Vapour Pressure of 4-Methylpyridine (MePy) over [Ni(MePy)$_4$(NCS)$_2$]·y(MePy) and [Cu(MePy)$_4$(NCS)$_2$]·2/3(MePy) Clathrates during Their Dissociation

E. A. UKRAINTSEVA, YU. A. DYADIN, N. V. KISLYKH,
V. A. LOGVINENKO and D. V. SOLDATOV
Institute of Inorganic Chemistry, Russian Academy of Sciences, Siberian Branch, 630090 Novosibirsk, Lavrentyeva 3, Russia.

Abstract. Strain measurement and quasiequilibrium thermogravimetry were used to study the dissociation processes of two clathrates, [Ni(MePy)$_4$(NCS)$_2$]·(MePy) and [Cu(MePy)$_4$(NCS)$_2$]·2/3(MePy), accompanied by the liberation of MePy into the gaseous phase. In the Ni clathrate dissociation process in the temperature range 298–368 K the liberated MePy was redistributed between the solid clathrate and gaseous phases; the MePy vapour pressure over the clathrate is a function of temperature and the guest content y, which agrees with the presence in the MePy–[Ni(MePy)$_4$(NCS)$_2$] system of a wide range of β-clathrate solutions, [Ni(MePy)$_4$(NCS)$_2$]·y(MePy). The same methods used to study the Cu clathrate dissociation resulted in conclusions different from those obtained for the dissociation process of the above clathrate: the process is described by the equation [Cu(MePy)$_4$(NCS)$_2$]·$\frac{2}{3}$(MePy)$_{solid}$ = [Cu(MePy)$_2$(NCS)$_2$]$_{solid}$ + $2\frac{2}{3}$(MePy)$_{gas}$; the temperature dependence of the MePy vapour pressure over the solid sample does not depend on its composition, which points to the absence from the system of solid solutions based on the clathrate. Standard changes of the enthalpy, entropy, and isobaric–isothermal reaction potential for the temperature range 292–325 K are equal to 178.6 ± 1.7 kJ (mole of clathrate)$^{-1}$, 463 ± 5.6 J (mole of clathrate)$^{-1}$ K^{-1}, and 40.4 ± 2.4 kJ (mole of clathrate)$^{-1}$, respectively.

Key words: Clathrate formation, vapour pressure, 4-methylpyridine, Ni(II), Cu(II), isothiocyanate.

1. Introduction

Clathrate formation in the systems MePy–[Ni(MePy)$_4$(NCS)$_2$] and MePy–[Cu(MePy)$_2$(NCS)$_2$] has been studied by various techniques [1–6]. The structures of the clathrates formed have been determined [7–9]. A feature shared by these clathrates is that their host components have the same general formula: [M(MePy)$_4$(NCS)$_2$]. However, the study of the properties of these clathrates reveals that they differ substantially and fundamentally in the way clathrate formation occurs in the systems.

In the Ni system a classic clathrate of tetragonal structure with the composition 1 : 1 (host : guest) forms. By removing the guest one can obtain an absolutely

vacant so-called β-framework which, though thermodynamically metastable, is quite stable kinetically [10] (this is the reason why it has been called an 'organic zeolite' [11]).

In contrast, as the study of the Cu system diagram revealed [5, 9, 12], the host complex exists only in two of the clathrates that form in the system: blue $1:2$ (monoclinic) and green $1:2/3$ (trigonal). Attempts to obtain a host complex as an individual phase by the removal of the guest were not successful, and study of the phase diagram showed that the compound $[Cu(MePy)_4(NCS)_2]$ has no stability range. The X-ray structural study of the clathrates demonstrated that the host molecule in various clathrates undergoes dramatic conformation transformations which causes drastic changes of colour [9, 12].

Investigations of the clathrate formation processes by obtaining the $P-T$, $P-x$, $P-t$, etc. relationships have been successfully used to obtain both their thermodynamic [13] and kinetic [5, 14] parameters. The study of the temperature dependence of the 4-methylpyridine equilibrium vapour pressure in the title systems makes it possible not only to learn about new properties of the above clathrates and to use them for obtaining thermodynamic values (ΔH, ΔS, ΔG) for the clathrate formation processes, but also to reach quite reliable conclusions on the nature (the stoichiometric aspect) of these compounds.
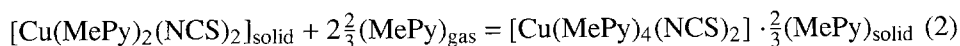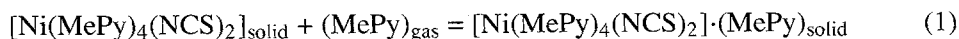
The present communication discusses the results of the study of the processes proceeding during the formation of MePy vapour from two clathrates, $[Ni(MePy)_4(NCS)_2]\cdot(MePy)$ and $[Cu(MePy)_4(NCS)_2]\cdot\frac{2}{3}(MePy)$.

