ORIGINAL ARTICLE

Vapour pressure of guest and thermodynamic stability of inclusion compounds [Ni(DBM)$_2$Py$_2$]*2G (DBM = dibenzoylmethanate anion, G = pyridine, tetrahydrofurane and chloroform)

E. A. Ukraintseva · D. V. Soldatov

Abstract Temperature dependences of the equilibrium vapour pressure of the guest molecules (G) over inclusion compounds [Ni(DBM)$_2$Py$_2$]*2G (DBM = C$_6$H$_5$COCHCOC$_6$H$_5$$^-$—dibenzoylmethanate anion; Py = pyridine; G = pyridine, tetrahydrofurane and chloroform) were investigated by means of the static membrane procedure. It was established using TGA and DTA methods that both of two guest molecules get detached at the first step of decomposition $1/2[Ni(DBM)_2Py_2]*2G_s = 1/2[Ni(DBM)_2Py_2]_s + G_{gas}$. The changes of thermodynamic parameters (ΔH_{av}^0, ΔG_{298}^0 and ΔS_{av}^0) in this process were determined on the basis of the experimental data.

Keywords Vapour pressure · Inclusion compounds · Complex dipyridinebis(dibenzoylmethanato)Ni(II) · Thermodynamic parameters

Introduction

Inclusion compounds based on metal complexes are the objects of supramolecular chemistry being under the most intensive investigation. The authors [1] described the synthesis and structures of the series of inclusion compounds of the complex dipyridinebis(dibenzoylmethanato)nickel(II) (host) with a number of organic solvents as the guest molecules (pyridine, benzene, acetone, tetrahydrofurane, chloroform, etc.). The studied compounds, described by formula [Ni(DBM)$_2$Py$_2$]*nG, (where DBM = dibenzoyl-methanate anion (C$_6$H$_5$COCHCOC$_6$H$_5$)$^-$, G = guest, n = 1 or 2) was shown to belong to one of three structural types: orthorhombic P2$_1$2$_1$2$_1$ (Z = 4); monoclinic C2/c (Z = 8) and monoclinic P2$_1$/п (Z = 2). However, at present there is a lack of data on their thermal and thermodynamic stability. Among the compounds of this series, only for [Ni(DBM)$_2$Py$_2$]*2(CH$_3$COCH$_3$) the temperature dependence of the equilibrium acetone vapour pressure during the dissociation process of this compound was obtained previously and the thermodynamic parameters of the process were determined [2]:

$$1/2[Ni(DBM)_2Py_2] * 2(CH_3COCH_3)_s \\ = 1/2[Ni(DBM)_2Py_2]_s + (CH_3COCH_3)_{gas}$$

The present investigation deals with the studies of thermal stability of three inclusion compounds [Ni(DBM)$_2$Py$_2$]*2G (G = pyridine, tetrahydrofurane and chloroform), determination of the thermodynamic parameters of the decomposition (formation) of these compounds and establishment of the boundaries of their existence. In [2–6] we successfully used the tensimetric method for studying the temperature dependences of the vapour pressure of guest molecules over clathrates to determine the thermodynamic characteristics of inclusion compounds of this type. This method that is sensitive and informative for the given class of compounds was used in this study.

Experimental

Synthesis and identification of the initial complex [Ni(DBM)$_2$Py] and its inclusion compounds with pyridine,

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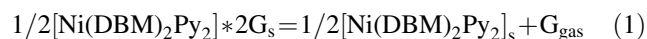
tetrahydrofurane and chloroform were described in [1, 2]. It was established that all the inclusion compounds are characterized by the guest to host ratio equal to 2:1 and crystallize in the monoclinic system with the space group C2/c (Z = 8) for the compound with pyridine guest molecule, and P2₁/n (Z = 2) for the compounds with tetrahydrofurane and chloroform guest molecules.

