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THERMOCHEMICAL STUDIES OF THE CLATHRATION OF AROMATIC GUEST COMPOUNDS BY THE HOST—$Ni(NCS)_2$ (4-METHYLPYRIDINE)$_4$ COMPLEX

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ABSTRACT

The enthalpy and thermokinetic course of clathration of some aromatic guest compounds (benzene, toluene, xylenes) were studied. The total enthalpy is analyzed in terms of steric fit between guest molecules and host crystalline structures. A two-step kinetic course of reaction is found.

INTRODUCTION

$Ni(NCS)_2(4\text{-}MePy)_4$ is a well-known clathratogenic substance able to absorb, on clathrate formation, many different chemical species varying, for instance, from Ar or O_2 to naphthalene derivatives [1—3]. Clathration enthalpy is an important factor influencing the stability of a clathrate formed with a particular guest component. Thus it is important for interpretation of clathration selectivity, when the guest consists of more than one component. Clathration has been known to be a very efficient absorption process particularly selective towards mixtures of molecules of different shapes, e.g. isomers [4] or even isotopomers [5]. The reaction

$$\alpha\text{-}Ni(NCS)_2(4\text{-}MePy)_4 + G_l \rightarrow \beta\text{-}Ni(NCS)_2(4\text{-}MePy)_4 \,.\, G \qquad (1)$$

where G stands for guest compound and the subscript "l" denotes liquid or solution phase, is an exothermic process; the corresponding enthalpy (ΔH_{clath}) usually reaches a few kcal per mole of the guest compound.

The aim of the present study is to critically evaluate the available enthalpy data concerning reaction (1) with aromatic guest (G) compounds. Numerous studies on selectivity of clathration reactions in which Werner MeX_2A_4-type complexes are involved as the host components were aimed at trying to correlate electronic effects of substituents at aromatic rings of the guest compound (substituted benzenes, naphthalenes) on the selectivity of clathration [6,7]. Instead, steric rather than electronic effects are of interest in the present work. The necessary basis of experimental data for the present analysis consists of our previously reported [8] data on the clathration of xylene isomers and their mixtures, thermochemical data on clathration reported by

Smith et al. [9,10], Allison and Barrer's data on isomeric heats of absorption [2], and enthalpies of clathration of benzene and toluene determined calorimetrically for the purpose of the present study, as well as the thermokinetic course of clathration of isomers of xylene at 25° C.

EXPERIMENTAL

Enthalpy measurements were performed using a BMR type calorimeter [11]. In order to obtain the experimental data which would enable determination of the function $w(t) = dQ(t)/dt$, i.e. thermokinetics, a suitable numerical data collection system was used. The total heat effects listed in Table 1 as well as the thermokinetic course [$w(t)$] were calculated using the

TABLE 1

Clathration enthalpy (ΔH_{clath}), molar volume (V_{mol}) and calculated density (d_x, from X-ray diffraction) of selected clathrates of $Ni(NCS)_2(4\text{-}MePy)_4$.

Content of the isomer in the guest (molar %)			ΔH_{clath} (kcal mole^{-1})		V_{mol} (cm^3)	d_x (g cm^{-3})
para	*meta*	*ortho*	Exp.	Calcd. [eqn. (7)]		
100	0.1	0.1	7.51		526.9	1.240
84.8	14.8	0.3	6.87	6.68	530.8	1.231
84.3	0.1	15.4	6.58	6.56	530.9	1.231
74.5	24.8	0.3	6.36	6.20	533.7	1.224
68.8	2.1	28.9	5.77	5.80	538.8	1.213
66.4	12.2	21.3	5.89	5.68	534.8	1.222
62.5	24.0	13.2	5.87	5.56	537.3	1.216
61.9	37.4	0.5	5.44	5.69	529.0	1.235
46.4	2.0	51.5	5.43	5.00	532.8	1.226
44.8	39.9	15.0	4.61	4.89	538.8	1.213
42.8	56.1	0.8	5.03	5.09	531.6	1.229
40.1	37.3	22.4	4.55	4.68	537.4	1.216
25.8	54.2	19.9	4.34	4.33	538.6	1.213
23.8	12.3	63.9	4.33	4.35	541.5	1.207
15.1	57.5	27.1	4.04	4.04	541.0	1.208
1.6	45.9	52.3	3.61	3.71	548.1	1.192
1.2	71.6	26.7	3.92	3.85	545.3	1.198
0.1	100	0.1	4.55		546.7	1.195
0.1	0.1	100	5.96 * 2.98 **		643.4	1.178
Benzene			4.80		505.5	1.237
Toluene			5.66		515	1.24

* Per mole of the host.