2. Experimental

2.1. SYNTHESIS AND ANALYSIS

The complexes $[Ni(MePy)_4(NCS)_2]$ and $[Cu(MePy)_2(NCS)_2]$ used in the synthesis of the title clathrates were obtained by Schaeffer's technique [15], i.e. by precipitation with MePy from aqueous solutions containing Ni(II) or Cu(II), and thiocyanate ions. Metal analysis was by EDTA titration. Elemental analysis (C, H, N) was carried out on a Carbo-Erba-1106 CHNS analyser. *Calcd.* for $[Ni(MePy)_4(NCS)_2]$ (%): Ni, 10.7; C, 57.1; N, 15.4; H, 5.2. *Found*: Ni, 10.7; C, 56.6; N, 15.4; H, 5.5. *Calcd.* for $[Cu(MePy)_2(NCS)_2]$ (%): Cu, 17.4; C, 46.0; N, 15.3; H, 3.9. *Found*: Cu, 17.4; C, 45.6; N, 15.1; H, 3.8.

To obtain the clathrates, the complexes were saturated with MePy vapour until the mass of the samples became constant, as described in ref. [11]. The number of MePy moles absorbed by one mole of each complex was equal to 1.06–1.08 and 2.69 for $[Ni(MePy)_4(NCS)_2]$ and $[Cu(MePy)_2(NCS)_2]$, respectively, which is in agreement with the following reactions:

$$[Ni(MePy)_4(NCS)_2]_{solid} + (MePy)_{gas} = [Ni(MePy)_4(NCS)_2]\cdot(MePy)_{solid} \qquad (1)$$

$$[Cu(MePy)_2(NCS)_2]_{solid} + 2\tfrac{2}{3}(MePy)_{gas} = [Cu(MePy)_4(NCS)_2]\cdot\tfrac{2}{3}(MePy)_{solid} \quad (2)$$
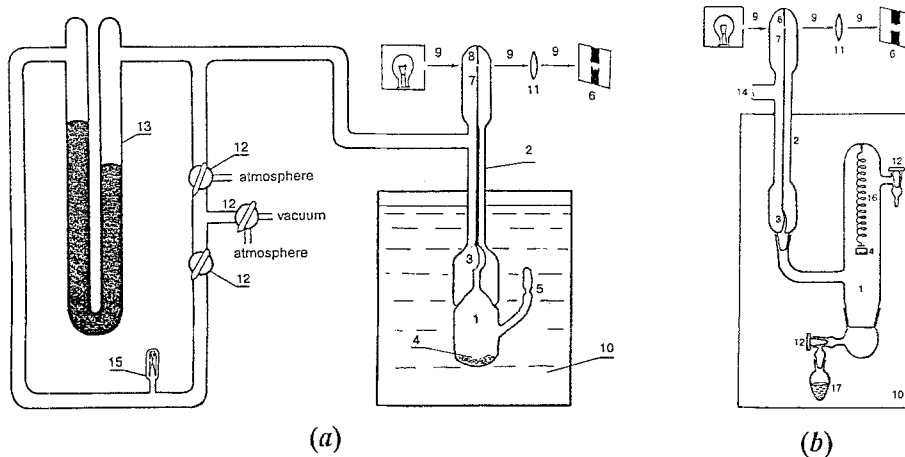
(a) (b)

Fig. 1. Devices for the determination of the $P–T$ (a) and $y–P$ (b) relationships for the clathrate dissociation processes. (1) Vacuum reactive vessel; (2) strain measurement cell; (3) glass spoon membrane; (4) sample (a) and cup with the sample on the uninterrupted weighing balance (b); (5) side-arm vessel projection for the removal of a portion of the volatile component (if nesessary); (6) screen; (7) movable rod; (8) immovable rod; (9) light beam; (10) water (a) and air (b) thermostat; (11) focusing lens; (12) taps; (13) mercury manometer; (14) outlet; (15) vacuum meter; (16) tungsten spring; (17) test tube with liquid MePy.

A somewhat greater amount of the sorbed MePy compared to the stoichiometric composition value (Equation 1) might be due to both adsorption of the excess MePy vapour on the surface of the clathrate powder and error in the determination of the composition of the initial complex.

In the synthesis of the complexes MePy marked 'pure' was used. To obtain the clathrates MePy was additionally purified by distillation over BaO and stored over P_2O_5.

