

The Structure–Properties Relations in Werner β -[Ni(NCS)₂(4-MePy)₄] Clathrates. Part 1. Sorption Equilibria and Guest to Host Influence in Solid β -[Ni(NCS)₂(4-MePy)₄] Clathrate – Gaseous Guest Systems

A. YU. MANAKOV^{1*} and J. LIPKOWSKI^{**}

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01 224 Warsaw, Poland.

(Received: 3 January 1997; in final form: 9 January 1997)

Abstract. Sorption equilibria have been studied in the systems solid β -[Ni(NCS)₂(4-MePy)₄] clathrate – gaseous guest (benzene, furan, tetrahydrofuran, propane, CH₂Cl₂, CH₂Br₂, methanol). Analysis of the experimental data shows that the solid–gas equilibrium in this system cannot be regarded as simple physical sorption by a rigid host lattice. It was found that the isosteric heats of guest sorption decrease with increasing guest uptake in all systems studied. The observed phenomena are interpreted as the result of a guest to host influence and guest–guest repulsion. The molecular model of guest sorption by the β -[Ni(NCS)₂(4-MePy)₄] host was suggested on the basis of combined analysis of sorption isotherms and the dependence of the isosteric heat of sorption on clathrate composition.

Key words: Werner clathrates, sorption equilibria, isosteric heats of sorption.

1. Introduction

A large number of different inclusion compounds whose host lattice is built from non-bonded or weakly bonded large molecules have been reported to date [1–4]. Compared to the availability of structural information, physicochemical data on such host–guest systems are relatively sparse and fragmentary. This group of inclusion compounds may be divided into two subgroups: those with a host lattice, which is stable only when completely filled by the guest molecules (for example, the clathrate β -[Zn(NCS)₂(4-MePy)₄]·(4-MePy), where MePy is 4-methylpyridine [5]); and those with a host lattice which preserves its structure after removal of part (or even all) of the guest molecules (some clathrates of gossypol [3], clathrates of the so-called β -phases of the [Ni(NCS)₂(4-MePy)₄] host [6]). Host–guest equilibria in these systems partially resemble equilibrium in systems with

* On leave of absence from Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, 630090, Novosibirsk, Lavrentyeva 3, Russia.

** Author for correspondence.

zeolites as hosts (especially for clathrates of the second group), and the realisation of reversible sorption–desorption cycles with such hosts is possible. The discovery of a great number of new types of ‘host’ substances with various possibilities for guest accommodation and host–guest interactions lead us to assume the possible importance of inclusion compounds with a host lattice constructed of independent or weakly-bonded molecules in the separation and modification of host (or guest) molecules. The typical host lattice of the second group of clathrates is ‘soft’, and distorts with changes of type or number of included guest molecules to achieve the most favourable configuration of van der Waals contacts or/and hydrogen bonding (available data for β -[Ni(NCS)₂(4-MePy)₄] clathrates are reported in [7], and for gossypol clathrates in [3]). The guest-to-host influence must be taken into account jointly with the assumption of different possible modes of guest accommodation (caused by peculiarities of host and guest geometry). Although it seems necessary for an understanding and correct interpretation of clathration equilibria, no systematic investigation of these phenomena has yet been performed for any host of the types discussed.

Clathrates with the β -[Ni(NCS)₂(4-MePy)₄] host lattice belong to the most studied (from both structural and physicochemical points of view) type of clathrates under consideration, because this host has been used as an adsorbent in the chromatographic separation of isomers of benzene derivatives and some other isomers [6, 8]. A significant number of X-ray structures of β -[Ni(NCS)₂(4-MePy)₄] clathrates with different guests have been determined [9–12]. The remarkable kinetic stability of this ‘empty’ host lattice allowed its structure to be determined by the X-ray method [13]. It was found that inclusion of guest molecules of different size and shape (and even complete removal of all guest molecules) does not significantly change the geometry of the host lattice. This fact facilitates the analysis of the guest to host influence and the interpretation of physicochemical data obtained for β -[Ni(NCS)₂(4-MePy)₄] – guest systems. The shape of the channels in a typical β -[Ni(NCS)₂(4-MePy)₄] clathrate is illustrated in Figure 1. The heterogeneity of sorption positions in the β -[Ni(NCS)₂(4-MePy)₄] phase allows different arrangements of guest molecules; the peculiarities of the channel geometry cause the effects of molecular recognition (localisation of guest molecules of different shape at different sorption positions [6, 11]). Studies of equilibria in solid clathrate – gaseous guest systems take advantage of the easy variations of guest activity over the clathrate phase (guest vapour pressure). Complications caused by solvent are eliminated in this case. This method may supply detailed information about guest accommodation and guest to host influence, but only one work on the topic has been published to date [14]. It has been established [6], that clathrates of the β -[Ni(NCS)₂(4-MePy)₄] host are typical solid solutions of guest molecules in a host matrix. Sorption isotherms of guest molecules such as methane, methanol, CH₃Cl were studied in [14]: it was shown that guest sorption by the β -[Ni(NCS)₂(4-MePy)₄] host is a complex process and the simple Langmuir equation is not valid in this case. All factors mentioned above played a role in our

