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A Thermokinetic Study of the Clathration of Isomeric Xylenes by the $Ni(NCS)_2(4\text{-Methylpyridine})_4$ Host

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Abstract. A detailed analysis of the thermokinetic course of the reaction α-$Ni(NCS)_2$(4-methylpyridine)$_4$ + xylene $\rightarrow$ β-$Ni(NCS)_2$(4-methylpyridine)$_4 \cdot$ (xylene) (at 25 °C), for 21 samples of pure *p*-xylene and *m*-xylene, as well as two- and three-component mixtures of the *o*-, *m*- and *p*-isomers was performed by using the dynamic optimization method. The mechanism of the reaction is discussed. Firstly, a relatively rapid $\alpha \rightarrow \beta$-phase transformation and uptake of 60–80% of the total guest takes place. Then follows the slower diffusion-controlled absorption of xylene up to the maximum filling corresponding to 1 : 1 guest/host stoichiometry.

Key words: Clathrate, inclusion compound, kinetics of clathration, thermokinetic analysis, xylenes-molecular inclusion of.

1. Introduction

Some Werner coordination complexes of the general formula MX_2A_4, (M is the divalent cation, X, is the anionic, and A is the neutral ligand) and particularly the $Ni(NCS)_2(4\text{-MePy})_4$ complex (4-MePy = 4-methylpyridine), are known to serve as suitable host components in the formation of inclusion compounds with a variety of guests [1–3]. The formation of the inclusion compounds is highly stereoselective and may conveniently be used for the separation of isomer mixtures [4] and even isotopomers [5]. A knowledge of the thermochemistry of the reactions is pertinent to comprehend their physicochemical nature and has thus been the subject of calorimetric studies since 1962 [6]. Recently, the overall heat of clathration (ΔH_{clath}) was resolved into four components

$$\Delta H_{\text{clath}} = \Delta H_{\alpha \rightarrow \beta_0} + \Delta H_{\beta_0 \rightarrow \beta} + \Delta H_{\text{evap}} + \Delta H_{\text{sorp}} \quad (1)$$

corresponding to single, virtual processes of, respectively:

- phase transformation of the solid nonclathrated α-form of the host into the 'empty' clathrate β structure ($\Delta H_{\alpha \rightarrow \beta_0}$),
- dilation of the β-host structure accompanying absorption of a given guest ($\Delta H_{\beta_0 \rightarrow \beta}$),
- evaporation (sublimation) of the guest (ΔH_{evap}), and
- uptake of the gaseous guest by the clathrate host structure (ΔH_{sorp}).

The thermochemical results also allowed the estimation of the role of the enthalpic and entropic contribution to the selectivity of clathration by $Ni(NCS)_2(4\text{-MePy})_4$ [7]. The recently stated two-step kinetic course of clathrate formation was surprising and prompted us to carry out a more detailed study, which is presented below.

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2. Experimental

The thermokinetic course of clathration was determined by analyzing the respective thermograms measured by means of a BMR microcalorimeter [8]. The clathration process (at 25 °C) was initiated by breaking a thin-wall glass ampoule containing 0.5 g of the solid α-$Ni(NCS)_2(4\text{-}MePy)_4$ complex in the calorimetric vessel containing 15 ml of liquid guest compound. The guest for clathration was presaturated with $Ni(NCS)_2(4\text{-}MePy)_4$ at 25 °C in order to avoid possible interference of the heat of dissolution of the solid substrate in the clathration heat effects.

Values of thermal power $W(t)$ were obtained by the dynamic optimization method [9], by means of the equation

$$q[u(t-\tau)] = \int_0^T [\Delta(t) - x(t)]^2 \mathrm{d}t$$

$$= \int_0^T \left[\Delta(t) - \int_0^t u(t-\tau) \times H(\tau)\mathrm{d}\tau\right]^2 \mathrm{d}t, \qquad (2)$$

where u denotes the calculated input function;
q stands for the function of discrepancy between the experimental and calculated functions;
$\Delta(t)$ stands for the observed temperature response of the calorimeter for the generated heat effect;
$W(t)$ is within the time (t) limits $<0, T>$;
$x(t)$ denotes the calculated temperature response of the calorimeter;
$H(t)$ is the unit step response of the system;
τ is the integration variable.