2.2. PRESSURE MEASUREMENT

Pressure was measured by the static method, using glass membrane spoon-type null-manometers [16, 17] (Figure 1). The MePy vapour pressure created by the sample (4) in a hermetically sealed reactive vessel (1) was equilibrated by regulating the external air pressure in the cell 2. When the pressure inside and outside the membrane (3) was the same, the pictures of the all-glass rods (7 and 8) on the screen (6) coincided. The outer compensating pressure was measured with the mercury manometer (13), using the KM-8 cathetometer with an accuracy of 0.01 mm. The sensitivity of the membranes was 0.03–0.1 mm Hg. The accuracy of the thermostatic control of the reaction volume and temperature measurement was 0.05 K (water or oil thermostat) or 0.5 K (air thermostat).

The clathrate [Ni(MePy)$_4$(NCS)$_2$]·(MePy) was used in two experiments aimed at the study of the MePy vapour pressure. The purpose of the first experiment was to study the temperature dependence of the vapour pressure over the clathrate.

The temperature of the sample was regulated with the water (or oil) thermostat 10 (Figure 1a). Four series of experiments were carried out in the temperature range 298–386 K. The series differed in the weight of the portions of the initial clathrate (151–333 mg), with the reaction volume being almost the same (30–32 ml).

The objective of the second experiment was to study the dependence of the guest MePy content in the clathrate matrix on its vapour pressure over the clathrate at constant temperature 318.5 ± 0.5 K (air thermostat 10, Figure 1b). The composition of the clathrate was determined with the help of an uninterrupted weighing balance with a coil spring made of tungsten wire 0.1 mm in diameter. The sensitivity of the balance was 0.2 mm/mg. The elongation of the spring was measured with the cathetometer. The weighed sample was selected so that the weight increase was in the range 40–50 mg. MePy vapour pressure in vacuum reactive vessel (1) was regulated by pumping MePy vapour out or pumping it into the reactive vessel from vessel (17).

The clathrate $[Cu(MePy)_4(NCS)_2] \cdot \frac{2}{3}(MePy)$ was used in two series of experiments carried out for the purpose of studying the temperature dependence of the MePy vapour pressure in the range 292–325 K. The series differed in the ratio of the weighed samples of the initial clathrate to the reactive volume. The process under study is absolutely reversible as equilibrium was approached from the point of view of both temperature and pressure. Equilibrium pressure is rapidly attained. Besides, the equilibrium pressure and equilibrium temperature occur essentially at the same time, and the velocities of the forward and the reverse processes are similar. Notice that to exclude the possibility of inclusion of water in the clathrate as an additional guest [5, 8], the synthesis of the clathrate, the filling of the membrane cell with the substance, and other procedures were carried out in a dry box desiccated with P_2O_5.

Pure MePy saturated vapour pressure was measured in the temperature range 291–361 K; the filling of the membrane cell with liquid MePy was also carried out in a dry box.

To determine the stoichiometry of the processes going on during the conversion of MePy from the clathrate into the vapour phase the quasiequilibrium thermogravimetry method [18] was used (Q-derivatograph). Standard crucibles (open, covered and labyrinth) were used as sample holders.

3. Results and Discussion

3.1. MePy VAPOUR PRESSURE IN $[Ni(MePy)_4(NCS)_2] \cdot (MePy)$ DISSOCIATION PROCESS
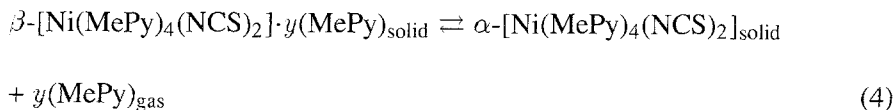
In the range 298–368 K in all the four series of the experiments to study the MePy vapour pressure over the clathrate versus temperature, different pressure values were obtained at the same temperature. This is clearly seen in Figure 2, which presents the relationship between the logarithm of pressure (here and below, the unit in which pressure is measured is mm Hg; 1 mm Hg = 133.322 Pa) on the inverse

temperature for two series with the weighed samples of the initial clathrate, 197 mg (series 1) and 355 mg (series 2), during the forward reaction, i.e. in the process of clathrate dissociation. The data obtained revealed that the equilibrium is divariant and includes two phases: a solid phase of variable composition and a gaseous one. The magnitude of the pressure in this case is affected both by temperature and the composition of the solid phase $[Ni(MePy)_4(NCS)_2] \cdot y\,(MePy)$, and, therefore, the latter is a solid solution resulting from the variable occupation of the cavities $(0 < y < 1)$ of the clathrate framework by the guest molecules of MePy [7]. This resulted in the realization in the strain measurement experiments of clathrate phases with different y values which was due to a different ratio of the weighed initial samples to the reaction volume and explains why the curves in series 1 and 2 do not coincide (Figure 2). The process of vapour formation is described by the equation:

$$\text{MePy (in the solid clathrate solution)} \rightleftharpoons \text{MePy(gas)} \qquad (3)$$
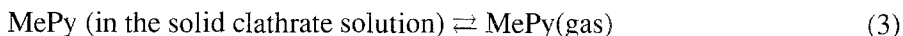
The slope of each line of the temperature dependence of the MePy vapour pressure changes at 346–347 K. This may be due to a slight change in the guest subsystem of the clathrate solid phase.

