



Phase Diagram of the Benzene–Dinitratotetrapyrindinecopper(II) (Guest–Host) System and Thermodynamic Parameters for the Host·2Guest Clathrate Dissociation

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Abstract. In the first part of the work, the phase diagram of the benzene —[CuPy₄(NO₃)₂] system has been determined in the –100 to +200 °C temperature range using DTA and solubility techniques. The only compound found in the system is the [CuPy₄(NO₃)₂]·2C₆H₆ clathrate. It is stable up to a temperature of +104.2(5) °C at which it melts incongruently to give liquid and the solid [CuPy₄(NO₃)₂] host phase. At 146.1(5) °C exfoliation into two liquid phases is observed, with the composition of the monotectic point being close to that of the clathrate. In the second part of the work, thermodynamic parameters of the clathrate dissociation have been determined from benzene vapour pressure strain measurements. For the process 1/2 [CuPy₄(NO₃)₂]·2C₆H₆ (solid) = 1/2 [CuPy₄(NO₃)₂] (solid) + C₆H₆ (gas) $\Delta H^\circ = 45.3(3)$ kJ/mole; $\Delta S_{298}^\circ = 126(1)$ J/(mole K); $\Delta G_{298}^\circ = 7.7(5)$ kJ/mole.

Key words: phase diagram, Werner clathrate, thermodynamic parameters, copper(II) complex

1. Introduction

Structural studies of the “MX₂·6Py” compounds (where M is a M(II) cation, X is a univalent acidogroup, and Py is pyridine) revealed their supramolecular nature [1–3]. Dozens of compounds of the above composition should be formulated as [MPy₄X₂]·2Py, the formula reflects the presence of two different molecular species in these phases. The clathrate behavior of the compounds was recently suggested, by replacing non-bonded pyridine in [CuPy₄(NO₃)₂]·2Py with benzene, tetrahydrofuran and chloroform [4] (the compounds may be considered as belonging to the so-called Werner clathrates [5]). It is necessary to mention that few other clathrates of [MPy₄X₂] complexes with non-pyridine guests were reported be-

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fore although they have structures completely different from each other and from that of the $[\text{MPy}_4\text{X}_2]\cdot 2\text{Py}$ compounds and weak host-to-guest bonding is usually observed. These are $[\text{CoPy}_4\text{Cl}_2]\cdot \text{CHCl}_3$ [6], $[\text{MPy}_4(\text{NCS}\cdot\text{I}_2)_2]$ ($\text{M} = \text{Co}, \text{Ni}$) [7], $[\text{CoPy}_4(\text{NCS})_2]\cdot 2\text{CHI}_3$ [8], $[\text{VPy}_4(\text{C}_6\text{H}_4\text{SO}_2\text{NCO})_2]\cdot 2\text{C}_4\text{H}_8\text{O}$ [9].

In spite of the rather extensive structural investigations of the $[\text{MPy}_4\text{X}_2]\cdot 2\text{Py}$ clathrates, only a few have been examined for the conditions of formation and other thermodynamic properties [10–14]. Now we present, for the first time, results of phase equilibrium studies on the formation of a $[\text{MPy}_4\text{X}_2]\cdot 2\text{G}$ compound with a non-pyridine (benzene) guest.

The $[\text{CuPy}_4(\text{NO}_3)_2]\cdot 2\text{C}_6\text{H}_6$ clathrate, considered here, has a molecular structure with guest species inside straight channels [4] and is isomorphous to its pyridine counterpart [15]. As the host complex may be isolated as an individual phase, the method of guest–host phase diagram determination to reveal all phases present in this binary system was used. In the second part of the work, the temperature dependence of the benzene vapour pressure over the clathrate was determined to obtain quantitative thermodynamic information for comparison with its pyridine-guest analogue [16].

2. Experimental

2.1. PHASE DIAGRAM DETERMINATION

Samples of all composition ranges were prepared mainly by mixing benzene and the $[\text{CuPy}_4(\text{NO}_3)_2]$ host complex. Benzene was of analytically pure grade and melted at $5.9(4)^\circ\text{C}$ (cf. 5.53 from lit.). The host complex was prepared and analyzed as in [4]. Also, samples of the crystalline benzene clathrate [4] and its mixtures with each component were used. The temperatures of the phase transitions and approximate values of the corresponding thermal effects were determined with the DTA-technique of the samples sealed in special glass ampoules, with 1 deg. per min. heating rate and sensitivity of 150° and 3° per scale for temperature and differential thermocouples, respectively. The solubility of the clathrate at 20 – 60°C was studied with the solubility method (at higher temperatures significant dissociation of the host complex occurred; this was easy to observe as both $[\text{CuPy}_4(\text{NO}_3)_2]$ complex and all its clathrates are dark-blue or violet-lilac while the $[\text{CuPy}_3(\text{NO}_3)_2]$ complex is light-blue). More details about the methods used can be found in our earlier papers [10, 13, 17].