** Per mole of the guest.

The estimated experimental standard deviations are: 0.5% of the given values of the guest content in the enclathrated mixture, 0.10 kcal mole^{-1} of the measured enthalpies (averaged), 1 cm^3 for the molar volume and thus 0.002 g cm^{-3} for the calculated density.

method of dynamic optimization [12]. 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 — benzene, toluene or xylenes — used for clathration were presaturated with $Ni(NCS)_2(4\text{-}MePy)_4$ at 25°C in order to avoid possible interference of heat of dissolution of the solid substrate in the clathration heat effects. Each measurement lasted approximately 200 min. The results given in Table 1 are averaged experimental results of four to five individual measurements.

RESULTS AND DISCUSSION

Table 1 summarizes the experimental results which are discussed below. Analyzing ΔH_{clath} values measured for the clathration of p-xylene and p-dichlorobenzene, Hart and Smith [9] have decomposed ΔH_{clath} into three components: $\Delta H_{\alpha\to\beta}$, ΔH_{evap} and ΔH_{sorp}, each corresponding to a single virtual process of, respectively, phase transformation of the host, transformation of the guest into a gas phase, and absorption of the gaseous guest by the clathrate structure of the host. More recent studies [13] have indicated that the host β-structure is quite "sensitive" to the amount and type of guest absorbed. Thus, there is no unique $\Delta H_{\alpha\to\beta}$ component since there is no unique β-phase. Lipkowski and Chajn [14] have assumed that at least the "empty" β-phase is independent of the type of guest and have determined $\Delta H_{\alpha\to\beta_0}$ as 0.8 kcal mole^{-1}. This being so, the clathration enthalpy, ΔH_{clath}, may be expressed as

$$\Delta H_{\text{clath}} = \Delta H_{\alpha\to\beta_0} + \Delta H_{\text{evap}} + \Delta H_{\beta_0\to\beta} + \Delta H_{\text{sorp}} \tag{2}$$

The first and second components (endothermic) are independent of the guest—host interactions in the clathrate. Endothermic $\Delta H_{\beta_0\to\beta}$, which corresponds to the dilatation process of the host structure (occurring on absorption of the guest), and exothermic ΔH_{sorp} define the energy of intermolecular interactions in the clathrate. The isosteric heat of sorption (q_{st}), defined [15] as

$$q_{\text{st}} = RT^2 \left(\frac{\partial \ln f}{\partial T}\right)_{n_s} \tag{3}$$

where f denotes the fugacity and n_s absolute sorption of the guest, may be regarded as a direct measure of ΔH_{sorp}. Thus, the difference between the values of the sum $\Delta H_{\text{clathr}} - \Delta H_{\alpha\to\beta_0} - \Delta H_{\text{evap}}$ determined by calorimetric techniques and the $q_{\text{st}} = \Delta H_{\text{sorp}}$ derived from the studies of temperature dependence of the guest equilibrium pressures over the clathrate may conveniently be used to estimate the $\Delta H_{\beta_0\to\beta}$ dilatation enthalpy. Availability of such data is, by now, limited to the benzene clathrate of $Ni(NCS)_2(4\text{-}MePy)_4$ for which both isosteric heat of sorption [2] and clathration enthalpy (present study) have been determined *. The corresponding values are $\Delta H_{\mathrm{clath}} = 4.80$, $\Delta H_{\mathrm{evap}} = 8.09$, $q_{\mathrm{st}} = 14.50$ and, as given above $\Delta H_{\alpha\to\beta_0} = 0.8$ kcal mole^{-1} **.

Hence the estimation for $\Delta H_{\beta_0\to\beta}$ gives the value 0.8 kcal mole^{-1}, which should be regarded as the enthalpy of dilatation of the host β-Ni(NCS)$_2$(4-MePy)$_4$ accompanying absorption of benzene. The "empty" β-phase has a molar volume of 471.6 cm^3 (lattice parameters: $a = 16.67$, $b = 22.54$ Å [16]) and the benzene clathrate, has a molar volume of 505.5 cm^3 ($a = 17.02$, $b = 23.18$ Å [17]).