In the range 298–368 K a constant MePy vapour pressure is established very rapidly, and practically at the same moment a constant temperature is achieved. At about 368 K the character of the MePy vapour formation process changes: the absolute pressure value increases stepwise; its temperature dependence changes; the time required for pressure to become constant increases, and becomes equal to 8–10 h in the course of the forward reaction. X-ray phase analysis revealed that the clathrate samples heated to a temperature of 373 K and higher contained a host α-phase which is not capable of including guest molecules [6]. It would be logical to assume that at a certain composition and temperature the divariant equilibrium (3) gives place to the monovariant one (4) which includes two solid phases and a gaseous one:

$$\beta\text{-}[Ni(MePy)_4(NCS)_2] \cdot y(MePy)_{\text{solid}} \rightleftharpoons \alpha\text{-}[Ni(MePy)_4(NCS)_2]_{\text{solid}}$$

$$+ \, y(MePy)_{\text{gas}} \qquad (4)$$

The process of MePy evaporation from the clathrate is not reversible after the samples are heated to a temperature of 368 K and higher. Having once fallen into condition 1a (Figure 2) the system does not return to condition 1 if it is simply cooled. The reverse process seems to be very slow, which results in the realization of a metastable condition with higher MePy vapour pressure in the system. The appearance of the host α-phase while $\beta\text{-}[Ni(MePy)_4(NCS)_2] \cdot y(MePy)$ is decomposing according to (4) and its slow reaction with MePy on cooling explains the phenomena observed in this study.

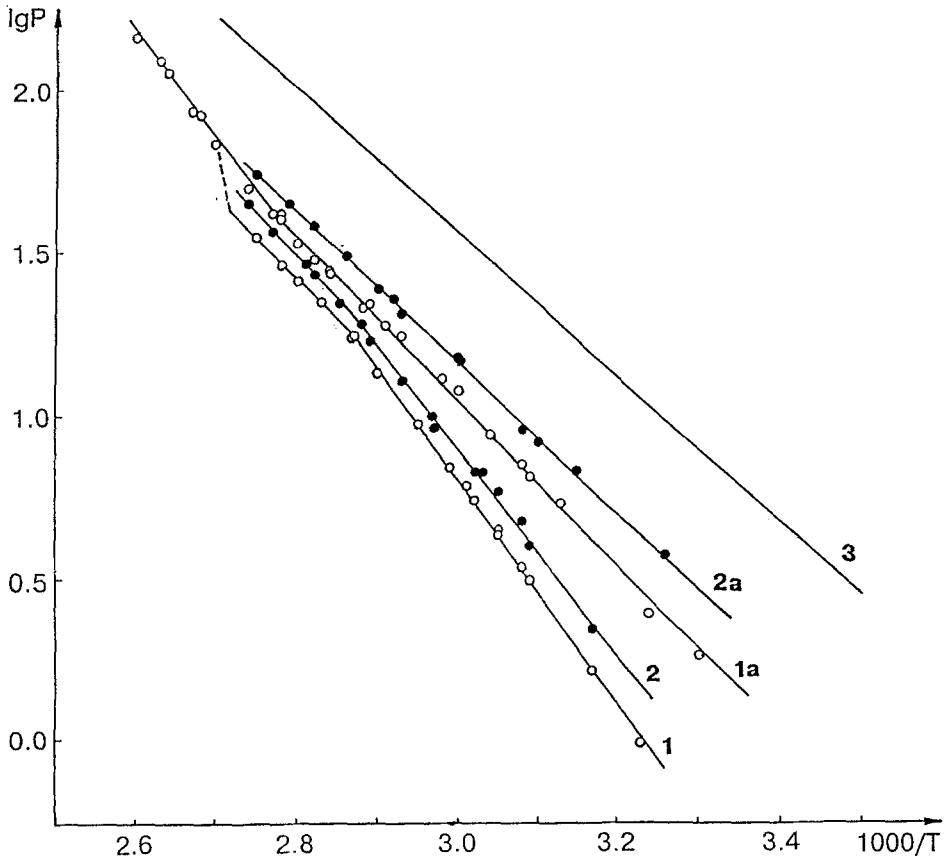Fig. 2.   Logarithm of 4-methylpyridine vapour pressure (mm Hg) over the clathrate [Ni(MePy)$_4$(NCS)$_2$]·y(MePy) versus inverse temperature (K): (1) and (2), two series with different initial clathrate weighed samples; 1a and 2a, the same series after heating the samples to 368 K. (3) Logarithm of the vapour pressure over liquid 4-methylpyridine versus the inverse temperature.