The temperatures and character of phase transformations were determined using DTA method and visually. For DTA, the samples with a mass of ∼20 mg in sealed thin-walled ampoules were heated at the rate of 5°/min. For visual observation, a microscope and the samples sealed in capillaries were used; they were heated at the rate of 0.5°/min. The stoichiometry of the processes of the first step of dissociation of inclusion compounds was determined with the use of thermogravimetric analysis method. A sample was heated in the quasi-equilibrium mode [7, 8] providing the permanent mass loss rate (q = 0.4 mg/min).
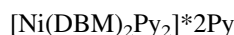
The guest vapour pressure over the inclusion compounds was measured by a static method using Pyrex membrane spoon-type null-manometers. The sensitivity of the membranes was ∼0.05–0.1 torr, the reaction volume (∼20 mL) was thermostated with the help of a water thermostat with the accuracy of 0.05 K. Details of this technique and the scheme of used experimental set-up were given elsewhere [3].

Results and discussion

Some characteristics of the phase transitions of the investigated compounds are listed in Table 1. It can be seen in Table 1 that the host complex is a very stable compound undergoing no changes up to its melting point, which is congruent and is accompanied by rather large endothermic effect. Inclusion compounds are less stable, melt with decomposition at rather low temperatures and with small endothermic effects. According to the data of thermogravimetric analysis, all of them lose both guest molecules at the first step of dissociation:

$$1/2[Ni(DBM)_2Py_2]*2G_s = 1/2[Ni(DBM)_2Py_2]_s + G_{gas} \quad (1)$$

The results of the guest vapour pressure studies will be considered individually for each compound.

$[Ni(DBM)_2Py_2]*2Py$

Dissociation of this clathrate is completely reversible, constant pressure is established rapidly both in the forward and in the reverse direction. Two series of experiments were carried out with this compound; the samples were weighed portions of 261 and 411 mg for about the same reaction volume. Pyridine vapour pressure is almost the same in both series. This is clearly seen in Fig. 1 representing the experimental data as the logarithmic dependence of pressure on reciprocal temperature. The temperature dependence of pressure exhibits a sharp bend. The results of both series were jointly treated with the least squares technique; they are described by the following equations:
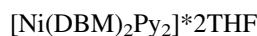
Before the bend $\log P = 8.46(5) - 2142(17)/T \quad (2)$

(Temperature range: 294–328 K, number of experimental points: 29)

After the bend $\log P = 7.60(3) - 1859(11)/T \quad (3)$

(Temperature range: 329–380 K, number of experimental points: 23)

The bend point (crossing of the shown curves) occurs at 328.7 K; it corresponds to incongruent melting of the clathrate (Table 1). Above the melting point, $[Ni(DBM)_2Py_2]_s$, saturated solution of the latter in pyridine and vaporized pyridine are in equilibrium. The pyridine pressure over the clathrate is very close to the saturated vapour pressure for pure pyridine. At 298 K, the pressure over the clathrate is 18.8 torr, while over pure pyridine it is 20.3 torr (Table 2).

$[Ni(DBM)_2Py_2]*2THF$

One set of measurements with the weighed portion of ∼155 mg was carried out. The temperature dependence of pressure exhibits a sharp bend corresponding to the incongruent melting of the clathrate.