The determination of the $W(t)$ function consists of looking for such a course of the input function $u(t)$ at which expression (2) reaches its minimum value. It is assumed that $W(t) = \hat{u}(t)$ for $\Delta(t) = x(t)$ at accuracy $\pm\varepsilon$ where ε stands for the mean discrepancy between the observed and calculated temperatures. Minimizations of the $q[u(t)]$ values were numerically performed by means of the conjugated gradient method. Calculations were done at a sampling time of 6 s so that the differences between $\Delta(t)$ and $x(t)$ did not exceed the experimental precision $\Delta(t)$.

The experiments on clathration were preceded by a standardization procedure performed with a calorimetric vessel containing 15 ± 0.1 ml of p-xylene and 500 ± 5 mg of α-$Ni(NCS)_2(4\text{-}MePy)_4$ in a glass ampoule. Two modes of standardizing measurements have been used by generating programmed amounts of heat in a heating coil situated in the vessel. At first, the heat amounts generated were of a constant power and magnitude, corresponding to the measured temperature effects observed on clathration. The results served to determine the heat loss coefficient (G), defined as the amount of heat exchanged, under stationary heat exchange conditions between the calorimetric vessel and its isothermic jacket. The values found for the different values of the generated thermal effects were 41.82; 42.60; 42.87; 42.09; 42.20; 42.88; 42.77 W/V; the averaged value being $G = 42.49 \pm 0.419$. The constancy of the G coefficient at the temperature differences considered is equivalent to the possibility of treating the calorimeter as a linear system. This assumption, as given above, makes it possible for the thermokinetic analysis to be performed. The second mode of standardization was based on the experimental determination of a thermogram $\Delta(t)$, which resulted as a consequence of the generation in the calorimetric vessel of a short-lasting heat effect of great amplitude (the determination of $H(t)$). At that stage it was assumed that the Dirac function corresponds to this impulse value within a time unit. The heat impulse was 3.0826 W for a duration of 2.100 s.

Finally, the applicability of the dynamic optimization method to studies of the clathration course was verified through the procedure in which:

(i) The heat generated in the calorimetric vessel was programmed as

$$W(t) = W_1 \exp(-t/T_1) + W_2[\exp(t^* - t/T_2) - \exp(t^* - t/T_3)]$$

where

$W_1 = 1.316 \times 10^{-1}$ W $\quad T_1 = 52$ s
$W_2 = 4.023 \times 10^{-2}$ W $\quad T_2 = 480$ s
$t^* = 168$ s $\quad T_3 = 240$ s.

(ii) The measured temperature response of the calorimeter ($\Delta(t)$) was analyzed by using the dynamic optimization method.

(iii) The reproduced course of the thermal power ($W(t)_{\text{calc}}$) obtained from the dynamic optimization, was compared to the course of the programmed thermal power ($W(t)$). In Figure 1 the results of such a standardization are illustrated by means of plots of experimental $\Delta(t)$, the course of the programmed thermal power $W(t)$ and the reproduced course of the thermal power $W(t)_{\text{calc}}$ obtained from the dynamic optimization.

