

Competitive Clathration of *p*-Xylene and *p*-Dibromobenzene by the [Ni(NCS)₂(4-Methylpyridine)₄] Host*

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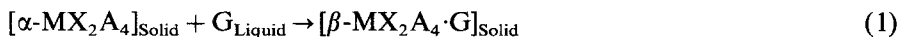
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Abstract. The selectivity of inclusion of *p*-xylene and *p*-dibromobenzene from their liquid mixtures by the host [Ni(NCS)₂(4-methylpyridine)₄] and the enthalpy of clathration were determined. *p*-Dibromobenzene is clathrated significantly more than *p*-xylene. The heats of clathration show a linear dependence upon the composition of the enclathrated mixture and are considered to be indicative of the conclusion that the guest–guest interactions are negligible from the thermochemical point of view. By comparing data presented herein with some literature data on competitive clathration an attempt to derive the entropy of guest exchange in the clathrate was performed.

Key words. Clathrate, inclusion compound, *p*-xylene/*p*-dibromobenzene mixture – molecular inclusion of.

1. Introduction

This study is part of a systematic thermochemical investigation of the equilibria of clathration of organic compounds ('guests') by the MX₂A₄-type Werner complexes ('host'), with particular emphasis on the selectivity of the inclusion processes. The process under investigation may be represented by the equation:



where G stands for a guest component which may be one-, two- or multicomponent.

Particularly interesting are the cases where the guest is a mixture and the compositions in the liquid material and in the solid inclusion compound are significantly different. In our previous papers [1, 2] attention has been paid to the selectivity of clathration of mixtures of isomers and, as the most suitable example, the xylene isomers were used as the guest components. The main conclusion of the studies cited above was that the molecular shape of the guest molecule is the factor determining its affinity to the *organic zeolite*, β -[Ni(NCS)₂(4-methylpyridine)₄]. When comparing these data with those on clathration of benzene and toluene we came to the conclusion that inclusion of the aromatic hydrocarbons shows the nature of a three-dimensional physical 'adsorption' rather than any chemical

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guest–host lattice bonding; the conclusion being in perfect accordance with the idea originally put forward by Allison and Barrer [3].

Next, it seemed very important to study the selective clathration of molecules which do not significantly differ in molecular shape and size while having chemically different substituents on the aromatic benzene ring. This study was aimed at this problem.

However, during the experimental work the paper by Smith and coworkers [4] appeared in which careful analysis of the basis for the selectivity of clathration by the host complex has been reported. Thus, in this paper we limit ourselves to some data and analyses which may, hopefully, supplement the work cited. The mixture chosen is *p*-xylene/*p*-dibromobenzene since the molecules of the two compounds are very much alike from the geometrical standpoint but, having no permanent dipole moments, differ significantly in the electronic properties of the methyl and bromine substituents. From the X-ray structure of the β -phase [8] it has been known that the adjacent guest molecules (*p*-xylene) in the clathrate have their substituents close to each other. Thus, if the guest–guest interaction contributes significantly to the enthalpy of clathration (and to the selectivity of the process) it should be observable by calorimetry.

2. Experimental

The guest (G) used as the substrate for clathration (according to the Equation (1)) was a solution of *p*-dibromobenzene (abbreviated to *p*-DBB) in *p*-xylene. The range of composition is thus limited by the solubility of solid *p*-DBB in *p*-xylene, which at room temperature reaches about 1/3 (mole/mole). Four concentrations of *p*-DBB/*p*-xylene (liquid phase) were used: 1/16; 1/8; 1/4 and that of a saturated solution (at 25°C), i.e. 1/3.1 (determined from experimental plots of density of the liquid phase). The *p*-DBB used (BDH, laboratory reagent) did not contain other DBB isomers in amounts detectable by gas chromatography.

The enthalpy of clathration was measured by using a BMR calorimeter [5]. The clathration process was (at 25°C) initiated by breaking a thin-walled glass ampoule containing 0.5 g (0.9137 mmole) of the solid α -[Ni(NCS)₂(4-methylpyridine)₄] complex in the calorimetric vessel containing 15 mL of liquid guest mixture. The guest for clathration was presaturated with a small amount of [Ni(NCS)₂(4-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. Presaturation did not alter significantly the composition of the liquid used.

The detailed procedures for the preparation of pure α -[Ni(NCS)₂(4-MePy)₄] substrate and details of the calorimetric method used have been described elsewhere [5, 6].

