ}(T) - T\Delta_{\text{fus}} S_{m,i}^{\circ}(T) \quad (2)$$

and

$$\Delta_{\text{fus}} H_{m,i}^{\circ}(T) = \Delta_{\text{fus}} H_{m,i}^{\circ}(T_{\text{fus},i}) + \int_{T_{\text{fus},i}}^T \Delta C_{pm,i} dT \quad (3)$$

$$\Delta_{\text{fus}} S_{m,i}^{\circ}(T) = \frac{\Delta_{\text{fus}} H_{m,i}^{\circ}(T_{\text{fus},i})}{T_{\text{fus},i}} + \int_{T_{\text{fus},i}}^T \frac{\Delta C_{pm,i}}{T} dT \quad (4)$$

where  $\Delta C_{pm,i} = C_{pm,i}^l - C_{pm,i}^s$  is the difference of molar isobaric heat capacities, where superscript l denotes liquid phase, s solid phase. Equations (3) and (4) are valid only if no solid–solid transition of pure crystals of substances 1 or 2 occurs between their melting temperature  $T_{\text{fus}}$  and temperature  $T$  as in our case. Thermodynamic description of solid–liquid equilibria with a solid–solid transition was given in our previous paper<sup>5</sup>.

Literature data<sup>4</sup> on molar enthalpies of fusion at normal melting temperatures  $\Delta_{\text{fus}} H_{m,1}^{\circ}(252.45 \text{ K}) = 10\,660 \text{ J mol}^{-1}$  for propanoic acid and  $\Delta_{\text{fus}} H_{m,2}^{\circ}(275.70 \text{ K}) = 6\,694.4 \text{ J mol}^{-1}$  for formamide were used when calculating activity coefficients. Calorimetric data of Martin and Andon<sup>6</sup> helped

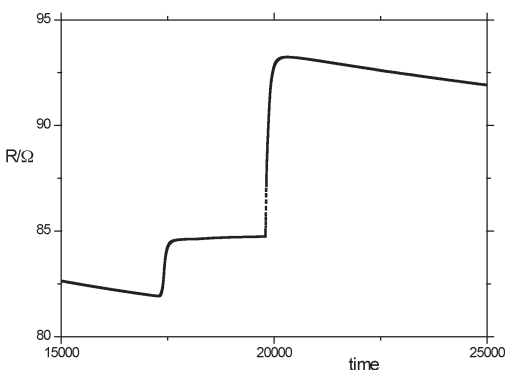


FIG. 4  
A leap during solidification (another concentration)

to fit the temperature dependence of  $\Delta C_{\text{pm},1}$  of propanoic acid  $\Delta C_{\text{pm},1} = 40.30 - 0.06473T$  and heat capacities of de Wit et al.<sup>7</sup> for formamide in the temperature range 200–270 K for liquid phase and 217–231 K for solid phase enabled to fit its temperature dependence as  $\Delta C_{\text{pm},1} = 83.71 - 0.2057T$ . The eutectic compositions were obtained from the intersection of the freezing-temperature lines. The melting temperature of the stable compound is  $T_{1,\text{fus}} = 261.25$  K and the eutectics are at  $x_1 = 0.226$  ( $T = 258.25$  K) and  $x_1 = 0.727$  ( $T = 240.60$  K).

Only the experimental points where pure solid propanoic acid or pure solid formamide is in equilibrium with liquid (i.e. the points most left and right in Fig. 5) can be used to calculate the activity coefficients in the propanoic acid (1)–formamide (2) system. The values with their standard

TABLE I  
Solid-liquid equilibria in the system propanoic acid (1)–formamide (2)