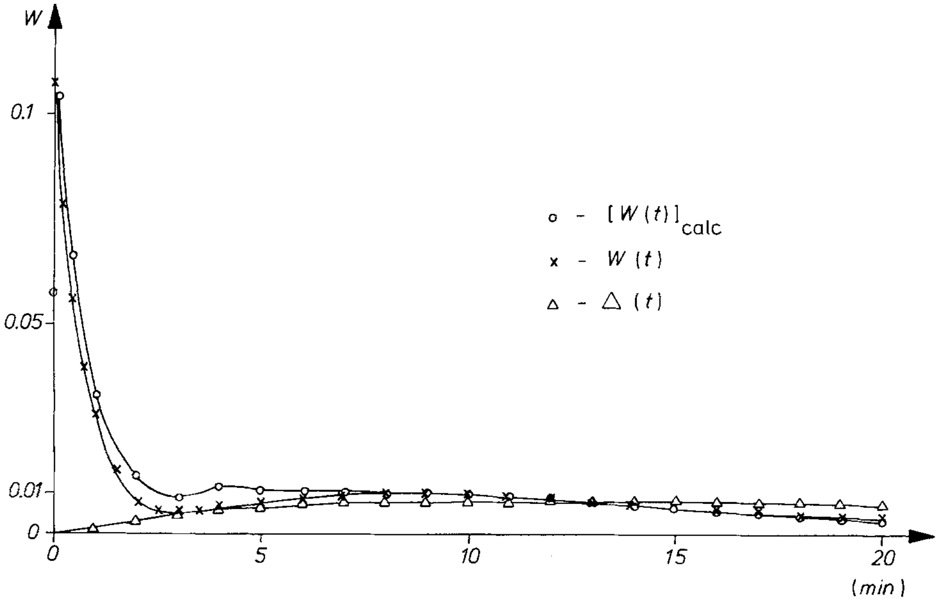

Fig. 1. Results of the verification of the applicability of the dynamic optimization method to reproducing the thermokinetic course of clathration. The curve with Δ represents the course of observed $\Delta(t)$ – the experimentally-measured response to that programmed in the calorimetric vessel thermal power $W(t)$ given here by the curve ×. Circles show the calculated thermal power obtained by dynamic optimization.

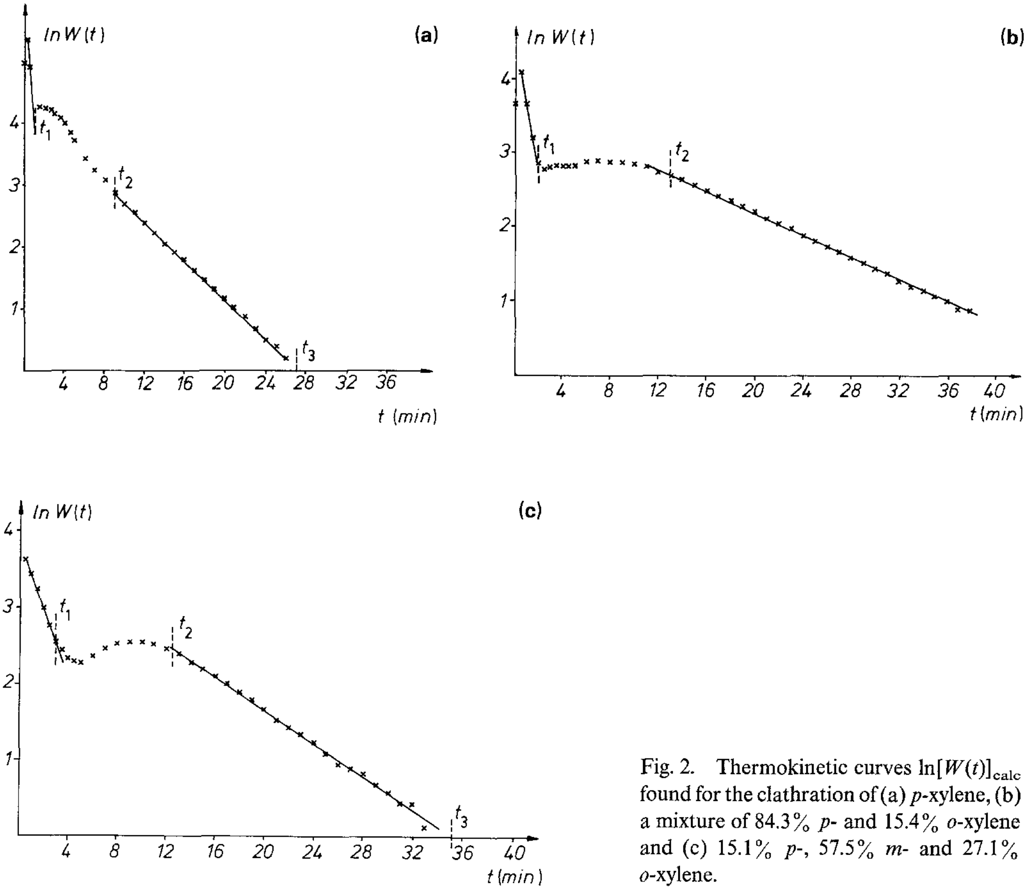

Fig. 2. Thermokinetic curves $\ln[W(t)]_{\text{calc}}$ found for the clathration of (a) *p*-xylene, (b) a mixture of 84.3% *p*- and 15.4% *o*-xylene and (c) 15.1% *p*-, 57.5% *m*- and 27.1% *o*-xylene.