The solid product of clathration was analyzed by thermogravimetry. This technique is quite suitable in the case studied because of the significant difference in the molar weights of *p*-DBB (235.92) and *p*-xylene (106.17). A typical thermogram is given in Figure 1a. As may be seen from this illustration, the guest evaporates from the sample within the first step of decomposition of the host [Ni(NCS)₂(4-MePy)₄]. The product at the end of step I has the composition [Ni(NCS)₂(4-MePy)₃]. Next, further decomposition of the complex proceeds. The best analytical results were

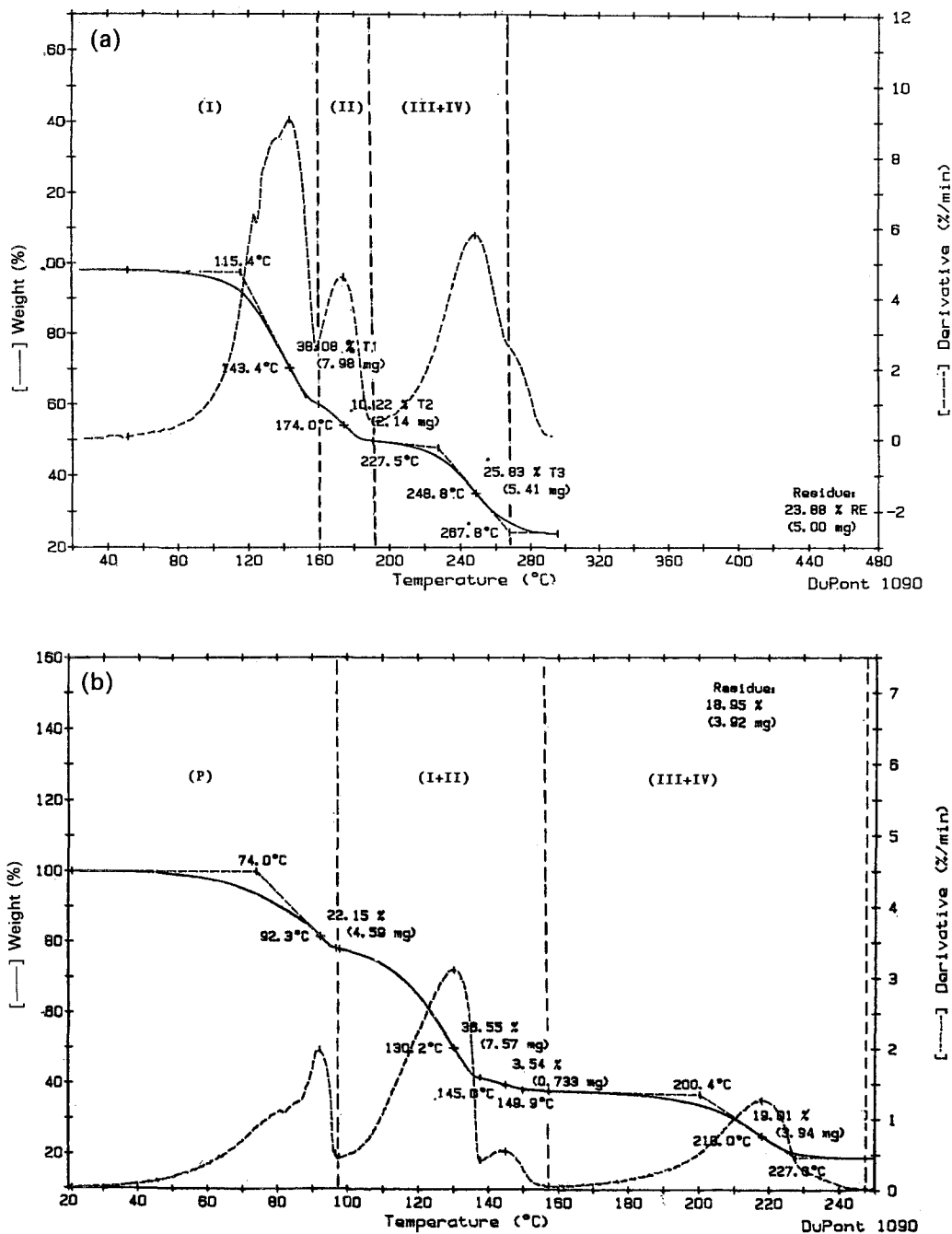


Fig. 1. (a) The course of thermal decomposition (TGA - solid line, DTG - broken line) of the *p*-DBB/*p*-xylene (guest) clathrate of $[\text{Ni}(\text{NCS})_2(4\text{-MePy})_4]$ (host). Sample size 20.96 mg, heating rate 10 deg/min., atmosphere - argon. (b) Thermal decomposition of a sample contaminated with an excess amount of *p*-DBB, which evolves in the preliminary step of the decomposition denoted 'P'. Sample size 20.71 mg, heating rate 2 deg/min. Notation I through IV refers to evaporation from the samples of the 1st through 4th 4-methylpyridine molecule.