The system was studied over the full concentration and -100 to 200°C temperature ranges. At higher temperatures the samples underwent irreversible changes showing strong exothermic effects. No significant kinetic complications were observed in the system. At the same time, the most serious difficulty was that the $[\text{CuPy}_4(\text{NO}_3)_2]$ complex dissociates significantly to the tripyridine complex in excess of benzene at elevated temperatures. For example, the dissociation is observable upon mixing the complex in benzene at 70°C and higher. Evidently, at

Table I. Coordinates of the liquidus curve experimental points in the title system

| [CuPy ₄ (NO ₃) ₂], mass-% | <i>T</i> , °C | Method | Phases in equilibrium |
|--|---------------|------------|---|
| 0 | 5.9(4) | DTA | <i>l</i> ₁ + C ₆ H ₆ (solid) |
| 0.031(1) | 20.0 | Solubility | <i>l</i> ₁ + [CuPy ₄ (NO ₃) ₂] \cdot 2C ₆ H ₆ |
| 0.083(2) | 40.0 | Solubility | <i>l</i> ₁ + [CuPy ₄ (NO ₃) ₂] \cdot 2C ₆ H ₆ |
| 0.112(6) | 50.0 | Solubility | <i>l</i> ₁ + [CuPy ₄ (NO ₃) ₂] \cdot 2C ₆ H ₆ |
| 0.163(4) | 60.0 | Solubility | <i>l</i> ₁ + [CuPy ₄ (NO ₃) ₂] \cdot 2C ₆ H ₆ |
| 82.0 | 157(1) | DTA | <i>l</i> ₂ + [CuPy ₄ (NO ₃) ₂] |
| 83.5 | 160(1) | DTA | <i>l</i> ₂ + [CuPy ₄ (NO ₃) ₂] |
| 87.8 | 162(2) | DTA | <i>l</i> ₂ + [CuPy ₄ (NO ₃) ₂] |
| 94.4 | 168(1) | DTA | <i>l</i> ₂ + [CuPy ₄ (NO ₃) ₂] |
| 96.1 | 172.2(6) | DTA | <i>l</i> ₂ + [CuPy ₄ (NO ₃) ₂] |
| 100 | 173.9(6) | DTA | <i>l</i> ₂ + [CuPy ₄ (NO ₃) ₂] |

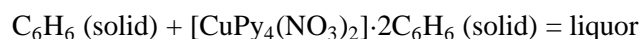
such conditions the system cannot be considered as a binary one and prominent location of the liquidus curve is not possible in this *T* – *X*-region.

2.2. STRAIN EXPERIMENTS

In the strain experiments, pressure was measured by the static method, using a glass membrane null-manometer [18, 19]. 2 g of the clathrate [CuPy₄(NO₃)₂] \cdot 2C₆H₆ (see [4] for synthesis and analysis) was placed into the reaction vessel; this was evacuated for a short time and sealed. Measurements were carried out in the range 290–346 K (17–73 °C). The equilibrium pressure was established quickly, both in the forward and backward approach to the required temperature. The *P*(*T*) experimental data were corrected for pyridine vapour pressure over the [CuPy₄(NO₃)₂] complex [16] and were approximated by the linear equation $\log P = A - B/T$ (*P*, torr; *T*, K), with the coefficients *A* and *B* refined by a least-squares technique.