3. Results and Discussion

Some typical examples of the thermokinetic course of the reaction

$$\alpha\text{-Ni(NCS)}_2\text{(4-MePy)}_4 + \text{G} \rightarrow \beta\text{-Ni(NCS)}_2\text{(4-MePy)}_4 \cdot G \qquad (3)$$

are given in Figure 2. There, three distinct stages may be specified:

I – a linear relationship between ln $W(t)$ and time, from $t = 0$ to $t = t_1$;

II – an intermediate step of complex characteristics (t_1 to t_2) and

III – a further linear relationship from t_2 until the end of the reaction. At some specific guest compositions, this step showed a more complex shape (Figure 3).

In Table I, the parameters describing the duration of the individual steps (t_1 through t_3) and the course of the third stage (A and B) are listed.

The results obtained clearly demonstrate that the overall duration of the clathration process studied depends strongly on the composition of the enclathrated guest. For instance, the reaction times observed for *m*- and *p*-xylene differ by a factor of approximately 2 (50 and 27 min, respectively). Respective times determined for two- and three-component mixtures of the xylene isomers vary from 30.5 to 90 min.

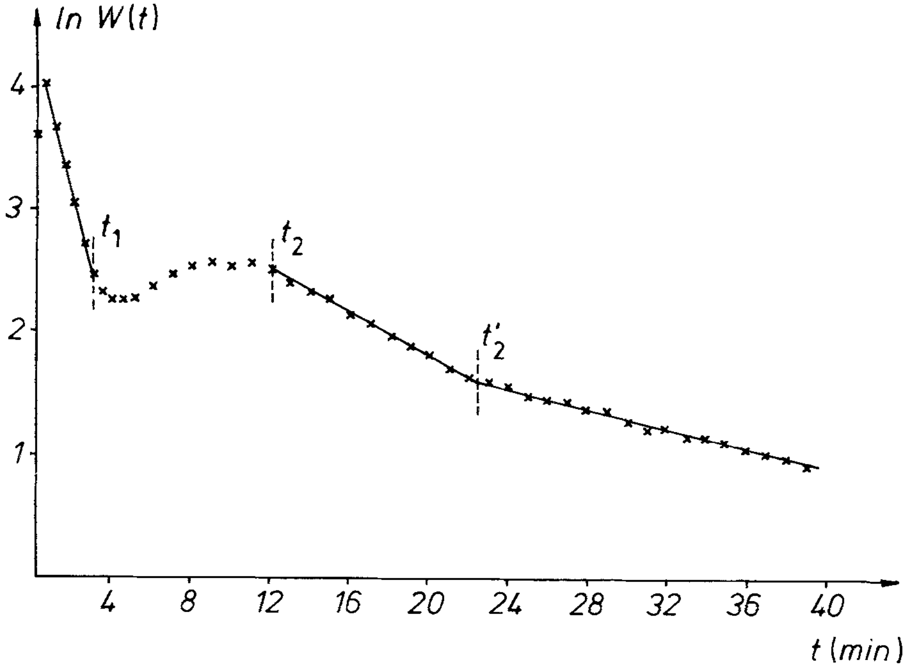

Fig. 3. Thermokinetic course $\ln[W(t)]_{\text{calc}}$ determined for the clathration of a mixture of 68.8% *p*-, 2.1% *m*- and 28.9% *o*-xylene.

A comparison of the duration of the different steps of the clathration process (t_1, t_2–t_1 and t_3–t_2, respectively) in Table I, indicates that the third step is the slowest and, thus, determines the overall duration of the reaction. No systematic relation has been found between the reaction time and the guest composition. Two-component mixtures are enclathrated at rather lower rates (mixtures Nos. 8, 9, 10, 11, 13, 14 in Table I) than either of the respective components alone, but with an exception for the mixture composed of 80% *p*- and 20% *o*-xylene (No. 16 in Table I). Apart from this exception, *o*-xylene, when mixed with *p*-xylene, seems to have a stronger influence in lowering the reaction rate than *m*-xylene (cf. Nos. 9 and 8 in Table I – 90 min for 46% *p*- and 52% *o*- while only 63.5 min for 43% *p*- and 56% *m*-). On the other hand, mixtures of *m*- and *o*-xylene (Nos. 1 and 2) as well as three-component mixtures (Nos. 3 through 7, 12, 15 and 18) are clathrated relatively fast (31.5 to 47 min).