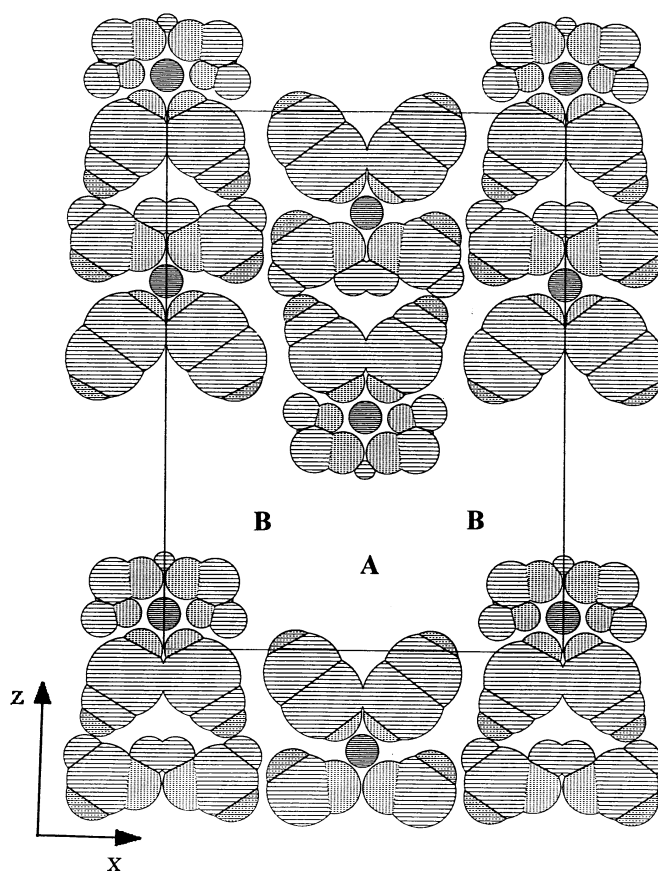


Figure 1. Typical [040] section of a β -[Ni(NCS)₂(4-MePy)₄] clathrate (guest molecules omitted). B and A 'absorption centers' with $\bar{1}$ and $\bar{4}$ local symmetry ('small cavity' and 'large cavity', respectively).

interest in investigating the chemical equilibria and isosteric heat of sorption in solid β -[Ni(NCS)₂(4-MePy)₄] clathrate-gaseous guest systems.

2. Experimental

The host [Ni(NCS)₂(4-MePy)₄] co-ordination complex was synthesised according to [15]. Samples of the β -[Ni(NCS)₂(4-MePy)₄]·benzene clathrate were prepared by putting α -[Ni(NCS)₂(4-MePy)₄] powder (particle size about 0.01 mm., as determined by microscopic observations) into a mixture of about 10% of 4-methylpyridine and 90% of benzene. Samples of the β -[Ni(NCS)₂(4-MePy)₄] phase with particle size 0.1–0.15 mm were prepared according to [16]. According to X-ray powder diffraction data, the pure β -[Ni(NCS)₂(4-MePy)₄]·yG phase was obtained. Samples of the empty β -[Ni(NCS)₂(4-MePy)₄] phase were obtained by

decomposition (guest desorption) of the benzene clathrate in a flow of air until the sample mass had stabilised.

Isotherms were investigated by using the experimental apparatus and procedure described in [17], with a Mettler AE100 balance and an external reservoir of guest vapour. The temperature in the apparatus was maintained with an accuracy of ± 0.2 °C, pressure was measured with a mercury manometer with an accuracy of ± 70 Pa. Sample sizes of 400–500 mg were used. Errors in determination of y (the number of guest molecules per single host molecule) were less than ± 0.05 for the isotherm with tetrahydrofuran, and less than ± 0.03 for other isotherms.

The dependencies of the pressure of the guest vapours over the clathrate versus temperature were determined in a glass chamber connected to a mercury manometer, vacuum system and source of guest vapours. Two modifications of the experimental apparatus with different internal volume were used (≈ 15 mL and ≈ 150 mL, with manometer diameter 7 and 22 mm respectively). The first modification was used for experiments at pressures > 2000 Pa, where measured values of the isosteric heat of sorption were not significantly influenced by capillarity. The second modification was used for experiments at lower pressures. In a typical run, about 1.5 g of large, well-formed crystals of the β -[Ni(NCS)₂(4-MePy)₄] clathrate with benzene were put into the apparatus, freed from benzene by long-term pumping at elevated temperatures and prepared for the experiment by repeated sorption and desorption of a given guest. The temperature was maintained with an accuracy of ± 0.05 °C, pressure was measured by a catetometer with an accuracy of ± 15 Pa for pressures greater than 2000 Pa and ± 7 Pa for smaller pressures.

3. Results and Discussion

3.1. PRELIMINARY EXPERIMENTAL DATA

To determine the experimental technique which should best be used for investigation of sorption isotherms, some preliminary experiments were performed with sorption of different guests into the empty β -[Ni(NCS)₂(4-MePy)₄] phase. As found in [16], only a limited (less than equilibrium) quantity of guests such as *p*-xylene and toluene were taken up after 30 min contact of guest with the powder of the empty host phase. The same results were obtained when tetrahydrofuran was used as a guest (size of host particles was 0.1–0.15 mm), significant scattering of guest uptakes by different samples of host took place in this case. The effect of a decrease of host particle size is illustrated in Table I. The host powder with about 0.01 mm particle size was used in all further experiments. An interesting effect, illustrated in Figure 2, was observed for all systems studied (the smallest effect was observed for systems with furan and benzene as guests) in the 10–35 °C temperature interval. Then guest uptake achieves ‘pseudoequilibrium’ and further increase of guest content became very slow (changes of sample mass could not be registered during 1 h).

Table I. Influence of size of host particles on guest uptake in the solid β -[Ni(NCS)₂(4-MePy)₄] clathrate-gaseous tetrahydrofuran system (pressure of guest vapours about 5000 Pa).

Temperature °C	Estimated size of host particles mm	Resulting host : guest ratio
19.9	0.1-0.14	1 : 0.34
30.1	0.1-0.14	1 : 0.32
19.9	0.01	1 : 0.37
39.1	0.01	1 : 0.44
19.9*	0.01	1 : 0.5
39.1*	0.01	1 : 0.47

* These points were obtained using the special technique described in the text.