Let us assume approximate enthalpies of dilatation for other clathrates of the same β-structure but different lattice parameters as equal

$$\Delta H_{\beta_0\to\beta_V} = 0.8\,\frac{V - 471.6}{505.5 - 471.6} = 0.0236(V - 471.6)$$

where V is the molar volume of a specific clathrate. Then, 1.01, 1.30 and 1.77 kcal mole^{-1} are obtained for toluene, *p*-xylene and *m*-xylene, respectively.

Allison and Barrer [2] have found linear correlations between isosteric heat of sorption (q_{st}) in the β-Ni(NCS)$_2$(4-MePy)$_4$ and condensability (boiling temperature and latent heat of vaporization) of several volatile guest compounds. The mean ratio of q_{st} to the latent heat was 2.0, which is usually interpreted as proof that there is no specific guest—host interaction [15b]. It seems interesting to analyze a corresponding relationship in the case of aromatic guests, beginning with benzene which was at the end of Allison's and Barrer's correlation. As the q_{st} values, we put

$$\Delta H_{\mathrm{sorp}} = \Delta H_{\mathrm{clath}} + \Delta H_{\alpha\to\beta_0} + \Delta H_{\beta_0\to\beta}$$

The results are given in Fig. 1. The points representing benzene and toluene define a straight line of slope very close to 2. *m*- and *o*-Xylene lie much below this line which reflects steric repulsive interaction between "cages" in the β-phase and branched molecules of *m*- or *o*-xylene. Ethylbenzene and *p*-xylene have similar ΔH_{sorp} values. Thus it seems that the linear shape of the guest molecule rather than its symmetry is important in fitting well the cavities within the host structure. The dashed vertical lines in Fig. 1 represent enthalpies of clathration of xylene isomers from different mixtures and will be discussed below.

When considering clathration of *n*-component guest mixtures, partial molar enthalpies of sorption $(H_{\mathrm{sorp}})_i$ or partial molar enthalpies of clathration $(H_{\mathrm{clath}})_i$ have to be introduced.

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* Few attempts have been reported in the literature on the subject of determining the clathration enthalpy of *p*-xylene or ethylbenzene from the dependence of vapour pressure over the clathrate phase on temperature. The results are less accurate because of the significant contribution of the partial pressure of the 4-methyl-pyridine (from thermal dissociation of the host complex) to the overall pressure.