Stable equilibrium		Metastable equilibrium	
$x_1$	$T, \text{K}$	$x_1$	$T, \text{K}$
0	275.54	0.3045	250.56
0.0992	268.26	0.3581	243.64
0.2140	259.13	0.3691	241.83
0.2837	260.66	0.4104	234.68
0.3314	261.21	0.4521	233.20
0.4104	260.53	0.4776	232.95
0.4521	259.06	0.5077	233.25
0.4776	257.69	0.5542	232.73
0.5661	251.53	0.6118	228.50
0.6113	248.56	0.6618	234.49
0.6447	246.50		
0.6569	245.63		
0.6758	244.14		
0.7469	241.58		
0.7990	244.44		
0.8894	248.02		
1.0000	252.54		

deviations are presented in Table II. The solubility is lower than the ideal one in both regions and shows a positive deviation from ideality ( $\gamma > 1$ ). To calculate standard deviations of the activity coefficients, the propagation law for independent quantities was used and the following errors in the input values were considered:  $s(T) = 0.1$ ,  $s(x) = 0.0005$  and  $s(\Delta_{\text{fus}}H^\circ) = 0.02\Delta_{\text{fus}}H_{\text{m},1}^\circ$ . The calculated activity coefficients were used to fit parameter of the regular solution model  $G^E/(RT) = Ax_1x_2$ , with  $A = 1.0522$ .

The system was investigated very carefully around the composition corresponding to the 2:1 adduct. No indication of such adduct was found. On the other hand two other solid adducts form in the measured system; the stable one  $\text{CH}_3\text{CH}_2\text{COOH}\cdot(\text{HCONH}_2)_2$  and the metastable one  $\text{CH}_3\text{CH}_2\text{COOH}\cdot\text{HCONH}_2$ . Both adducts exist in the solid phase but are unstable in the liquid phase. (There is no point of discontinuity on the liquidus curve at  $x_1 = 0.333$  for the stable solid and  $x_1 = 0.5$  for the metastable solid.) It means that the following dissociation reactions<sup>8</sup> take place:



for the 1:2 adduct with equilibrium constant  $K_1 = a_{\text{A}}a_{\text{B}}^2$  and

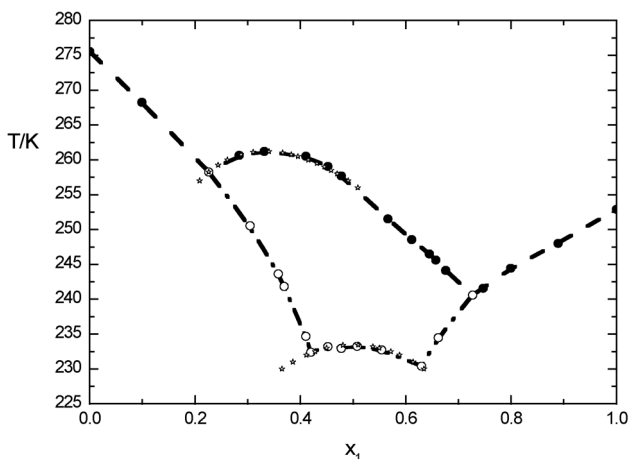


FIG. 5

Solid-liquid equilibrium data for the system propanoic acid (1)-formamide (2); ● experimental data for the stable region, ○ experimental data for the metastable region, \* calculated values; dashed line, graphically smoothed experimental data in the stable region; dash-and-dotted lines, graphically smoothed experimental data in the metastable region



for the 1:1 adduct with an equilibrium constant  $K_2 = a_A a_B$ , where  $a_i = \gamma_i x_i$  stands for activity,  $\gamma_i$  for activity coefficient,  $x_i$  for mole fraction of  $i$ -th component in the liquid phase and subscripts A, B for propanoic acid and formamide, respectively.

Extrapolating melting temperature of the 1:2 adduct to  $T_{1,\text{fus}} = 261.25$  K and that of the 1:1 adduct to  $T_{2,\text{fus}} = 233.35$  K and knowing the activity coefficients of liquid formamide and propanoic acid for  $x_1 = 0.333$  and equimolar mixture,  $K_1$ ,  $K_2$  and the corresponding  $\Delta_{\text{diss}}G^\circ = -RT \ln K$  can be calculated at the melting temperature (Table III).