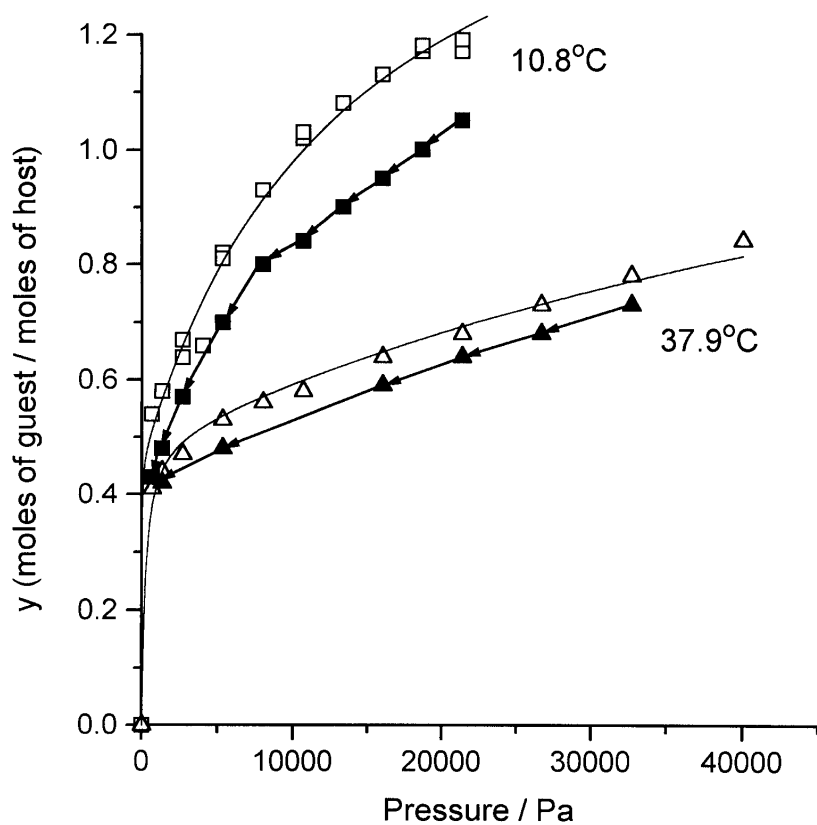


Figure 2. Sorption of CH₂Cl₂ guest into the β -[Ni(NCS)₂(4-MePy)₄] phase. Equilibrium sorption isotherms (open symbols) were obtained using the special technique described in the text. Solid symbols represent 'pseudoequilibrium' points which were obtained by sorption of vapours into the empty β -[Ni(NCS)₂(4-MePy)₄] phase at the guest pressure, corresponding to the 'highest' symbol. Arrows show the direction of guest vapour pressure decrease.

A special experimental technique was used in our experiments to achieve the true equilibrium state. CH_2Cl_2 , CH_2Br_2 , THF and benzene were used as guests, samples of the empty β - $[\text{Ni}(\text{NCS})_2(4\text{-MePy})_4]$ phase were exposed (0.1–1 h) to guest vapours at a pressure greater than the pressure over a saturated solution of the $[\text{Ni}(\text{NCS})_2(4\text{-MePy})_4]$ complex compound in the respective liquid solvent. After that, the pressure of guest vapours was reduced and the composition of the equilibrium clathrate was recorded after the sample mass reached a constant value. In the case of propane and furan as guests, the equilibrium state was assumed if saturation proved to be independent of the way the final pressure of the guest was reached. Reproducible experimental results were obtained by using this technique, the limit values of host : guest ratio obtained were in good agreement with the stoichiometry of the respective clathrates [9–11].

An explanation of the observed phenomena may be suggested as follows. Let us discuss one spherical particle of the host phase with ‘sorption positions’ situated in the three-dimensional system of channels. When a guest molecule occupies a ‘sorption position’, it blocks diffusion of the guest molecules through this part of the channel. When a particle of the empty host phase is in contact with vapours of the guest, the molecules of the latter may occupy ‘sorption positions’ close to the surface of the particle and begin to diffuse into the internal layers. If exchange of molecules between the gas phase and the external layer of the particle is faster than exchange between external and internal layers, the situation is that the concentration of vacant ‘adsorption centres’ in the internal part of the particle remains greater than the equilibrium concentration (‘defects’), and these ‘defects’ slowly diffuse in the internal part of the crystal, occasionally annihilating guest molecules from the external part of the particle. A change of equilibrium pressure of guest vapours causes a rapid change of guest concentration in the ‘external’ part, and significantly slower changes in the ‘internal’ part of the particle. An increase of particle radii increases the volume of the ‘internal’ part of the crystal, hence deviations from equilibrium stoichiometry become higher.

3.2. SORPTION ISOTHERMS AND ISOSTERIC HEATS OF GUEST SORPTION IN THE β -PHASE

Experimental isotherms of sorption of different guests by the β - $[\text{Ni}(\text{NCS})_2(4\text{-MePy})_4]$ phase are shown in Figures 3 and 4. Sorption isotherms for methanol guest are reported in [14]. Single crystal X-ray structures of the clathrates under investigation (except for the clathrates with propane and CH_2Br_2 as guests, which were obtained only by sorption of gaseous guest into the empty host phase) are reported in [9–11]; four different modes of guest molecule arrangements in the solid clathrate were reported for the guests. Brief information about the localisation of guest molecules will be given in this section.