3. Results

Figure 1 shows the phase diagram of the C₆H₆–[CuPy₄(NO₃)₂] system; the coordinates of the liquidus curve experimental points are listed in Table I. Except for the original components, only one compound forms in the system; this one is the clathrate with the 1 : 2 (host : guest) stoichiometry which is in good agreement with the previously determined crystal structure of the clathrate [4]. The clathrate solubility is low at temperatures close to room temperature; the eutectic



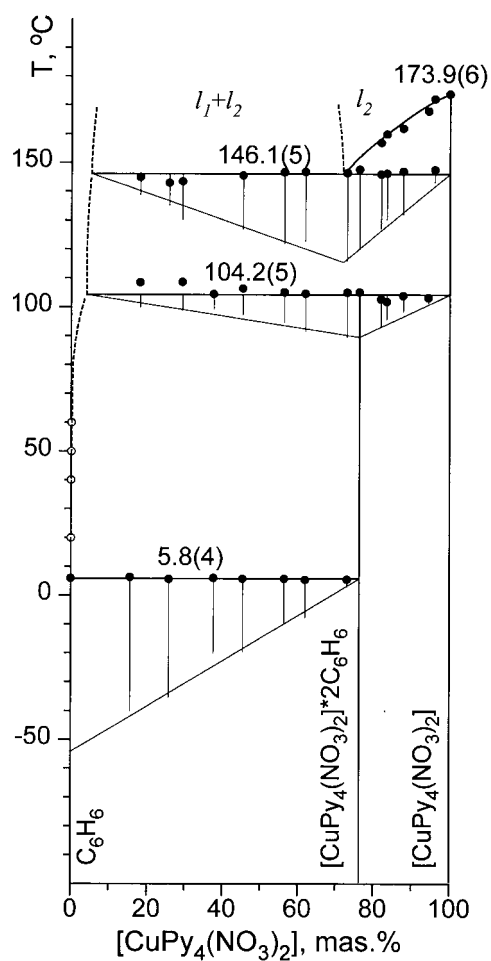
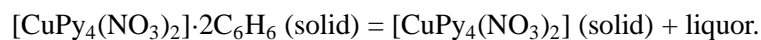
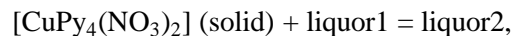


Figure 1. The phase diagram of the title system. Open and solid circles represent the points obtained by the solubility and DTA methods, respectively. Vertical segments about DTA-points indicate relative magnitudes of the phase transition thermal effects (Tammán triangle).

is degenerate and its temperature of 5.8(4) °C practically coincides with the benzene melting point. At 104.2(5) °C the clathrate melts incongruently forming the solid host complex:



At 146.1(5) °C the mixture undergoes a monotectic transformation to form liquid of another composition:



where pale-blue liquor1 (l_1) has a composition close to pure benzene while dark-blue liquor2 (l_2) is enriched with the complex. The monotectic point composition

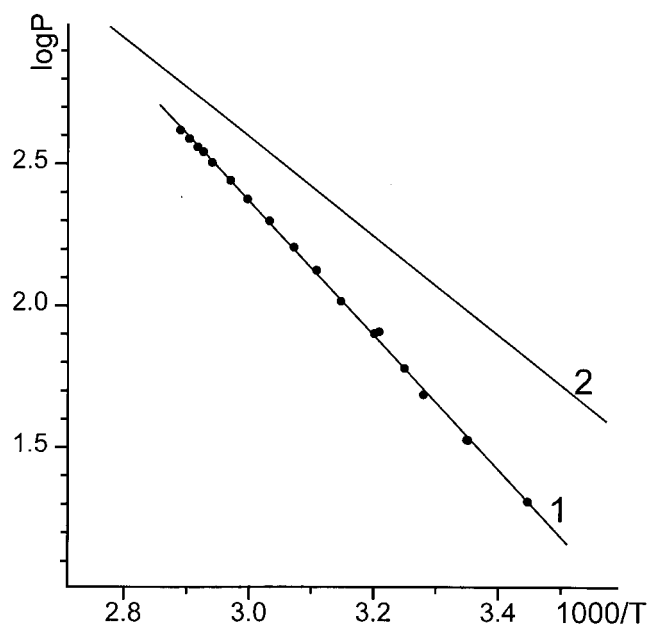


Figure 2. Logarithm of benzene vapour pressure versus the inverse temperature: (1) over the clathrate [CuPy₄(NO₃)₂] \cdot 2C₆H₆; (2) over neat benzene (P , torr; T , K).

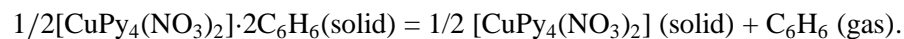
of ca. 72% of the complex is close to the composition of the clathrate which does not exist at this temperature. Above the monotectic line there are areas of two co-existing liquors (that is well observed visually, too), of liquor2, and of co-existing liquor2 and the solid complex [CuPy₄(NO₃)₂]. The latter melts congruently at 173.9(6) °C.