TABLE II  
Activity coefficients for the system propanoic acid(1)-formamide(2)

$x_1$	$T, \text{K}$	$\gamma_1 \pm s(\gamma_1)$	$\gamma_2 \pm s(\gamma_2)$
1	252.54	1.000 ± 0.002	
0.8894	248.02	1.023 ± 0.002	
0.7990	244.44	1.057 ± 0.003	
0.7469	241.58	1.064 ± 0.003	
0	275.54		1.000 ± 0.001
0.0992	268.26		1.025 ± 0.002
0.2140	259.13		1.063 ± 0.002

TABLE III  
Thermodynamic data for dissociation of acid-formamide adducts

Compound	$\Delta_{\text{diss}}G^\circ, \text{J mol}^{-1}$ at the compound melting point	$\Delta_{\text{diss}}S^\circ, \text{J K}^{-1} \text{mol}^{-1}$	$\Delta_{\text{diss}}H^\circ, \text{J mol}^{-1}$
$\text{CH}_3\text{CH}_2\text{COOH} \cdot (\text{HCONH}_2)_2$	2716	37	12 382
$\text{CH}_3\text{CH}_2\text{COOH} \cdot \text{HCONH}_2$	1868	32	9 335
$(\text{CH}_3\text{COOH})_2 \cdot \text{HCONH}_2$	4190	44	15 800

Knowing  $\Delta_{\text{diss}}S^{\circ}$ , it is possible to calculate the value of  $\Delta_{\text{diss}}G^{\circ}(T) = \Delta_{\text{diss}}G^{\circ}(T_{\text{fus}}) - \Delta_{\text{diss}}S^{\circ}(T - T_{\text{fus}})$  and equilibrium concentration for selected  $T < T_{\text{fus}}$  from the equation  $\Delta_{\text{diss}}G_1^{\circ} = -RT \ln (a_A)_{\text{eq}}(a_B)_{\text{eq}}^2$  for the adduct of the 1:2 type or  $\Delta_{\text{diss}}G_2^{\circ} = -RT \ln (a_A)_{\text{eq}}(a_B)_{\text{eq}}$  for the 1:1 adduct. Calculated equilibrium compositions are represented by stars in Fig. 5. The calculation of equilibrium compositions was performed for various  $\Delta_{\text{diss}}S^{\circ}$ , the values given in Table III are those which best fitted the experimental data. The recently calculated thermodynamic values of dissociation of the 2:1 adduct found in the acetic acid(1)–formamide(2) system<sup>3</sup> are given in the last line of Table III. Surprisingly we found the stable 1:2 and the metastable 1:1 but no 2:1 adduct in the present system. Therefore, we carried out theoretical calculations of the relative stability of particular adducts using the standard computer program<sup>9</sup> Gaussian 03W and the 6-31G\* basis<sup>10</sup> of atomic orbitals. The calculations were carried out with a full optimization of the molecular geometry (Fig. 6). From the obtained molecular energies we calculated the association enthalpies of all three kinds of adducts formed by formamide and acid. The enthalpy difference was calculated as the difference between enthalpies of the adduct and individual molecules. We have found that the enthalpy difference decreases in the order: (acid)<sub>2</sub>–formamide < acid–(formamide)<sub>2</sub> < acid–formamide for both acetic and propanoic acids. Calculations were done for acids and formamide in the perfect gas state at 0 K and they indicated the adduct of two acid molecules and one formamide molecule as the most stable adduct. This result corresponds with our experimental observation for the acetic acid–formamide system. However, in the present propanoic acid–formamide system we only found two remaining adducts with the same stability as calculated. The query why we did not observe the expected 2:1 adduct in

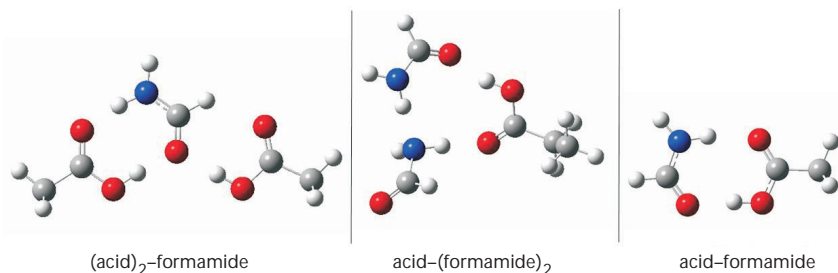


FIG. 6

Calculated molecular geometry of the adducts found in a solid phase: gray sphere, carbon; blue sphere, nitrogen; small sphere, hydrogen; red sphere, oxygen



the present system remains not answered. As to the results of theoretical calculation, it should be noted that the obtained results correspond to the perfect gas state and not to a real situation in the solid state.

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