** 1 kcal = 4.18 kJ; the figures report enthalpy data expressed in both units.

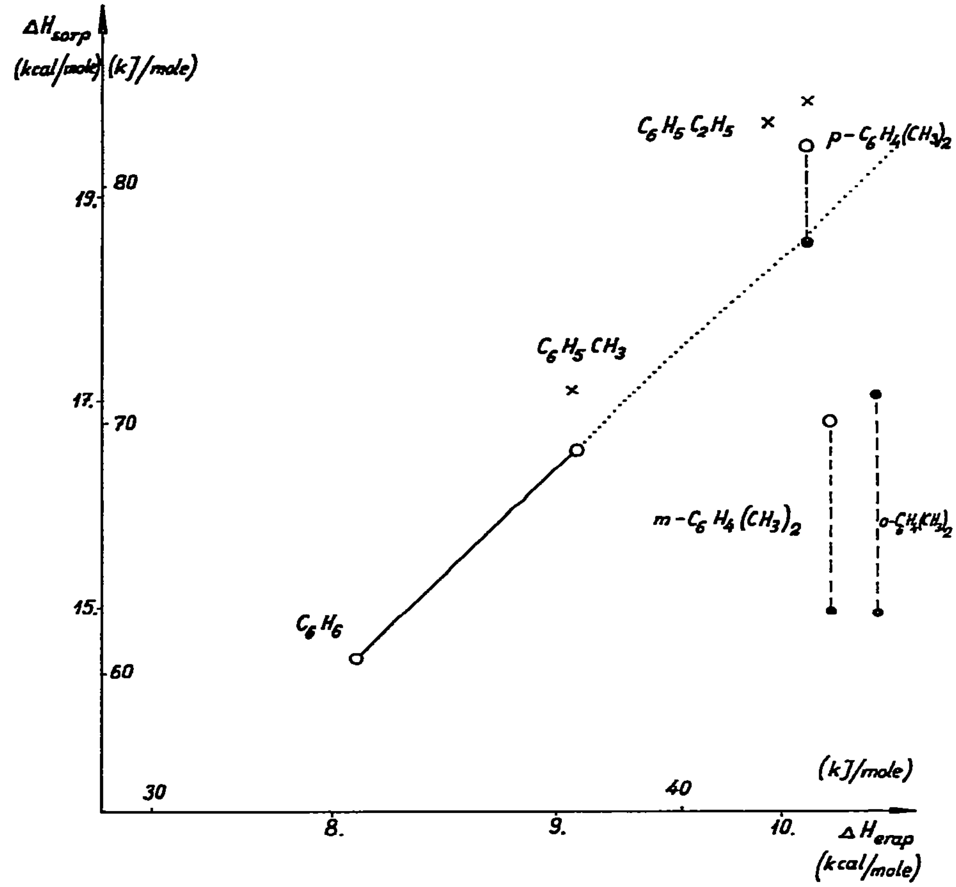

Fig. 1. Correlation between enthalpy of sorption (ΔH_{sorp}) of some aromatic guests in the β-Ni(NCS)$_2$(4-MePy)$_4$ clathrates and heats of liquefaction (ΔH_{evap}) of the guests. (o) Our data; (x) data reported by Smith and co-workers (refs. 9 and 10); (●— — —●) ranges of partial molar enthalpies of clathration [$(H_{\text{sorp}})_i$] of the respective isomers (cf. text).

Then

$$\Delta H_{\text{clath}} = \sum_i (H_{\text{clath}})_i \tag{4}$$

and

$$\Delta H_{\text{sorp}} = \sum_i (H_{\text{sorp}})_i \tag{5}$$

Values of H_{sorp} are perhaps more interesting than H_{clath} from the point of view of selectivity of the sorption processes but, because of some uncertainty in determining the $\Delta H_{\beta_0 \to \beta}$ enthalpy, H_{clath} should rather be used in interpretations of calorimetric data on ΔH_{clath} measured as a function of the quantitative composition of the guest.

As a model system of the guest component for studies on steric effects in the guest—lattice interactions in the β-Ni(NCS)$_2$(4-MePy)$_4$ clathrates, we have chosen a mixture of isomeric xylenes. Such a choice enables the electronic effects in the guest—host interactions to be neglected. Moreover, there is no need for any solvent when performing experiments at room temperature and hence the eventual solvent effects are avoided.

The dependence of ΔH_{clath} upon guest composition [8] is very complex. Attempts have failed to interpret these data on the assumption that the $(H_{\text{clath}})_i$ values are either constant or, alternatively, related to the molar volume of the clathrate. Thus it seems obvious that the $(H_{\text{clath}})_i$ must be dependent on the composition of the guest in the clathrate, and that molar volume of the clathrate phase does not adequately represent the shape and size of cavities in the clathrate.

The best fit of calculated and experimental ΔH_{clath} data has been attained by assuming that partial molar enthalpy of clathration $(H_{\text{clath}})_i$ is a linear function of the content of the *i*-th guest in the enclathrated guest mixture, as given below

$$(H_{\text{clath}})_o = 2.41 + 2.17\, y_o \tag{6a}$$
$$(H_{\text{clath}})_m = 3.20 + 1.35\, y_m \tag{6b}$$
$$(H_{\text{clath}})_p = 6.01 + 1.50\, y_p \tag{6c}$$

and

$$\Delta H_{\text{clath}} = (H_{\text{clath}})_o y_o + (H_{\text{clath}})_m y_m + (H_{\text{clath}})_p y_p \tag{7}$$

where y is the molar fraction of a given isomer in the enclathrated mixture and the subscripts o, m, p denote *ortho-*, *meta-* and *para*-xylenes (in the experiments we are referring to, $y_o + y_m + y_p = 1$). Clearly, eqn. (7) may be regarded as an expansion of the ΔH_{clath} into a Taylor sequence with respect to y_i. Fairly good agreement between $(\Delta H_{\text{clath}})_{\text{calc}}$ and $(\Delta H_{\text{clath}})_{\text{exp}}$ (Table 1) may suggest that guest—guest intermolecular interactions in the clathrate phase do not significantly contribute to the clathration enthalpy; the sequence in eqn. (7) not containing mixed expressions.