Before bend, $\log P = 10.2(5) - 2876(148)/T, \quad (4)$

(Temperature range: 294–319 K, number of experimental points: 6),

After bend, $\log P = 5.30(6) - 1285(20)/T, \quad (5)$

Table 1 The parameters of phase transformations

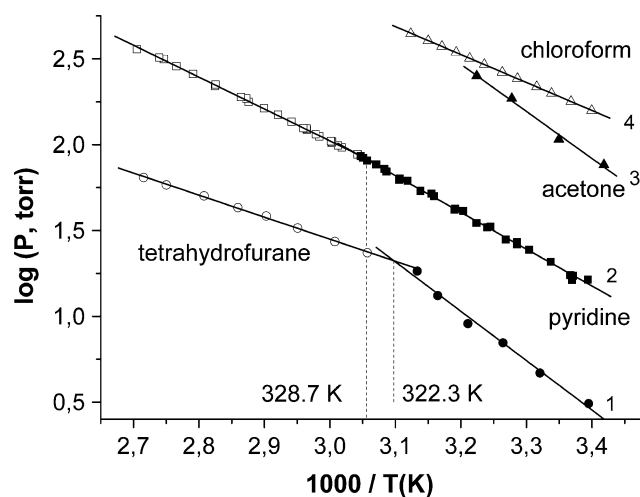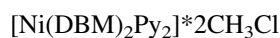| Compound	Melting temperature (K)	Estimated heat of fusion (kJ/mol)	Character of fusion (visually observations)
$[Ni(DBM)_2Py_2]$	485	47.1	Congruent
$[Ni(DBM)_2Py_2]*2(TGF)$	∼327	12.0	Incongruent
$[Ni(DBM)_2Py_2]*2Py$	339	18.7	Incongruent
$[Ni(DBM)_2Py_2]*2(CHCl_3)$	319	14.4	Incongruent
$[Ni(DBM)_2Py_2]*2(CH_3COCH_3)$	∼331	27.9	Incongruent

Fig. 1 Temperature dependences (T, K) of the equilibrium vapour pressure (P, torr) of the guest over inclusion compounds [Ni(DBM)$_2$-Py$_2$]*2G, G = tetrahydrofurane (1), pyridine (2), acetone (3) and chloroform (4)

(Temperature range: 327–368 K, number of experimental points: 8), crossing (the bend point) occurs at 322.3 K.

Errors in determining the coefficients of Eq. 4 are rather large. This is caused by the fact that somewhat overestimated pressure values are obtained at cooling after melting of the sample; no complete reversibility of the process was observed. Because of this, only the data obtained while approaching the equilibrium from low temperatures (on heating) were used.
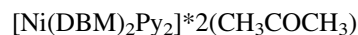
[Ni(DBM)$_2$Py$_2$]*2CH$_3$Cl

The sample under investigation was a crystalline dry substance; the weighed portion of about 700 mg was taken. Within the investigated temperature range 293–320 K, the dissociation of the clathrate is a reversible process; the equilibrium pressure is rapidly established except for the first measurements at room temperature. Pressure values are high (at 21 °C the pressure value is already 158 torr, at 47 °C it is 444 torr) and close to the saturated vapour pressure for pure chloroform (for these temperatures the pressure values are 163 and 465 torr, respectively). With a good accuracy, the experimental data are described with equation:

$$\log P = 7.73(1) - 1628(2)/T \qquad (6)$$

(Temperature range: 292–320 K, number of experimental points: 12)

Above 320 K, measurements were not carried out due to the technical reasons.

[Ni(DBM)$_2$Py$_2$]*2(CH$_3$COCH$_3$)

The results of the investigation of this compound, similar in composition to the previous one, were described in detail in [2]; here we present the quantitative data in order to compare with those for the above-described clathrates. The temperature dependence of acetone vapour pressure in this system is described with equation:

$$\log P = 11.2(5) - 2742(16)/T \qquad (7)$$

The dependences given in the Eqs. 2–7 together with the experimental values of vapour pressure of the guest are presented in the Fig. 1.

One can see in Table 2 that pyridine and chloroform vapour pressure over inclusion compounds [Ni(DBM)$_2$-Py$_2$]*2G at 298 K is close to the vapour pressure for the pure solvent, while vapour pressure of tetrahydrofurane and acetone decreases substantially when they get included into the host lattice. Comparing these data with similar data for the inclusion compounds based on copper complex [CuPy$_4$(NO$_3$)$_2$]*2G, one can see that the latter, especially the compound containing pyridine as the guest, demonstrate a substantial decrease of the solvent vapour pressure on their inclusion into the lattice of [CuPy$_4$(NO$_3$)$_2$].