As mentioned above, the overall reaction time is mainly defined by the slowest, third step of the process. A comparison of the (t_3–t_2) values found for molecules of different shapes, suggests a diffusion mechanism for this step. Both from previously reported studies [7] on liquid *p*-xylene absorption by the $\mathrm{Ni(NCS)_2(4\text{-}MePy)_4}$ host complex and from the illustration given in Figure 4, it may clearly be seen that after a time comparable to t_1, the solid no longer contains the α-phase of the host. Thus, in the third, and perhaps also the second stages of the reaction, no phase transformation takes place. The smallest t_3 value among all guest systems studied is that found for the *p*-isomer of xylene. This result indicates the easier diffusion of 'linear' molecules rather than 'branched' *m*-xylene, which is in accord with the results of liquid chromatographic studies on isomer separation [10].

Table I. Composition of enclathrated xylenes, given as mole percent of the total guest (y_p, y_m, y_O), the end time of individual steps of clathration (t_1, t_2, t_3), and kinetic parameters (A, B) of the third, linear step of the reaction described by the expression $A \cdot e^{-t/B}$ (where two sets of values are given, the process has the course as illustrated in Figure 3). In addition, the two last columns report the overall enthalpy of sorption (ΔH_{sorp}) and molar volumes of the clathrates (V_{mol}). The last values are taken from [7], the enthalpy of sorption was calculated from the corresponding enthalpy of clathration taken from [7] by using the equation $\Delta H_{\mathrm{sorp}} = \Delta H_{\mathrm{clath}} - \Delta H_{\alpha \to \beta_0} - \Delta H_{\mathrm{evap}} - \Delta H_{\beta_0 \to \beta}$, where $\Delta H_{\alpha \to \beta_0}$ stands for the experimentally determined enthalpy [14] of the phase transformation $\alpha \to \beta_0$ ('empty' β-form), equal to 3.56 kJ mol^{-1}; ΔH_{evap} represents the enthalpy of the evaporation of the guest and $\Delta H_{\beta_0 \to \beta}$ stands for the enthalpy of dilation of the host lattice on the absorption of the guest, estimated by means of the expression $\Delta H_{\beta_0 \to \beta} = 0.096(V - 471.6)$; V denoting the molar volume of the clathrate.

No.	y_p (%)	y_m (%)	y_O (%)	t_1 (min)	t_2 (min)	t_3 (min)	A	B	$-\Delta H_{\mathrm{sorp}}$ (kJ/mol)	V_{mol} (cm^3/mol)	$-\Delta H_{\mathrm{clath}}$ (kJ/mol)
1	1.2	71.6	26.7	2.5	11.5	31.5	41.5	500	69.68	545.3	16.24
2	1.6	45.9	52.3	2.2	9.5	31.5	48.2	482	68.99	548.1	15.11
3	9.5	48.5	41.6	2.0	13.0	31.5	85.6	427	69.64	539.2	16.82
4	15.1	57.5	27.1	3.0	12.5	35.0	47.0	549	69.80	541.0	16.90
5	25.8	54.2	19.9	3.0	8.0	34.0	35.7	573	70.81	538.6	18.16
6	37.5	25.7	36.5	3.0	12.0	31.0	61.7	449	71.34	540.1	18.54
7	40.1	37.3	22.4	2.0	13.5	31.0	83.5	446	71.45	537.4	19.00
8	42.8	56.1	0.8	2.0	20.5	63.5	18.9	1278	72.67	531.6	21.01
9	46.4	2.0	51.5	2.0	9.5	90.0	33.1	580	74.95	532.8	22.68
					18.0		7.58	2666			
10	54.5	0.1	45.3	1.5	12.0	75.5	27.8	725	–	–	23.56
					20.5		9.25	2080			
11	61.9	37.4	0.5	1.8	10.5	51.0	22.2	927	74.12	529.0	22.76
12	66.4	12.2	21.3	1.8	8.5	30.5	60	453	74.72	534.8	24.60
13	68.8	2.1	28.9	3.0	13.0	61.0	35.7	674	74.62	538.8	24.10
					22.5		12.8	1360			
14	74.5	24.8	0.3	1.5	14.0	63.0	16.2	1334	78.25	533.7	26.57
15	77.4	14.3	8.1	2.0	8.5	47.0	27.1	870	77.44	527.8	26.19
16	79.5	0.2	20.1	2.5	10.5	32.0	56.0	506	77.23	529.4	25.57
17	84.3	0.1	15.4	2.0	14.0	48.0	43.6	754	79.03	530.9	27.49
18	84.5	8.4	6.9	1.5	11.0	43.0	32.3	571	78.14	521.9	27.49
19	84.8	14.3	0.3	2.5	9.0	48.0	30.0	836	80.19	530.8	28.70
20	<0.1	100	<0.1	1.5	14.0	50.0	136	1170	72.38	546.7	19.04
21	100	<0.1	<0.1	1.0	9.0	27.0	68.4	380	82.51	526.9	31.42