The study of the y–P dependence at constant temperature (desorption isotherm, Figure 3) for [Ni(MePy)$_4$(NCS)$_2$]·(MePy) has also revealed that this clathrate cannot be classified with constant composition compounds because of the absence of a plateau from the desorption curve.

This equilibrium type is also confirmed by the shape of the mass loss curves obtained under quasiequilibrium conditions (Figure 4). Varying the temperature during the loss of the guest supports the above conclusion about the presence of a solid solution. However, after some of the guest is lost, i.e. at certain composition and temperature, the temperature becomes constant, and the remainder of the guest MePy is lost in the narrow temperature range. This points to the changing character of the clathrate thermal dissociation process which is in agreement with
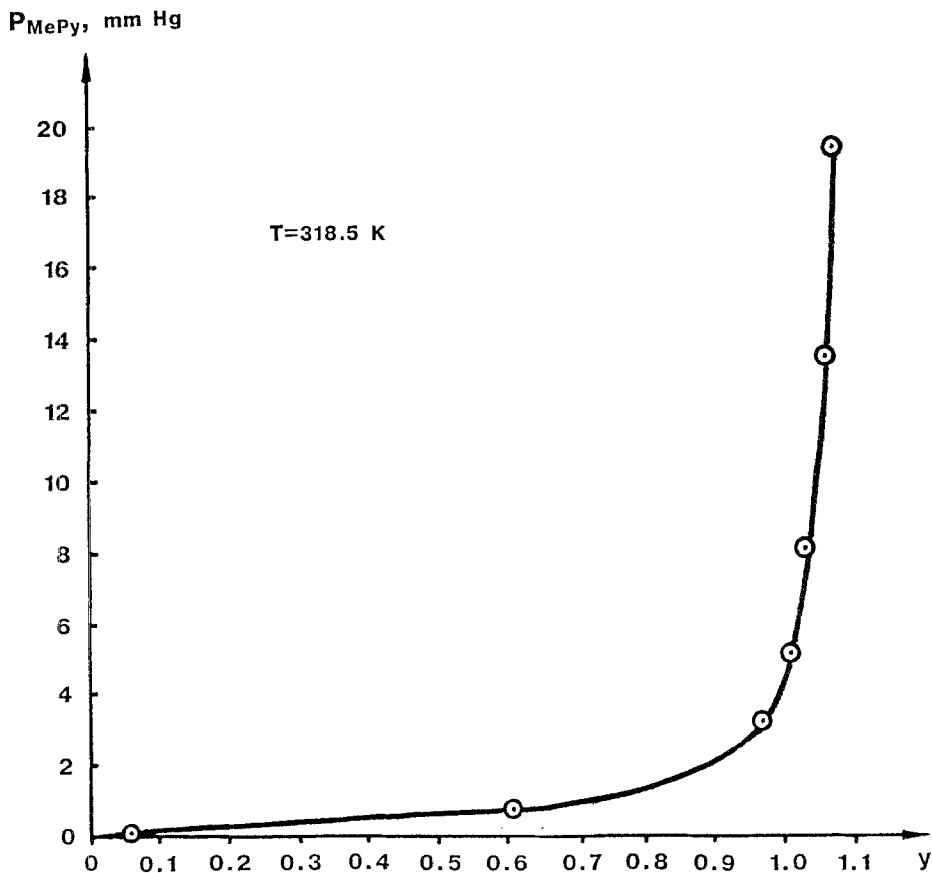
P_{MePy}, mm Hg

Fig. 3.   Desorption isotherm for the clathrate $[Ni(MePy)_4(NCS)_2]\cdot y(MePy)$; y changes from 1 to 0, $T = 318.5$ K.

the experiments on the temperature dependence of the MePy pressure over the clathrate.