Benzene molecules occupy ‘small cavities’ (positions B in Figure 1), which corresponds to the maximum 1 : 1 host : guest ratio. Furan molecules occupy

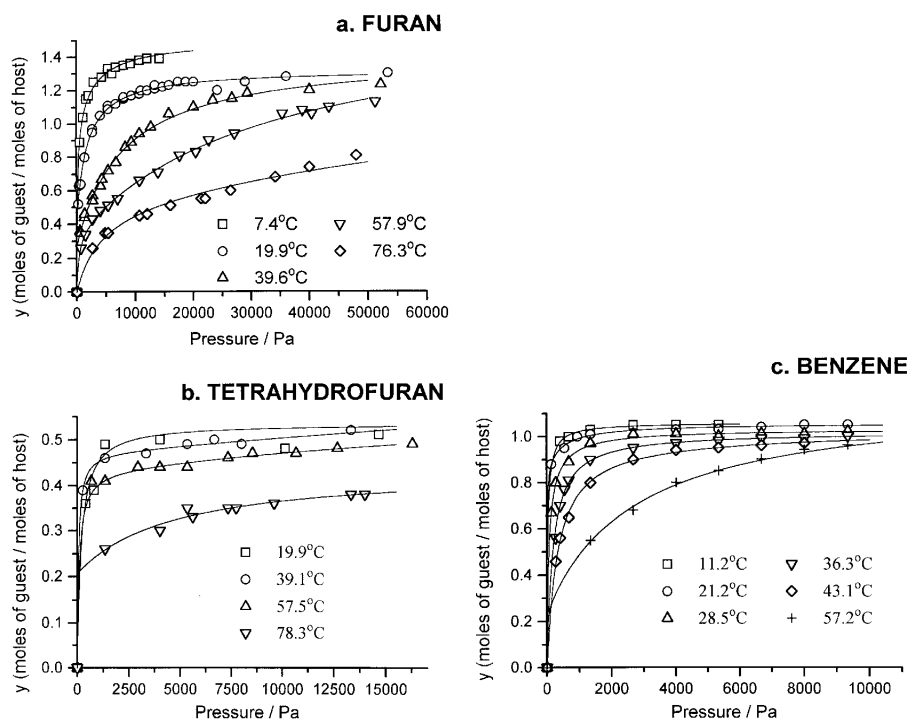


Figure 3. Sorption isotherms of furan (a), tetrahydrofuran (b) and benzene (c) in the β -[Ni(NCS)₂(4-MePy)₄] phase clathrate.

both A and B type ‘sorption positions’ with the experimentally stated 1 : 1.5 limit host : guest stoichiometry, and tetrahydrofuran occupies only A type positions (1 : 0.5 limit host : guest ratio). Allocation of some CH₂Cl₂ molecules in a ‘large cavity’ (position A in Figure 1) with limit ‘nonideal’ 1 : 1.2 host : guest ratio was reported for this guest. As reported in [10] four methanol molecules occupy A type positions (or, equivalently, two methanol molecules occupy B type positions) with ideal stoichiometry 1 : 2 host : guest ratio. Based on the rules for guest allocation [11] the same modes of guest accommodation with the same ideal stoichiometries may be suggested for such pairs as CH₂Cl₂ and CH₂Br₂, tetrahydrofuran and propane.

The principal nonstoichiometry of β -[Ni(NCS)₂(4-MePy)₄] clathrates causes significant deviations of clathrate composition from the ideal stoichiometry [6, 15], but out of the mother solution most β -[Ni(NCS)₂(4-MePy)₄] clathrates rapidly lose guest molecules, which complicates the analytical determination of the composition of these clathrates. The 1 : 1.05 and 1 : 1.83 limit host : guest ratios were reported for the benzene and methanol clathrates, respectively [15]; similar values were obtained in sorption experiments (Figure 3). Comparatively slow (composition of crystals removed from mother solution, remains practically unchangeable over

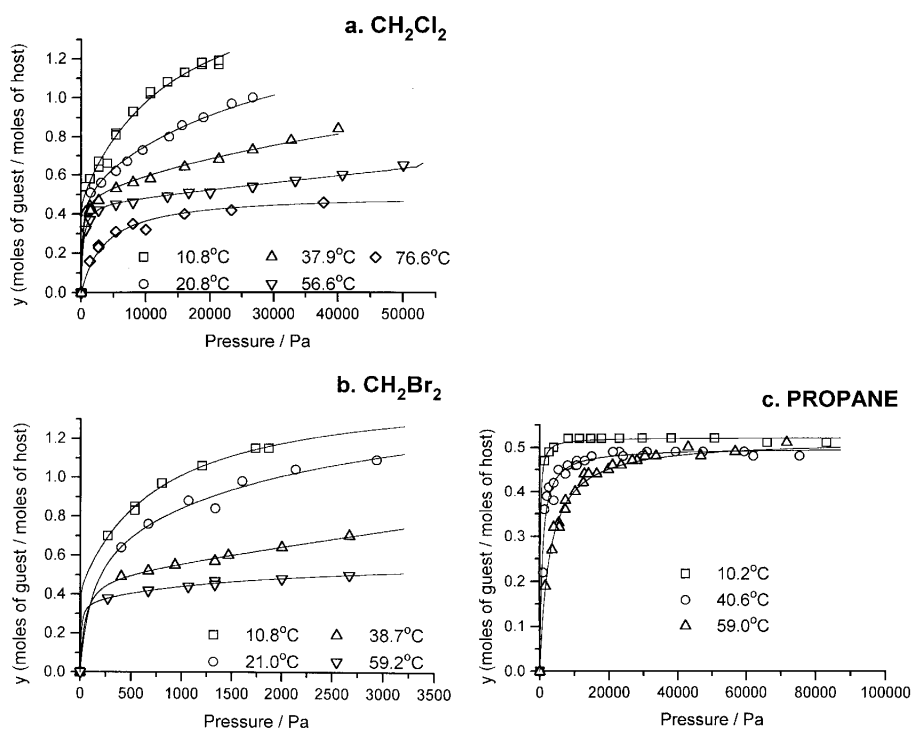


Figure 4. Sorption isotherms of CH₂Cl₂ (a), CH₂Br₂ (b) and propane (c) in the β -[Ni(NCS)₂(4-MePy)₄] phase clathrate.