The first linear step of reaction (3) should be related to the uptake of some guest and the simultaneous $\alpha \to \beta$ phase transformation, according to the results of X-ray diffraction studies (Figure 4). The $\alpha \to \beta$ lattice reconstruction was formerly found [13] to occur within 1–2 min when using *p*-xylene as the guest. In the present studies, we can extend this result to the clathration of *m*-xylene and xylene mixtures. A typical X-ray powder image is represented in Figure 4 for the example of the clathration of *m*-xylene. Pure *o*-xylene forms an inclusion compound with $Ni(NCS)_2(4\text{-}MePy)_4$ but of a different crystal structure to the β-phase [4] and so is not considered here.

Following the van der Waals theory of clathrate solutions [11] it should be assumed that the resulting β-phase, being thermodynamically stable, has some 'cavities' filled with guest

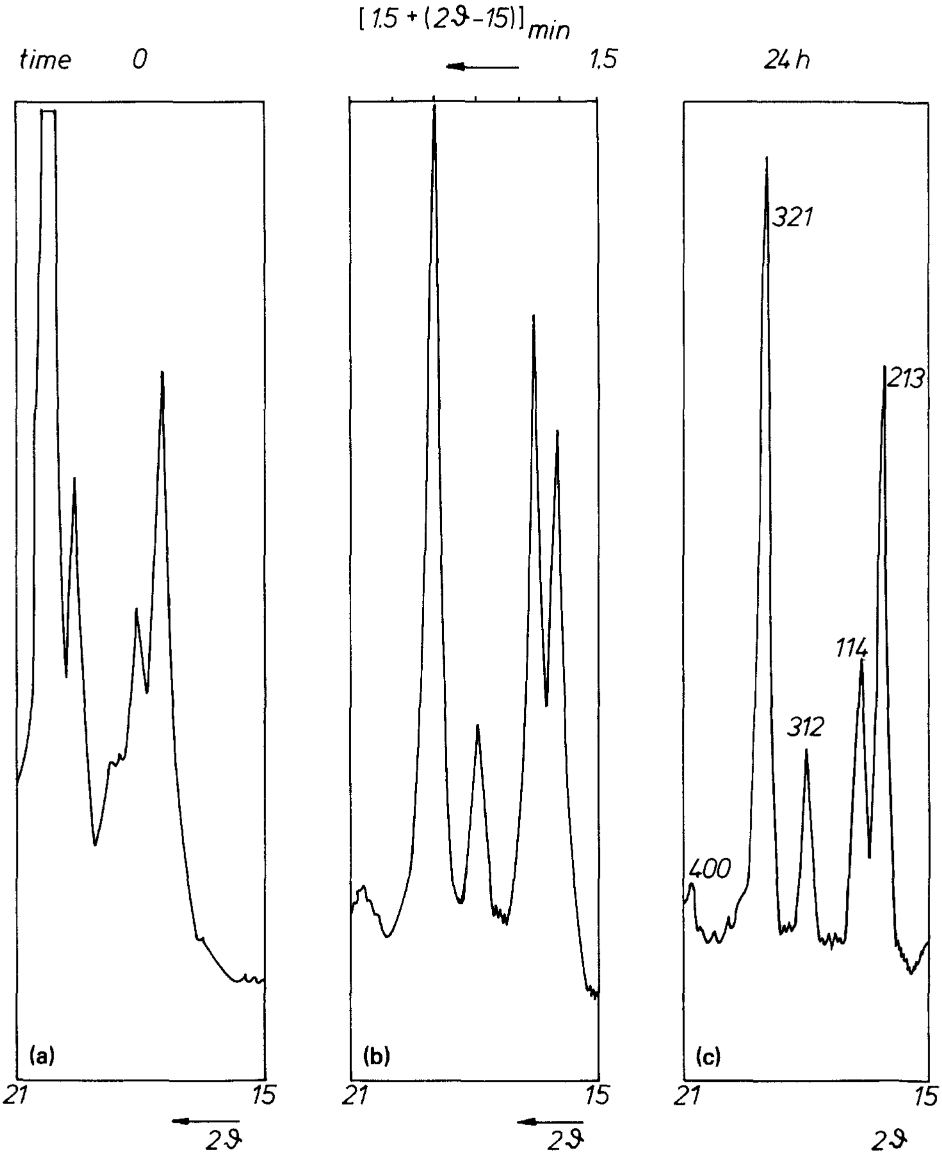

Fig.4. X-ray powder diffraction with (CuK_α) of: (a) the solid substrate of clathration – α-$Ni(NCS)_2(4\text{-}MePy)_4$; (b) the $Ni(NCS)_2(4\text{-}MePy)_4$ sample 1.5 min after contacting patterns liquid *m*-xylene at 25 °C (the diffractogram was taken at 1° 2ϑ/min scanning rate, thus different reflections were recorded at different times – as given by the upper scale), and (c) the sample after 24 h in contact with *m*-xylene.

molecules so that Equation (4) is fulfilled

$$\ln(1 - y_{\min}) = -z \frac{\Delta G}{RT} \tag{4}$$

where ΔG represents a change of Gibbs free energy, when going from the α-host to the empty β-host lattice, $y_{\min}$ stands for the minimum fraction of the cavities which must be occupied in order to make the clathrate host structure thermodynamically stable, and z is a constant equal to the number of cavities divided by the number of host molecules in a given structure.

Hart and Smith [6] suggest a value close to 0.6 for $y_{\min}$ when p-xylene is the guest in the β-Ni(NCS)$_2$(4-MePy)$_4$ phase. In recent studies [7], it has been shown that upon substitution of some of the p-xylene molecules with other molecules, e.g., m-xylene, the molar volume of the solid phase varies, even when the total amount of guest component remains constant. Consequently, different $y_{\min}$ values should be expected for different guests. For instance, if the dilation-contraction process of the β-host is assumed to be an isoentropic one within the $\Delta V = V_1 - V_2$ range of molar volumes, then