Thus, the techniques used allow us to draw reliable conclusions concerning the nature of the clathrate formation process and the presence in the system of solid clathrate solutions. The inference that the clathrate $[Ni(MePy)_4(NCS)_2]\cdot y(MePy)$ is a compound of variable composition (iskhoric solution [19]) agrees well with Brzozowski's and Broniarek's conclusions about the dependence of the clathrate equilibrium composition on the MePy concentration in aqueous solution [2] and Lipkowski's conclusions based on the X-ray phase analysis of a series of the clathrate desorbed samples [7]. Among the factors responsible for this kind of clathrate nature in the MePy–$[Ni(MePy)_4(NCS)_2]$ system is the stability of the host complex itself. That is why it would be interesting to use the above techniques, particularly the precision strain-measurement one, in the study of a clathrate with a host which is unstable as a separate phase. We will show below that this choice
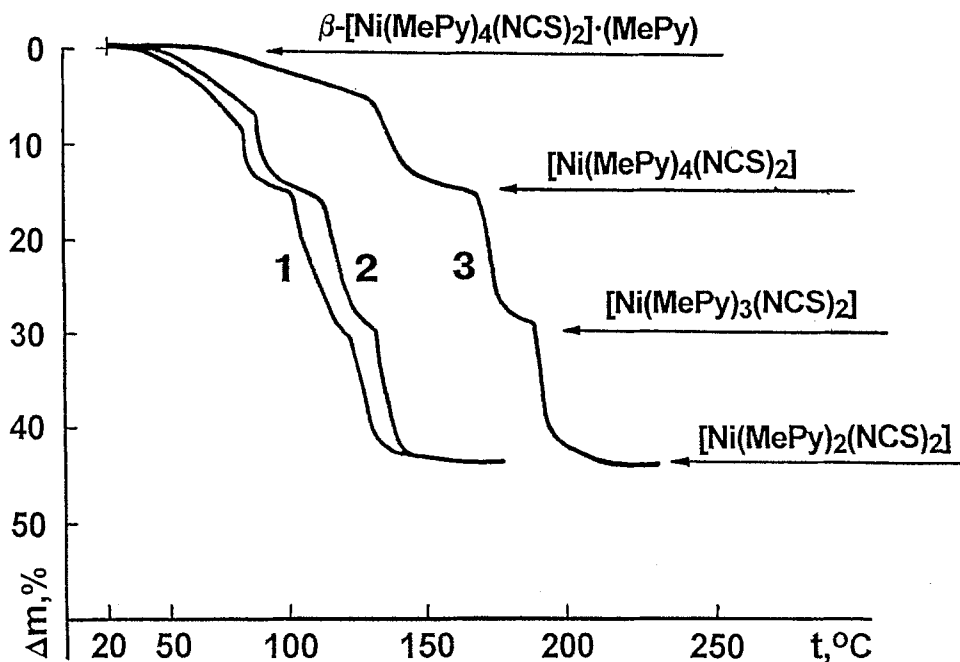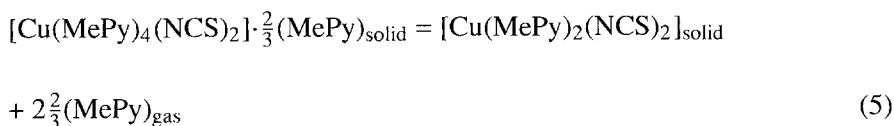
Fig. 4.   Mass loss curves for the clathrate [Ni(MePy)$_4$(NCS)$_2$]·(MePy); heating program: quasiisothermal; $q = 0.3$ mg/min; sample holders: (1) open, (2) covered, and (3) labyrinth crucibles.

of methods is justified, and completely different results were obtained for one of the clathrates in the MePy–[Cu(MePy)$_2$(NCS)$_2$] system.

3.2. MePy VAPOUR PRESSURE IN [Cu(MePy)$_4$(NCS)$_2$]·$\frac{2}{3}$(MePy) DISSOCIATION PROCESS

Experimental data on the temperature dependence of the MePy equilibrium vapour pressure over the clathrate are presented in Figure 5. The relation between the components does not affect the value of the MePy equilibrium pressure within the limits of experimental error, which points to the monovariant character of the clathrate dissociation process, and since during the experiment one of the samples had the composition close to that of the clathrate, we can state that, unlike the Ni system, this system has practically no range of solid solutions. According to quasiequilibrium thermogravimetry (Figure 6) the clathrate dissociation follows the reaction:
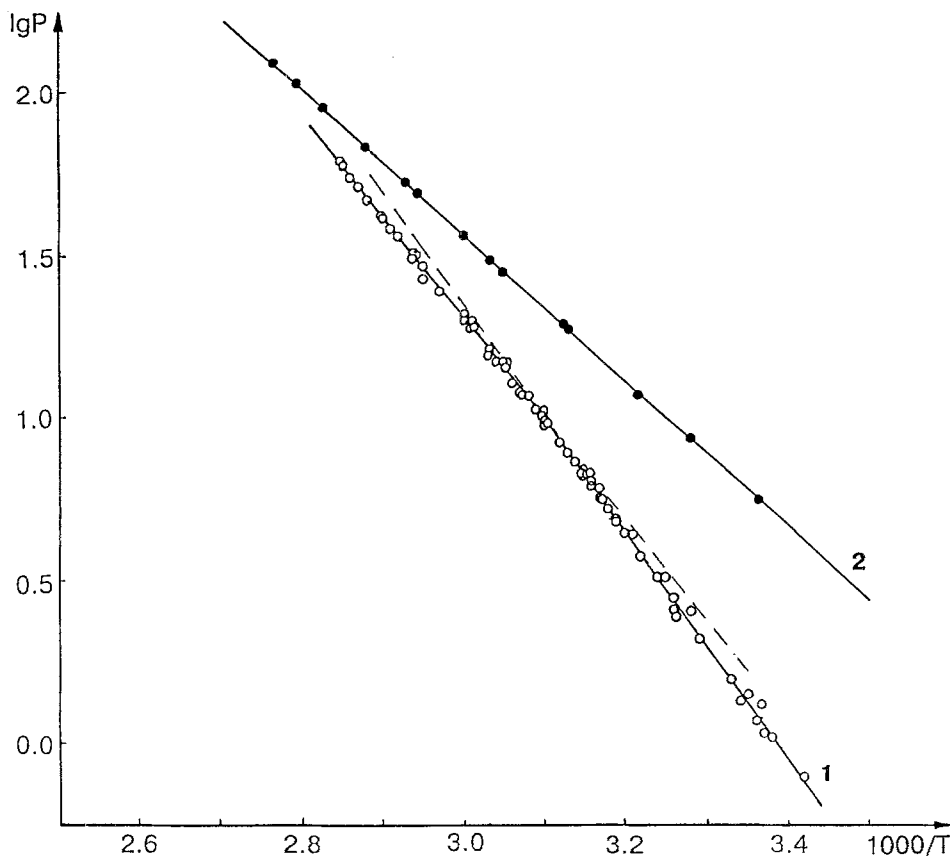
$$[Cu(MePy)_4(NCS)_2]\cdot\tfrac{2}{3}(MePy)_{solid} = [Cu(MePy)_2(NCS)_2]_{solid}$$