The data on the temperature dependence of the benzene vapour pressure over the clathrate are presented in Figure 2. In the studied temperature range (17–73 °C) they are approximated by the equation (for this equation and Figure 2 the temperature is in Kelvin units):

$$\log P = (9.46 \pm 0.05) - (2366 \pm 17)/T \quad (18 \text{ experimental points}).$$

Extrapolation of the dependence to higher temperatures shows the benzene pressure over the clathrate would reach that over neat benzene liquid approximately at 107 °C (380 K), the value being in good agreement with the upper limit of the clathrate stability from the phase diagram.

Thermodynamic parameters calculated from the found $P(T)$ dependence for the clathrate dissociation process



are as follows:

$$\Delta H_{\text{av}}^\circ = 45.3(3)\text{kJ/mole}; \Delta S_{298}^\circ = 126(1)\text{J/(mole K)}; \Delta G_{298}^\circ = 7.7(5)\text{kJ/mole}$$

4. Discussion

Formation of the complex-2benzene compound observed in the title system assumes a pure supramolecular type of this phase organization. Evidently, no significant interaction is possible between the hydrophilic coordinatively saturated Cu-complex and benzene. Indeed, the solubility of both $[\text{CuPy}_4(\text{NO}_3)_2] \cdot 2\text{C}_6\text{H}_6$ and $[\text{CuPy}_4(\text{NO}_3)_2]$ in benzene is low suggesting weak interactions between the system components in solution. Nevertheless, the 1 : 2 molar ratio results in the clathrate phase which is thermodynamically stable up to 104 °C. Above this temperature the clathrate decomposes to solid host and liquid of composition close to the pure benzene component. Further heating provides more evidence of both the chemical disaffinity and spatial complementarity of the components. At 146° the host complex melts in benzene to a dark-blue liquid (l_2 , see Figure 1) which does not mix with the light-blue liquid consisting mainly of benzene (l_1). This disfoliation extends at least up to 200 °C. Remarkably, the maximum mixing corresponds more or less to the 1 : 2 (complex : benzene) ratio, the same as in the clathrate phase. Although no more evidence is available, one can assume formation of clathrate-like solution structures at these conditions in the system. These might be some heteromolecular associates and aggregates, the crystal structure of the solid $[\text{CuPy}_4(\text{NO}_3)_2] \cdot 2\text{C}_6\text{H}_6$ clathrate [4] being assumed as a possible model for them [20]. Actually, the system may demonstrate the formation of “liquid clathrates” which was earlier suggested for some aqueous solutions [21] and was studied extensively for the systems of organoaluminium compounds with aromatics [22].

The thermodynamic driving force for the $[\text{CuPy}_4(\text{NO}_3)_2] \cdot 2\text{C}_6\text{H}_6$ clathrate formation is significantly lower in comparison with that for the $[\text{CuPy}_4(\text{NO}_3)_2] \cdot 2\text{Py}$ clathrate ($\Delta H_{\text{av}}^\circ = 74.6(9)$ and $57.2(3)$ kJ/mole; $\Delta S_{298}^\circ = 197(3)$ and $145(9)$ J/(mole K); $\Delta G_{298}^\circ = 15.9(5)$ and $14.1(4)$ kJ/mole for the 31–60 and 60–105 °C T -ranges, respectively) [16] even if differences in evaporation characteristics for benzene and pyridine ($\Delta H_{\text{evap}}^\circ = 33.5(1)$ (C_6H_6) and $39.3(2)$ (Py) kJ/mole) are taken into account. This suggests the dispersion van der Waals forces and interactions involving guest dipole contribute commensurably to the overall sorption energy during guest inclusion. As formation of the benzene clathrate is thermodynamically quite favorable, moreover, small polar molecules may result in more stable clathrates with this host.

Thus, the $[\text{CuPy}_4(\text{NO}_3)_2] \cdot 2\text{C}_6\text{H}_6$ clathrate forming in the title system is characterized by an extensive stability area in the $T - X$ -space as suggested by the phase diagram determination and significant driving force to its formation as determined quantitatively with the strain measurement. These results, along with the structural study [4], give basis for the existence of numerous clathrates resulting from replacing non-bonded pyridine with other guest species in the original $[\text{MPy}_4\text{X}_2] \cdot 2\text{Py}$ compounds, the clathrates cited in this work being the only ones reported to date.

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