$$\ln(1 - y'_{\min}) = -\frac{\Delta G + \Delta V \cdot a}{RT} \tag{5}$$

where $y'_{\min}$ denotes the new minimum filling extent but ΔV and a stand for, respectively, the volume dilation and the enthalpy of dilation per cm^3 of the β-host.

This equation is illustrative only, particularly because data on the molar volumes of clathrates at the three-phase equilibrium: α-Ni(NCS)$_2$(4-MePy)$_4$ + β-Ni(NCS)$_2$(4-MePy)$_4 \cdot y_{\min}$ (xylene) + liquid xylene, are not available. However, in view of the difference between the β-phase volumes containing m-xylene and p-xylene at $y = 1$ being as much as 24 cm^3, one could expect differences in $y_{\min}$ of approximately 0.2. On the basis of the above considerations, we assume that at the end of the first kinetic step of reaction (3), we obtain a clathrate β-phase with significantly more than half of the cavities occupied by the guest molecules. Kinetic constants k of the expression $A\,e^{-kt}$ are within the range 8×10^{-3} to $15 \times 10^{-3}\,s^{-1}$ at this step. The accompanying heat effects obtained by integrating the thermokinetic curves within the $0 - t_1$ time intervals fall within the 4–7 kJ mol^{-1} range. If the enthalpy of the $\alpha \rightarrow \beta$ phase transformation, of the order of 5 kJ mol^{-1} [7] is added, the heat evolved is still much lower than $y_{\min} \cdot \Delta H_{\text{sorp}}$; ΔH_{sorp} denoting the total enthalpy of sorption. The reason for that would be a dependence of the differential enthalpy of sorption upon the geometry of the host structure. In our previous study [7], we have reported a strong relationship between the partial molar enthalpy of clathration of a given guest and its content in the enclathrated mixture. It seems evident that the relation between the partial molar enthalpy of clathration and the guest should be even stronger when, as in steps II and III, there is the best guest-cavity fit, and host-lattice expansion occurs. Thus, increasing the amount of guest absorbed should result in an increase of the differential enthalpy of clathration and should be observed by means of the relatively great contribution of steps II and III to the overall heat evolved. The heat amounts obtained by integrating the thermokinetic curves within the t_1 to t_3 time intervals are between 12–25 kJ mol^{-1}and fully support the conclusion given above.