1–2 mm) decomposition of the tetrahydrofuran clathrate allowed us to weigh crystals of the clathrate before and after decomposition, giving a 1 : 0.51 limit host : guest ratio. The sorption data are in good agreement with this result (Figure 3). The same limit stoichiometry may be suggested for the propane clathrate based on the sorption data. The ideal limit stoichiometry was observed by the present authors in experiments on the sorption of furan saturated vapours in the empty β -[Ni(NCS)₂(4-MePy)₄] phase at about 0 °C.

The concept of different ‘sorption positions’ which are available for the guest molecules in the channels of the β -[Ni(NCS)₂(4-MePy)₄] phase was suggested in [11]. The following types of position may be defined on the basis of X-ray structural data. If a guest molecule has a tendency to be localised in a ‘large cavity’, localisation of a first guest molecule in the cavity may be called a ‘first sorption position’, a second guest molecule goes into a ‘second sorption position’, and so on. Localisation of a first guest molecule in a ‘small cavity’ leaves unoccupied the residual space in a ‘large cavity’ – a second sorption position. It should be underlined that ‘over-stoichiometric’ guest molecules may be regarded as included at another type of sorption position with a small degree of filling. When comparing β -[Ni(NCS)₂(4-MePy)₄] clathrates with benzene and furan as guests one can see

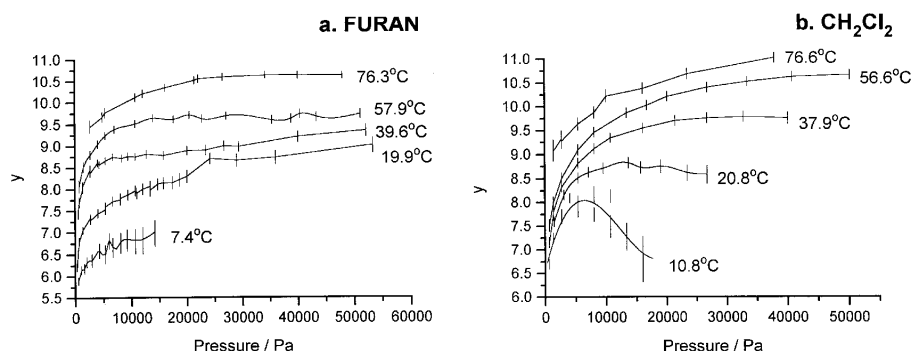


Figure 5. $\ln(p(1-\theta)/\theta)$ guest vapour pressure plot for furan (a) and CH_2Cl_2 (b) isotherms. ($K = \ln(p(1-\theta)/\theta)$).

that a decrease of guest molecular size from a six-membered to a five-membered ring causes additional filling of the second type of positions by the same guest. An example of filling of residual free space in the β - $[\text{Ni}(\text{NCS})_2(4\text{-MePy})_4]$ clathrate with benzene by another guest (ethanol) is also known [11]. By analysing the shape of the sorption isotherms it may be seen that they very often have inflexion points at compositions which approximately correspond to the 1 : 0.5 or 1 : 1 host : guest ratios. This may be interpreted as a completion of guest inclusion on one possible type of 'sorption position' and the start of guest inclusion onto the second position.

As a first step of treatment we tested the validity of the simple Langmuir equation for representation of our experimental data. The $\ln(p(1-\theta)/\theta)$ versus p plots (where p is the equilibrium pressure of guest vapours and $\theta = \text{guest content/limit guest content ratio}$) for furan and CH_2Cl_2 sorption isotherms are shown in Figure 5. It may be concluded that sorption of guest molecules by this host cannot be described as simple physical sorption, which agrees with the conclusion reached in [14]. Similar results were obtained for sorption of other guests. The main part of the sorption isotherms in the β - $[\text{Ni}(\text{NCS})_2(4\text{-MePy})_4]$ host phase, which were studied in this work and in [14] correspond to type 1 of the Brunauer classification, but sorption isotherms of some 'light' molecules (including methanol and methane) belong to types 4 or 5 [14].

Guest to host influence, guest-guest interactions and specific host-guest interactions may cause deviations from the simple Langmuir sorption equation in the systems under consideration. Since non-Langmuir behaviour is characteristic of guests with very different chemical natures and localisation in the channels of the host lattice (benzene, tetrahydrofuran, CH_2Cl_2), specific host-guest interactions cannot be regarded as playing a significant role in clathrates of this host. It should be mentioned that structure analysis of the β - $[\text{Ni}(\text{NCS})_2(4\text{-MePy})_4]$ host lattice does not allow us to exclude the possibility of such interactions, but their existence was not detected [6]. The same conclusion may be drawn about the possibility of guest-guest specific interactions. The possible influence of specific interactions

on the properties of β -[Ni(NCS)₂(4-MePy)₄]-guest systems will not be discussed. Dipole-dipole host-guest interactions were found in another Werner host-guest system [18].

Values of the isosteric heat of sorption (q_{st}) were calculated for different clathrate compositions from data on the variation of equilibrium guest vapour pressure over the clathrate with temperature (in ± 5 °C intervals from the mean value of temperature) as described in [19]. The data obtained are shown in Figure 6 and Table II. Because $q_{st} = -\Delta\bar{H}$ ($\Delta\bar{H}$ is the partial molar heat of guest sorption), a greater value of the isosteric heat of sorption means a more exothermic sorption process and hence a more energetically favourable configuration of the host-guest system. The large scatter of the experimental points allowed us to draw only qualitative conclusions. Values of the isosteric heats of guest sorption decrease with increasing guest content in the clathrate phase (which contradicts the results reported in [14]).

3.3. INTERPRETATION OF THE EXPERIMENTAL DATA

As mentioned earlier, in [11] we suggested the hypothesis about the heterogeneity of 'sorption positions' in the β -[Ni(NCS)₂(4-MePy)₄] phase, and the types of positions which are available for guest molecules of different size and shape were analysed. The data presented in this work allow us to discuss the process of guest inclusion in more detail. The common scheme of sorption of guest molecules, studied in this work, into the empty β -[Ni(NCS)₂(4-MePy)₄] phase may be represented in the following way.