The influence of y_i on the respective $(H_{\text{clath}})_i$ (eqns. 6a—c) is in each case positive and very significant. This indicates the great ability of the β-Ni(NCS)$_2$(4-MePy)$_4$ host structure to "adapt" its sorption centres to the shape and size of the guest molecules. When p-xylene is predominant in the enclathrated mixture its partial molar enthalpy of clathration is higher than that observed at low y_p values. Because of similar relationships between $(H_{\text{clath}})_o$ and y_o, and $(H_{\text{clath}})_m$ and y_m; it seems reasonable to assume that the shape and size of the cavites in the clathrate can be modified by the guest molecules occupying them. Similar concepts have recently been proposed to interpret LC chromatographic results of isomer separations in which different β-Ni(NCS)$_2$(4-MePy)$_4$ sorbents were used as the stationary phase [18]. Very recent X-ray crystallographic investigations [19] demonstrate that the molecular structure of the host in the β-Ni(NCS)$_2$(4-MePy)$_4$ phases is independent of the guest. Thus, the intramolecular energy of the host may be regarded as constant and the effects described above may be treated as variations of guest—host intermolecular energy according to steric fit: cavity—guest molecule.

Clathration of xylenes by Ni(NCS)$_2$(4-MePy)$_4$ is "*para*-selective", i.e. the p-xylene content in the enclathrated guest mixture (y_p) is higher than that in the mixture of liquid xylenes (x_p), being equilibrated with the solid clathrate. It is interesting to compare differential enthalpy

$$H_{s,o} = \left(\frac{\partial \Delta H_{\mathrm{clath}}}{\partial y_p}\right)_{\substack{y_o + y_p = 1 \\ y_m = 0}} \tag{8}$$

or

$$H_{s,m} = \left(\frac{\partial \Delta H_{\mathrm{clath}}}{y_p}\right)_{\substack{y_m + y_p = 1 \\ y_o = 0}}$$

of substitution processes

β-Ni(NCS)$_2$(4-MePy)$_4$(*o*-xylene) + *p*-xylene

$\rightleftharpoons$ β-Ni(NCS)$_2$(4-MePy)$_4$(*p*-xylene) + *o*-xylene

and

β-Ni(NCS)$_2$(4-MePy)$_4$(*m*-xylene) + *p*-xylene

$\rightleftharpoons$ β-Ni(NCS)$_2$(4-MePy)$_4$(*p*-xylene) + *m*-xylene (9)

with the corresponding equilibrium constants

$$K_{s,o} = \frac{x_o y_p}{x_p y_o} \qquad K_{s,m} = \frac{x_m y_p}{x_p y_m} \tag{10}$$

The comparison clearly shows (Fig. 2) that the selectivity towards a two- or multicomponent guest system is not simply related to the partial molar enthalpies of clathration of the components of the guest mixture. The highest selectivities are even observed at low *p*-xylene concentrations in the β-clathrate, where $(H_{\mathrm{clath}})_p$ is lower than at high y_p. This effect should be ascribed to the entropy factor. When passing to lower y_p concentrations, some dilatation of the clathrate lattice occurs — this enables possible disordering of the *p*-xylene molecules. However, it must be pointed out that the type of selectivity is still in agreement with the sequence of enthalpies of clathration of single components: *para* > *meta* > *ortho*.

Within the β-phase the "adaptation" of the host lattice to the shape and size of the guest is made by drawing aside or pushing together the host molecules of constant geometry. However, it is known [20] that the Ni(NCS)$_2$(4-MePy)$_4$ molecule is able to adopt different conformations of the MePy and NCS ligands. Guest molecules of geometry not well fitted to the cavities in the β-phase can alter the conformation of the host and, consequently, molecular packing in the crystal and its physicochemical properties, e.g. selectivity. A good example is provided by the guest *o*-xylene which, when its concentration in the clathrate amounts to ca. $y_o = 0.65$, forms γ-clathrate [4] of entirely different form to the β-phase crystalline structure and even stoichiometry (2 : 1, guest/host). This γ-structure is "*ortho*-selective". Attempts have failed to obtain either the "empty" γ-phase or a series