This fact that the vapour pressure of pyridine guest molecules in the system [Ni(DBM)$_2$Py$_2$]*2Py does not depend on the mass of the initial clathrate phase provided the reaction volume is the same testifies that the investigated equilibrium is monovariant and the studied compound may be considered as the inclusion compound of constant composition. This conclusion has been extended on the inclusion compounds of the complex [Ni(DBM)$_2$Py$_2$] with tetrahydrofurane and chloroform.

Using the coefficients given in the Eqs. 2–7, that express the temperature dependences of equilibrium vapour pressure of the guest, the changes of standard enthalpy, entropy and isobaric–isothermal potential of the process I were

Table 2 Vapour pressure (torr) of the guest over inclusion compounds [Ni(DBM)$_2$Py$_2$]*2G, [CuPy$_4$(NO$_3$)$_2$]*2G and over pure solvents at 298 K[a]

Host\Guest	Pyridine	Tetrahydrofurane	Chloroform	Acetone
[Ni(DBM)$_2$Py$_2$]	18.8 (0.93)[a]	3.6 (0.02)	189 (0.98)	101 (0.44)
[CuPy$_4$(NO$_3$)$_2$]	1.3 (0.06) [9]	41 (0.23) [9]	111 (0.44) [9]	No data
Pure solvent	20.3 [11]	176 [12]	193 [12]	230 [12]

[a] The ratios of guest vapour pressure above inclusion compound to the saturated vapour pressure for pure solvent are given in round brackets

Table 3 Thermodynamic parameters of processes $1/2[Ni(DBM)_2Py_2]*2G_s = 1/2[NiPy_2(DBM)_2]_s + G_{gas}$ (1) and $[Ni(DBM)_2Py_2]*2G_{melt} = [Ni(DBM)_2Py_2]_s + G_{gas}$ (2)

G		Range, T (K)	ΔH_{av}^0 (kJmol^{-1})	ΔG_{298}^0 (kJmol^{-1})	ΔS_{av}^0 (Jmol^{-1}K^{-1})
Py	(1)	294–328	41.0 (3)	9.16 (6)	107 (1)
	(2)	329–380	35.6 (2)	–	–
TGF	(1)	294–319	55 (3)	13.1 (1)	141 (9)
	(2)	327–368	24.6 (4)	–	–
CHCl$_3$	(1)	293–320	31.3 (1)	3.45 (9)	93.3 (1)
Acetone	(1)	292–310	53 (3)	4.74 (7)	160 (10) [2]

calculated. Their numerical values are given in the Table 3. It is seen that the enthalpies of dissociation of the compounds investigated are within the usual range for inclusion compounds of this type. For example, for the compound $[CuPy_4(NO_3)_2]*2G$, with the same guest molecules, this range is 45–74 kJ/mol guest$_{gas}$ [9]. However, if we arrange the guest molecules in the order of decreasing enthalpies of their binding with the host complex, the sequences will be different. For $[Ni(DBM)_2Py_2]*2G$, it will be as follows:

Tetrahydrofurane > pyridine > chloroform,

while for $[CuPy_4(NO_3)_2]*2G$ it will be:

Pyridine > tetrahydrofurane > chloroform.

The minimal values of changes of isobaric-isothermal potential have the inclusion compounds of the complex $[Ni(DBM)_2Py_2]$ with chloroform and acetone as the guests (3.45 kJ/mol of the guest and 4.74 kJ/mol of the guest, respectively). For the comparison, the value of isobaric–isothermal potential change for the dissociation process of inclusion compound of the complex $[CuPy_4(NO_3)_2]$ with chloroform (4.88 kJ/mol of the guest) is close to the given values [9]. This explains the experimental observations that when obtaining some of these compounds (with chloroform, acetone), sometimes not inclusion compounds but the crystals of the host complex $[Ni(DBM)_2Py_2]$ or its mixture with the inclusion compound get crystallized from the corresponding solutions.

So, as it has been already demonstrated in [10], the stability of inclusion compounds is affected both by the nature of the host component and by the nature of the guest component.

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