The geometry of the host lattice in the 'empty' β -[Ni(NCS)₂(4-MePy)₄] phase illustrates the most energetically favourable configuration of the host-host interactions for this metastable clathrate lattice. Inclusion of the guest molecules distorts the host lattice. The configuration of the host-host contacts becomes less favourable, but very energetically favourable host-guest interactions compensate for this loss in energy. As discussed earlier, only nonspecific van der Waals interactions exist in host-guest systems with the β -[Ni(NCS)₂(4-MePy)₄] host, hence the efficiency of these interactions is the determining factor for heat effects in such systems. Two possible modes of distortions of the host lattice geometry may be postulated; being located at a 'sorption position' a guest molecule distorts the geometry of only the neighbouring part of the host lattice and inclusion of the guest molecule causes a change of geometry of the whole host lattice. In the first case a gradual decrease of q_{st} should be expected, the second situation corresponds to a first-order phase transition and abrupt changes of q_{st} should occur. The phenomenon discussed may be regarded as examples of guest to host influence; modification of the host lattice by the included guest molecules then changes the properties of the given host-guest system. Experimentally observed changes of q_{st} at the clathrate composition corresponding to the filling of one type of sorption position (Table II, Figure 6) confirms the model discussed earlier. Similar phenomena were observed when co-sorption of different guest molecules, which occupy the same type of

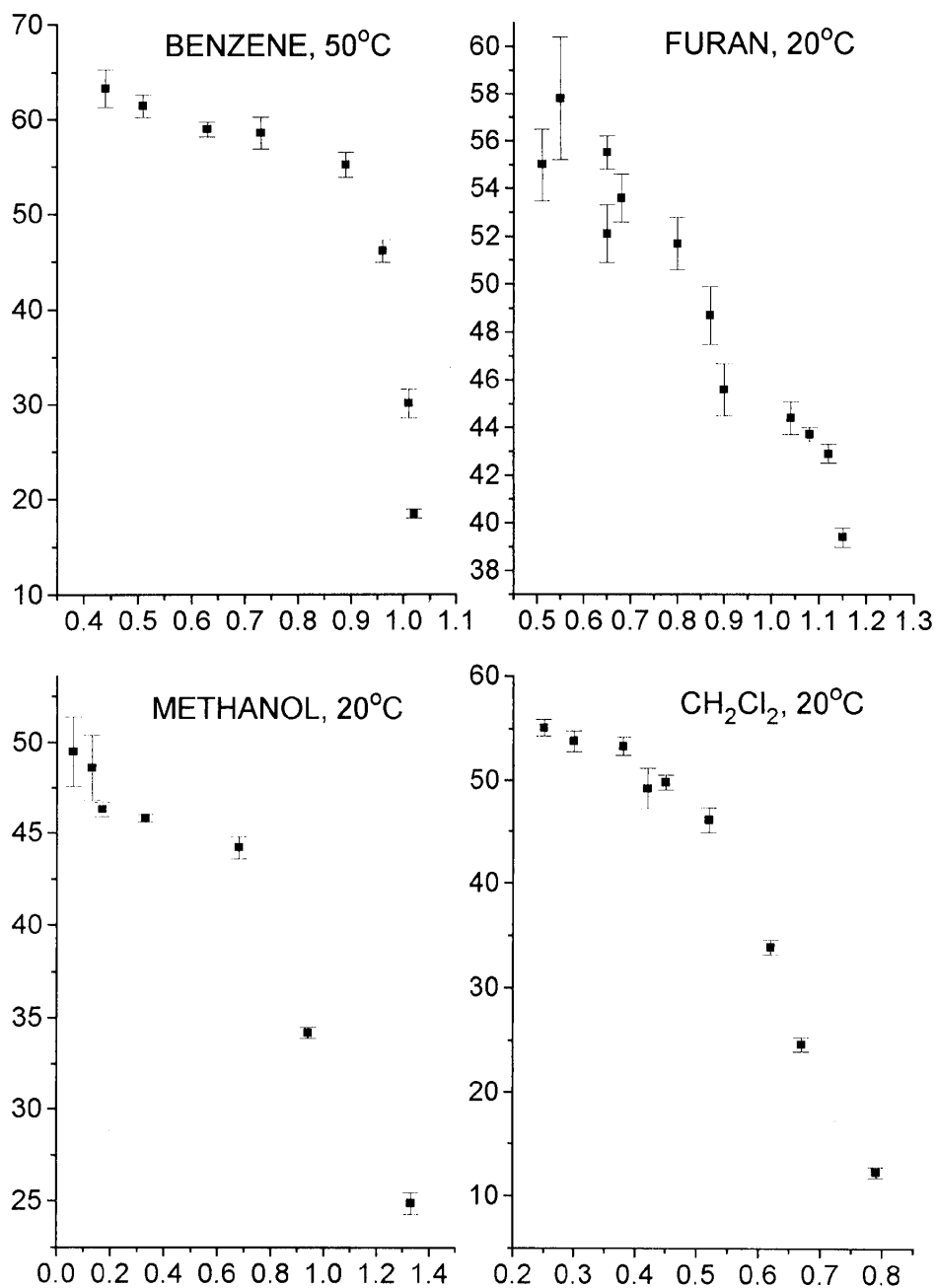


Figure 6. Dependence of the isosteric heats of guest sorption from guest uptake for sorption of different guests into the β -[Ni(NCS)₂(4-MePy)₄] host phase. Values of the isosteric heats of guest sorption (kJ/mol) are shown on the vertical axis, compositions of the clathrate phase (guest molecules per one host molecule) are shown on the horizontal axis.