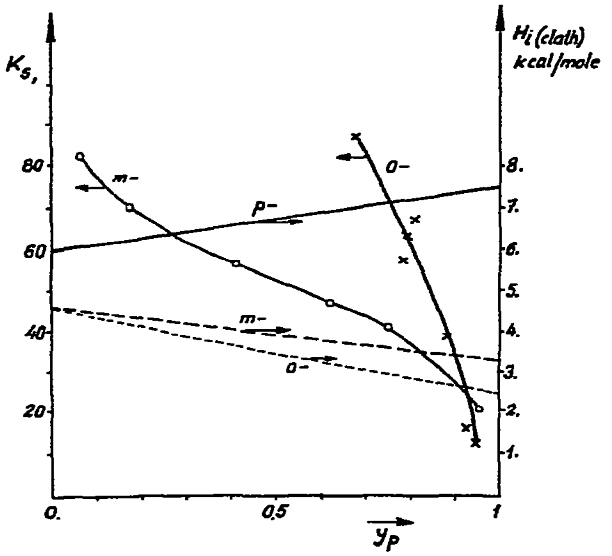

Fig. 2. Relationships between the equilibrium constants of the substitution of guest *m*-xylene ($K_{\mathrm{s.m}}$) or *o*-xylene ($K_{\mathrm{s.o}}$) with *p*-xylene in the β-Ni(NCS)$_2$(4-MePy)$_4$ clathrate confronted with partial molar enthalpies of clathration $[(H_i)_{\mathrm{clath}}]$ of the respective xylene isomers.

of γ-phases of varying guest content and the crystalline structure qualitatively unaffected. Thus no estimate has been made for the $\Delta H_{\alpha\to\gamma}$ enthalpy, and the $\Delta H_{\mathrm{clath}}$ measured for the γ-samples are not comparable in terms of guest—host interactions with the $\Delta H_{\mathrm{clath}}$ determined for the β-structure clathrates. It should be mentioned, however, that the possibility of host structure adaptation (dilatation—contraction) in order to adsorb guest molecules of different shapes and sizes is also observed for the γ-phase. *o*-Xylene may be replaced by larger molecules — naphthalene and methylnaphthalenes form γ-clathrates of similar molecular packing and the same stoichiometry. However, there is a large difference between the two methylnaphthalene (MeN) clathrates. The 2-MeN and the 1-MeN isomers form, with the Ni(NCS)$_2$(4-MePy)$_4$ as the host, two crystallographically different structures in which the host complex adopts a significantly different conformation of the ligands around the Ni—N coordination bonds [21,22]. Thus, within the host, not only intermolecular but also intramolecular van der Waals energy contributes as a variable part of the $\Delta H_{\mathrm{clath}}$ when considering enthalpies of clathration by the Ni(NCS)$_2$(4-MePy)$_4$ complex.

In Fig. 3 the thermokinetic course of the clathration [eqn. (1)] is given for two examples, with *p*-xylene (a) and a *m*-/*p*- mixture (b) as the guest component. The Fig. proves the rather complex kinetics of the reaction. Thus some additional information was collected by other techniques: X-ray powder diffraction (performed on separate samples but under the same physicochemical conditions as the calorimetric measurements) suggests the phase transformation $\alpha \to \beta$ is completed in a few minutes (not more than ca. 2—3 min) but dilatometric measurements, given in Fig. 4, indicate that sorption of the guest lasts significantly longer. Thus it may be assumed