In the steps II and III, we assume a similar physicochemical process, i.e., an uptake of the guest by the β-clathrate. The complex course of the thermokinetic curves in II and the large variety observed at different compositions of the guest may be attributed to the dilatation of the host structure and, in particular:

- the endothermic effect of dilation of the host structure contributes to the measured enthalpy, and
- the partial molar enthalpies of absorption of individual guests are dependent on the extent of dilation of the host framework.

We regard the second effect as dominant. The variety of curve shapes, from a 'plateau' (Figure 2b) to a local maximum (Figure 2c) may be understood if one takes into account the possibility of a complex variation of individual differential enthalpies during dilatation, e.g., the heat of absorption of *p*-xylene would reach a maximum at $V \approx 527$ cm^3 and decrease at higher volumes of the clathrate lattice [7].

Let us assume that, at clathrate compositions close to maximum filling, the heat effect is a direct measure of the reaction rate, as might be suggested by the linear shape of the curve at step III. Then, for a diffusion-controlled process, an approximate equation [12] may be written

$$\ln\left(1 - \frac{Q_t}{Q_{t_3}}\right) = ln\,\frac{6}{\pi^2} - \frac{D\pi^2 t}{r^2} \tag{6}$$

where D stands for the mean coefficient of diffusion, r denotes the linear size of the absorbing crystals and Q_t and Q_{t_3} represent the amounts of heat evolved in the $t_2{-}t$ and $t_2{-}t_3$ periods of time. Thus, derived $D\pi^2/r$ values are equal to 9.6×10^{-4} s^{-1} and 4.9×10^{-3} s^{-1} for *m*- and *p*-xylene, respectively. Provided the crystals' radii were of the same order in the *p*- and *m*-xylene products of clathration, diffusion of *p*-xylene through the solid is faster, even though the *p*-xylene structure has a lower porosity than the *m*-xylene one by about 20 cm^3 (see Table I).

Quantitative interpretation of guest diffusion in the third step of clathration becomes non-realistic when the guest is a mixture of isomeric *p*-, *m*- and *o*-xylenes. The presumed dependence of the mean coefficients of diffusion of the individual guest components upon the porosity of the host framework (molar volume), which should be taken into account, is not known. Moreover, complex mechanisms may play a role. For instance, the slower absorption of mixtures of *p*-/*o*-xylene or the *p*-/*m*-xylene than of the *p*- and *m*-isomers alone could be attributed to 'blocked diffusion' [12]; the values of t_3 determined for these mixtures are greater than those observed for individual isomers. Some mixtures are, however, by contrast absorbed at greater rates than expected (*m*-/*o*-xylene mixtures and 1 : 1 : 1 *m*-/*o*-/*p*-xylene).

The heat evolved in step III of the thermokinetic course of *p*-xylene clathration (Figure 2a) is calculated as 6.3 kJ mol^{-1}. If this value is compared to the overall heat (31.4 kJ mol^{-1}) plus 3.6 and 5.3 kJ mol^{-1}, which correspond to the $\alpha \rightarrow \beta_0$ phase transition and the $\beta_0 \rightarrow \beta$ dilation, respectively, then absorption of approximately 16% of the total guest *p*-xylene should be assumed for the third step.

The results and discussion given above suggest that the analysis of the thermokinetic course of clathration is a convenient procedure for studying the mechanisms of clathration, which otherwise would be difficult. Conventional X-ray diffraction is rather slow and permits us to specify only which crystalline phase, α- or β-, is present at a given point of the course of the reaction. Attempts to study the clathrate structure dilation effects in steps II and III failed because of the low accuracy attainable, compared to the dilation effects, though some increase of the lattice parameters *a* and *c* of the order of 0.1 Å during steps II and III might be postulated. The previously reported [7] determination of the volume of some of the reacting systems as a function of time, allowed the assumption of guest absorption in steps II and III but could not be used as a basis for quantitative kinetic analysis due to the unknown course of dilation of the solid phase during reaction.

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