Table II. Isosteric heats of guest sorption (q_{st}) into the β -[Ni(NCS)₂(4-MePy)₄] clathrate for different equilibrium pressures of the gaseous guest (compositions of the clathrate phase were established by interpolation of the studied sorption isotherms).

P/P_a	y^1	q_{st} kJ/mol	P/P_a	y^1	q_{st} kJ/mol
Benzene 20 °C			507	0.25	51.1 ± 1.0
280	0.91	72.1 ± 3.0	587	0.28	49.9 ± 1.0
560	0.95	62.2 ± 2.4	1053	0.34	48.6 ± 0.6
1000	0.99	44.3 ± 1.6	4186	0.54	48.8 ± 0.8
2213	1.01	43.4 ± 0.5	5905	0.59	48.7 ± 0.6
2306	1.01	39.6 ± 1.0	8931	0.67	48.0 ± 0.4
3199	1.02	35.8 ± 0.7	11917	0.75	47.2 ± 0.4
4199	1.02	33.1 ± 0.6	12797	0.77	43.3 ± 0.6
5932	1.04	21.0 ± 0.3	Methanol 20 °C		
6238	1.04	17.3 ± 1.0	280	0.06	49.5 ± 1.9
Benzene 50 °C			560	0.13	48.6 ± 1.8
413	0.44	63.3 ± 2.0	724	0.17	46.3 ± 0.4
693	0.51	61.4 ± 1.2	1240	0.33	45.8 ± 0.2
1173	0.63	58.9 ± 10.8	2213	0.68	44.2 ± 0.6
2280	0.73	58.5 ± 1.7	3026	0.94	34.2 ± 0.3
4187	0.89	55.1 ± 1.3	4332	1.33	24.9 ± 0.6
6387	0.96	46.1 ± 1.2	CH ₂ Cl ₂ 20°C		
10053	1.01	30.1 ± 1.5	373	0.25	55.1 ± 0.8
10266	1.02	18.5 ± 0.5	427	0.30	53.8 ± 1.0
Furan 20°C			587	0.38	53.3 ± 0.9
307	0.51	55.0 ± 1.5	706	0.42	49.2 ± 2.0
333	0.55	57.8 ± 2.6	826	0.45	49.8 ± 0.7
573	0.65	55.5 ± 0.7	1413	0.52	46.1 ± 1.2
573	0.65	52.1 ± 1.2	2826	0.62	33.9 ± 0.7
613	0.68	53.6 ± 1.0	3932	0.67	24.6 ± 0.7
1080	0.80	51.7 ± 1.1	7518	0.79	12.3 ± 0.5
1480	0.87	48.7 ± 1.2	THF 20°C		
1760	0.90	45.6 ± 1.1	1840	0.497	38.4 ± 0.3
4399	1.04	44.4 ± 0.7	2400	0.498	32.0 ± 0.9
5732	1.08	43.7 ± 0.3	3160	0.500	32.5 ± 0.6
7731	1.12	42.9 ± 0.4	5160	0.502	26.8 ± 0.3
9598	1.15	39.4 ± 0.4	6145	0.503	29.5 ± 0.4
Furan 50° C			8665	0.504	27.5 ± 0.3
427	0.23	46.8 ± 1.2	9944	0.505	25.4 ± 0.2

¹ y = guest to host molar ratio.

position (*ortho*-, *meta*- and *para*-xylene), was studied [20]. It was found that values of the heats of sorption are a maximum for the pure guest components, and pass through a minimum when different types of guest molecules are included. The

most likely explanation of this fact is non-effective interactions between differently distorted (by different guests) parts of the host lattice. According to [21] the formation of superstructures has not been observed in systems with mixed guest, the same situation could be expected for systems with less than 100% filling of sorption positions by the guest. This question will be additionally discussed in Part 2 of the present work.

After complete filling of one type of sorption position, a less energetically favourable arrangement of the guest molecules in another type of position begins. This manifests itself in an inflection of the isotherms and faster (or, possibly, abrupt) changes of q_{st} . The composition of the corresponding clathrate phase depends dramatically on the size and shape of the guest molecule. For guests such as tetrahydrofuran and CH_2Cl_2 (Figure 4) this composition is close to the 1 : 0.5 host : guest ratio, which corresponds to complete filling of 'large cavities' by a single guest molecule. Inclusion of the second tetrahydrofuran molecule in a 'large cavity' (filling of the second type of sorption position) requires significant distortions of the host lattice and causes strong guest (position 1) – guest (position 2) repulsion. Both factors explain the rapid decrease of q_{st} . After filling of about 2% of the second type of sorption position, inclusion is stopped, which corresponds to the horizontal part of the sorption isotherms. Inclusion of another guest for which the 1 : 0.5 limit host : guest ratio and localisation of one guest molecule in a 'large cavity', observed in X-ray experiments (methylcellosolve [11]) or postulated based on studying the sorption isotherms (propane, this work), may be expected to proceed in the same way. Allocation of more than one guest molecule of the smaller size (CH_2Cl_2 , CH_2Br_2) in a 'large cavity' is energetically favourable. Filling of a second sorption position and even a small part of the third (third guest molecule in a 'large cavity') significantly distorts the host lattice [11] (undoubtedly, guest–guest contacts in this case are also very close, which causes strong guest–guest repulsion). This manifests itself in a significant decrease of the isosteric heat of guest sorption. Comparison of the sorption isotherms of three molecules of similar size and shape (propane, CH_2Cl_2 , CH_2Br_2 , Figure 4) allows one to illustrate the influence of the chemical potential of the guest molecule (proportional to the mass of guest molecule) on the mode of inclusion. The greater chemical potential of the CH_2Cl_2 and CH_2Br_2 molecules allows (at low temperatures) inclusion of these guest molecules in less energetically favourable positions. At higher temperatures the inclusion isotherms of all three guests are very similar. Inclusion of guest molecules of small size (methanol, methane, ethane [14]) is insignificantly different from that discussed above. A greater number of similar small molecules (and, probably, of triatomic linear molecules [11, 14]) may be effectively allocated in a 'large cavity'. A significant difference in energy between the first and second 'sorption positions' may explain the existence of type 4 sorption isotherms, which were reported in [14], for methane, ethane and CH_3Cl .