$$+\; 2\tfrac{2}{3}(MePy)_{gas} \qquad\qquad\qquad (5)$$

Fig. 5. Logarithm of 4-methylpyridine vapour pressure over the clathrate [Cu(MePy)$_4$(NCS)$_2$]·$\frac{2}{3}$(MePy) versus inverse temperature (1) and logarithm of the vapour pressure over liquid 4-methylpyridine versus inverse temperature (2).

The formation of the [Cu(MePy)$_2$(NCS)$_2$] complex from the clathrate in the course of MePy vapour formation has also been confirmed by the X-ray analysis of the desorbed clathrate samples [6].

The curve of the temperature dependence of the MePy vapour pressure over the clathrate has a break at 325 K (Figure 5) which might be due to a slight change in the guest subsystem [20]. This dependence is described by the equations:

At T = 292–325 K $\quad \log P = (11.96 \pm 0.11) - (3494 \pm 33)/T$

$$(6)$$

(40 exp. points)

At T = 325–351 K $\quad \log P = (10.74 \pm 0.07) - (3101 \pm 23)/T$

$$(7)$$

(29 exp. points)
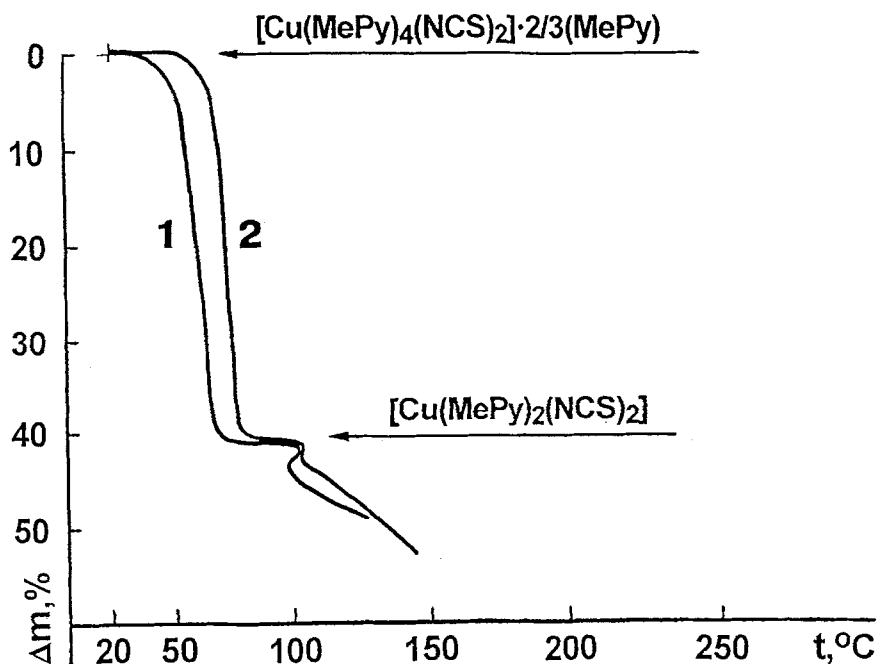
Fig. 6.   Mass loss curves for the clathrate $[Cu(MePy)_4(NCS)_2] \cdot \frac{2}{3}(MePy)$; heating program: quasiisothermal; $q = 0.3$ mg/min; sample holders: (1) open, (2) covered crucibles.