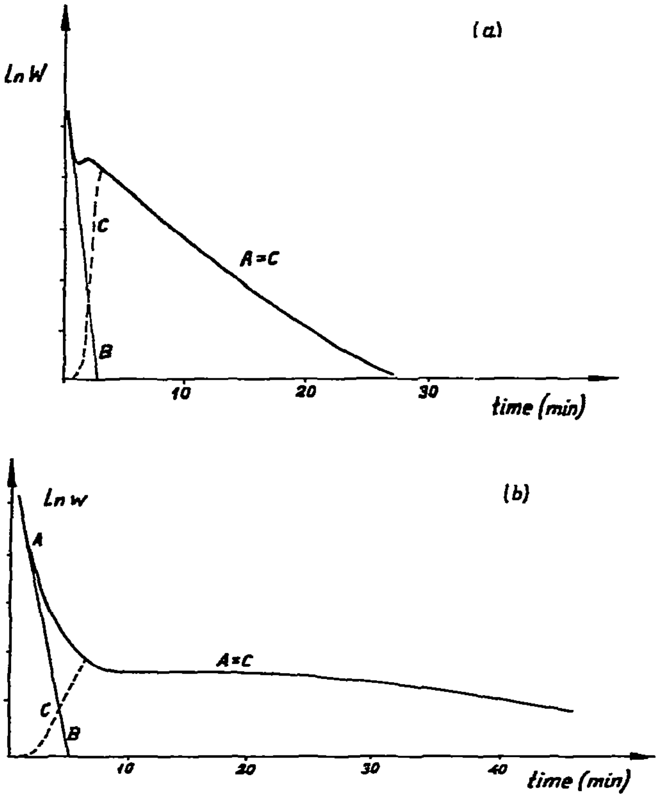

Fig. 3. The thermokinetic course of clathration of (a) p-xylene and (b) mixture of m- and p-xylene by the $Ni(NCS)_2(4\text{-}MePy_4)_4$ complex: ln $w(t)$ plotted against time (curve A) and its resolution into two components B and C (cf. text). (a) $y_p = 1.0$; (b) $y_m = 0.6$, $y_p = 0.4$.

that the clathration is a two-step process:

(I) at this stage relatively fast reconstruction and simultaneous guest absorption occur but some cavities in the clathrate remain unoccupied

$$\alpha\text{-}Ni(NCS)_2(4\text{-}MePy)_4 + x(\text{xylene}) \rightarrow \beta\text{-}Ni(NCS)_2(4\text{-}MePy)_4 \cdot x(\text{xylene})$$

(II) Step (I) is followed by xylene uptake to full occupancy of the cavities

$$\beta\text{-}Ni(NCS)_2(4\text{-}MePy)_4 \cdot x(\text{xylene}) + (1-x)(\text{xylene}) \rightleftharpoons \beta\text{-}Ni(NCS)_2(4\text{-}MePy)_4 \cdot (\text{xylene})$$

Periods of time in which particular steps are completed as well as the overall time of the reaction differ greatly according to the composition of the guest. The overall time of clathration is determined mainly by the slowest step (II) which, in turn, seems to be controlled by diffusion of the guest through the solid clathrate. This conclusion results from a comparison of reaction times which increase in the sequence: benzene (2 min) < toluene (7 min) < p-xylene (27 min) < m-xylene (50 min). The longest reaction times, up to ca. 90 min, are observed when the guest is a mixture of xylene isomers. Analogous effects, observed on absorption by zeolites, were ascribed to hindered diffusion [15c].

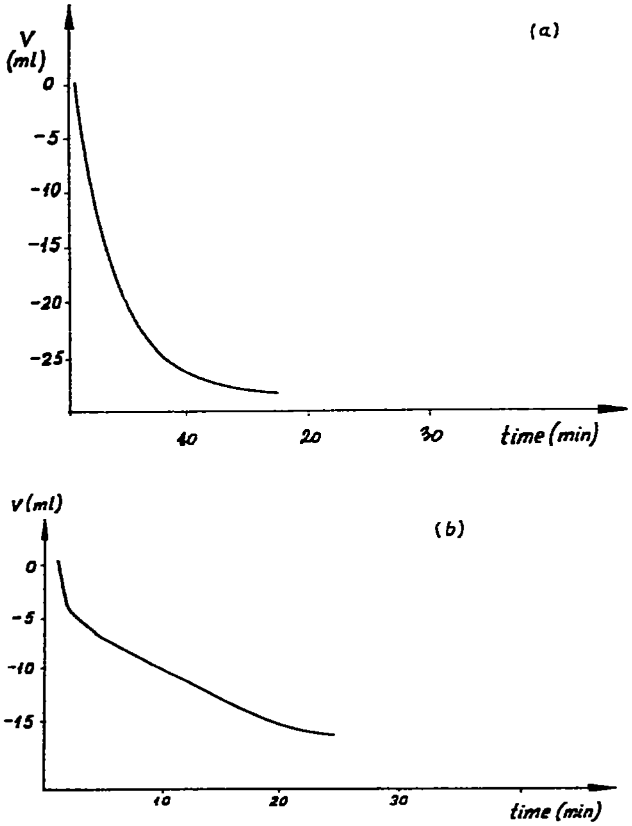

Fig. 4. Dilatometric curves of the total volume of reactants vs. time in the reacting systems of Fig. 3. The volume is given in cm^3 per mole of the host complex. (a) $J_p = 1.0$.

No quantitative interpretation of the shapes of curves C in Fig. 3 was attempted in view of the dependence of $(H_{\mathrm{clath}})_i$ on the composition of the guest (described above). Hence w(t) vs. time need not quantitatively represent the reaction rate.

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