Finally, some remarks concerning guest–guest interactions should be made. Analysis of the clathrate structures and some molecular mechanics calculations

[22] show that interactions between guest molecules under consideration which occupy the same sorption positions are rather insignificant. The role of guest–guest interactions between molecules occupying different sorption positions was discussed earlier.

Flat parts of guest molecules of suitable size (width is not more than the width of a benzene ring, a change of a toluene guest molecule to the slightly wider *ortho*-xylene molecule makes the formation of β -type clathrates impossible [6]) are localising in a ‘small cavity’ of the β -[Ni(NCS)₂(4-MePy)₄] host lattice [6, 11]. This phenomenon may be regarded as an example of ‘molecular recognition’ of a molecular fragment of definite size and shape by the host lattice. An insignificant inflection of the guest molecule dramatically changes the mode of guest sorption. Comparison of the sorption isotherms and modes of sorption of furan and tetrahydrofuran (Figure 3) gives a good illustration of this behaviour. The cases of occupation of a ‘small cavity’ by a guest molecule and localisation of a guest molecule in a ‘large cavity’, close to the centre of inversion, should be distinguished [11]. In our opinion only cases when the molecular contour includes a centre of inversion may be regarded as ‘allocation of a guest molecule in a small cavity’. Inflection points in room-temperature isotherms with benzene and furan as guests correspond to about 1 : 1 host guest stoichiometry (Figure 3). Inflections may be observed at similar compositions for q_{st} – composition dependencies for benzene guest molecules (Figure 6, Table II). Our knowledge allows us to interpret it as occupation of all (or main part) of the ‘small cavities’ by the corresponding guest molecule. Further occupation of residual ‘sorption positions’ in ‘large cavities’ are less energetically favourable because of strong guest–guest repulsion and distortion of the host lattice. The greater volume of the benzene molecule causes a plateau in the sorption at about 5% filling of ‘large cavities’; the sorption of furan molecules goes up to the stoichiometric limit. Studying the dependence of q_{st} upon composition of the solid clathrate at 50°C (Figure 6) showed that values of the isosteric heat of sorption decreases with increasing temperature. Finally, it should be mentioned that furan molecules may be located in both types of cavities [11], but on the basis of the present experimental data we cannot with certainty localise the furan molecule at all stages of sorption.

References

1. J.L. Atwood, J.E.D. Davies, and D.D. MacNicol (eds.), *Inclusion Compounds*, Vol. 4, Oxford University Press (1991).
2. L. Lavelle and L.R. Nassimbeni: *J. Incl. Phenom.* **16**, 25 (1993), and references therein
3. B.T. Ibragimov, S.A. Talipov, and P.M. Zorky: *Supramol. Chem.* **3**, 147 (1994).
4. G. Tsoucaris, J.L. Atwood, and J. Lipkowski (eds.): *Crystallography of Supramolecular Compounds*, NATO ASI Series, Series C: Mathematical and Physical Sciences, Vol. 480, Kluwer Academic Publishers, Dordrecht (1984).
5. J. Lipkowski, D.V. Soldatov, N.V. Kislykh, N.V. Pervukhina, and Yu.A. Dyadin: *J. Incl. Phenom.* **17**, 305 (1994).

6. J. Lipkowski: 'Inclusion compounds formed by Werner MX_2A_4 coordination complexes', in J.L. Atwood, J.E.D. Davies, and D.D. MacNicol (eds.), *Inclusion Compounds*, Vol. 1, Academic Press, London (1984), pp. 59–103.
7. J. Lipkowski and S. Majchrzak: *Roczn. Chem.* **49**, 1655 (1975).
8. D. Sybilska and E. Smolkova-Keulemansova: 'Applications of inclusion compounds in chromatography', in J.L. Atwood, J.E.D. Davies and D.D. MacNicol (eds.), *Inclusion Compounds*, Vol. 1, Academic Press, London (1984), pp. 173–239.
9. J. Lipkowski, K. Suwinska, G.D. Andreetti, and K. Stadnicka: *J. Mol. Struct.* **75**, 101 (1981).
10. E. Rodulfo de Gil and I.S. Kerr: *J. Appl. Crystallogr.* **10**, 315 (1977).
11. A.Yu. Manakov, J. Lipkowski, K. Suwinska, and M. Kitamura: *J. Incl. Phenom.* **26**, 1 (1996).
12. D.R. Bond, G.E. Jackson, and L.R. Nassimbeni: *S. Afr. J. Chem.* **36**, 19 (1983).
13. G.D. Andreetti, G. Bocelli, and P. Sgarabotto: *Cryst. Struct Commun.* **1**, 51 (1972).
14. S.A. Allison and R.M. Barrer: *J. Chem. Soc., A* 1717 (1969)
15. W. Kemula, J. Lipkowski, and D. Sybilska: *Roczn. Chem.* **48**, 4 (1974).
16. A.Yu. Manakov and J. Lipkowski: *Thermochim. Acta* **227**, 199 (1996).
17. L.J. Barbour, K. Achleitner, and J.R. Greene: *Thermochim. Acta* **205**, 171 (1992).
18. L. Pang, E.A.C. Lucken, and G. Bernardinelli: *J. Incl. Phenom.* **13**, 63 (1992).
19. R.M. Barrer: *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*, Academic Press, London (1978).
20. J. Lipkowski, P. Starzewski, and W. Zelenkiewicz: *Polish J. Chem.* **56**, 349 (1982).
21. J. Lipkowski: unpublished results.
22. P. Starzewski: Ph.D. thesis, Warszawa (1982).