TABLE   I.   Thermodynamic   characteristics   of   the reaction $[Cu(MePy)_4(NCS)_2] \cdot \frac{2}{3}(MePy)_{solid} \rightleftharpoons [Cu(MePy)_2(NCS)_2]_{solid} + 2\frac{2}{3}(MePy)_{gas}$.

Temperature range, K	ΔH° kJ (mole of clathrate)$^{-1}$	ΔS°_{298}, J (mole of clathrate)$^{-1}$ K^{-1}	ΔG°_{298}, kJ (mole of clathrate)$^{-1}$
292–325	178.6 ± 1.7	463.4 ± 5.6	40.4 ± 2.4
325–351	158.5 ± 1.2	401.1 ± 3.6	38.9 ± 1.6

Standard changes of enthalpy, entropy, and the isobaric–isothermal potential of process (5) obtained from this dependence are cited in Table I.

Thus, clathrate formation in the Cu system has some obvious features. In contrast to the Ni system, the Cu system lacks a broad, metastable range of solid clathrate solutions. Moreover, even if the system has a stable range of solutions, it is extremely narrow and it cannot be observed in the strain-measurement experiment. The most plausible cause of these features is the instability of the $[Cu(MePy)_4(NCS)_2]$ host complex, the molecules of which, unlike those of the similar Ni species, are not capable of forming their own phase and are realized only in clathrate phases due to contact stabilization by the guest molecules [12].

3.3. Saturated Vapour Pressure of Liquid MePy

The data obtained are presented in Figure 5. The temperature dependence of the base vapour pressure is described by the equation:

At $T = 297\text{--}361$ K $\quad \log P = (8.26 \pm 0.06) - (2232 \pm 5)/T$

(14 exp. points) (8)

The MePy evaporation enthalpy obtained from the equation equals 42.7 ± 0.1 kJ/mole; the known literature data are 45.19 kJ/mole [21] and 40.00 kJ/mole [3].

Acknowledgements

References

1. W. Kemula, J. Lipkowski, and D. Sybilska: *Rocz. Chem.* **48**, 3 (1974).
2. S. Brzozowski and M. Broniarek: *Rocz. Chem.* **48**, 1213 (1974).
3. J. Chajn, J. Lipkowski, and W. Zielenkiewicz: *Rocz. Chem.* **51**, 1431 (1977).
4. J. Lipkowski and J. Chajn: *Rocz. Chem.* **51**, 1443 (1977).
5. G.V. Gavrilova, N.V. Kislykh and V.A. Logvinenko: *J. Therm. Anal.* **33**, 229 (1988).
6. N.V. Kislykh, Yu.A. Dyadin, N.V. Pervukhina, I.V. Davydova, and N.V. Podberezskaya: *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **3**, 76 (1989); *Chem. Abstr.* **111**, 141646n (1989).
7. J. Lipkowski and S. Majchrzak: *Rocz. Chem.* **49**, 1655 (1975).
8. N.V. Pervukhina, N.V. Podberezskaya, I.V. Davydova, N.V. Kislykh, and Yu.A. Dyadin: *J. Incl. Phenom.* **13**, 9 (1992).
9. J. Lipkowski, Yu.A. Dyadin, and N.V. Kislykh: manuscript.
10. G.D. Andreetti, G. Bocelli, and P. Sgarabotto: *Cryst. Struct. Commun.* **1**, 51 (1972).
11. S.A. Allison and R.M. Barrer: *J. Chem. Soc. A* 1717 (1969).
12. Yu.A. Dyadin and N.V. Kislykh: *Mendeleev Commun.* 134 (1991).
13. M.R. Caira, L.R. Nassimbeni, N. Winder, E. Weber, and A. Wierig: *Supramol. Chem.* **4**, 135 (1994).
14. L.J. Barbour, K. Achleitner, and J.R. Greene: *Thermochim. Acta* **205**, 171, 1992.
15. W.D. Schaeffer, W.S. Dorsey, D.A. Skinner, and C.G. Christian: *J. Am. Chem. Soc.* **79**, 5870 (1957).
16. C.G. Jackson: *J. Chem. Soc.* **99**, 1066 (1911).
17. A.V. Suvorov: *Termodinamicheskaya khimiya paroobraznogo sostoyaniya. Tenzimetricheskiye issledovaniya geterogennykh ravnovesij*, pp. 46–51. Khimiya, Leningrad (1970) (in Russian).
18. F. Paulik and J. Paulik: *J. Therm. Anal.* **5**, 253 (1973).
19. Yu.A. Dyadin, G.N. Chekhova, and N. P. Sokolova: *J. Incl. Phenom.* **5**, 187 (1987).
20. The thermal effect corresponding to this fracture was not observed in the course of the study of the system phase diagram which might be due to its being small, or some other reasons.
21. E.F.H. Herington and I.F. Martin: *Trans. Faraday. Soc.* **49**, 154 (1953).