obtained by comparing the weight loss within step III (release of the last two MePy ligands) and that of the combined steps I + II. The difference (I + II) - III may be considered as the mass of the guest in the clathrate and the average molar weight (m_0) of the guest may thus be derived. By assuming a guest/host molar ratio equal to unity (in accordance with all relevant data available) we obtain $m_G = xM_{\text{xylene}} + (1-x)M_{\text{DBB}}$; and thus $x = (m_G - M_{\text{DBB}})/(M_{\text{xylene}} - M_{\text{DBB}})$; x standing for the molar content of *p*-xylene in the enclathrated mixture.

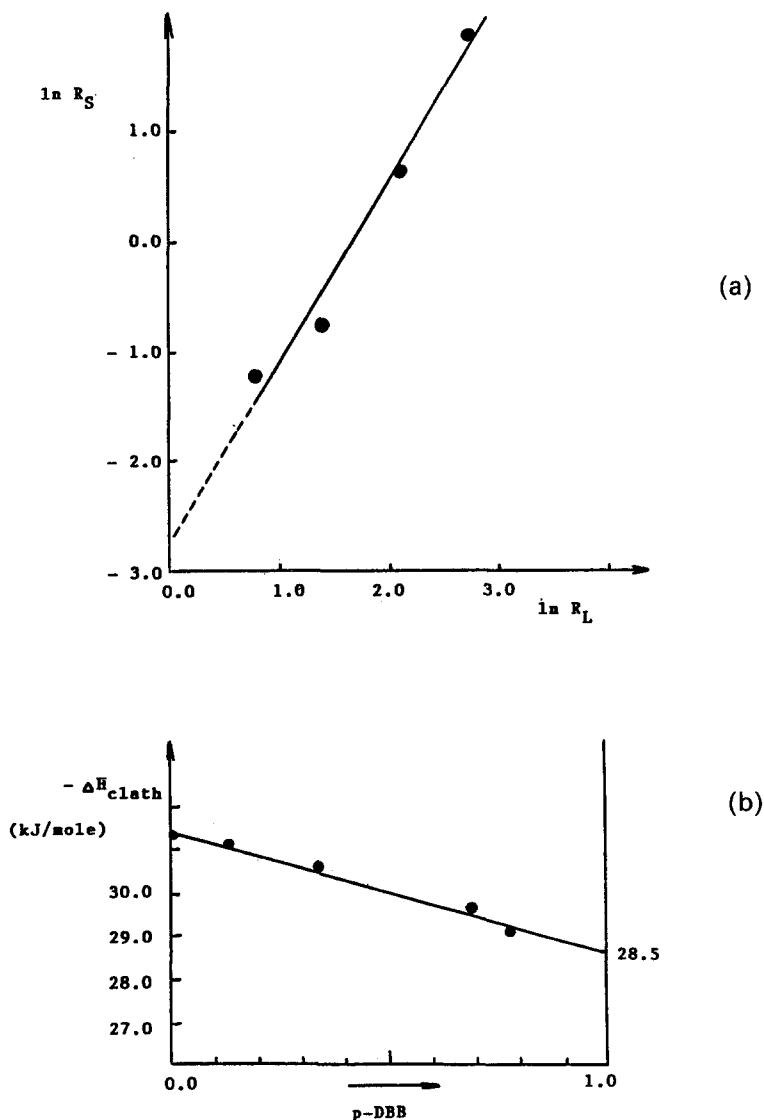


Fig. 2. (a) Distribution of *p*-xylene/*p*-dibromobenzene between liquid and solid phases. R_L and R_S refer to *p*-xylene/*p*-DBB molar ratio in the liquid (L) and solid (S) phases. (b) Enthalpy of clathration of the *p*-xylene/*p*-dibromobenzene guest mixture plotted against composition of the enclathrated mixture (mole per mole of guest).

It should be noted here that the clathrate was not washed with any solvent before thermogravimetry; the samples were just patted with some cotton wool and filter paper and then left to dry in the open air for about 30 minutes. When using concentrated *p*-DBB solutions one may suspect that the solid samples prepared as described above may contain some extra amount of *p*-DBB, as the solid admixture, in addition to the amount enclathrated. To check this, every sample was submitted to a DSC analysis. *p*-DBB shows the melting point at 86.9°C and, if present in the sample, an endothermic heat effect should be observed in DSC curves at the temperature where no significant decomposition of the clathrate takes place. Such an endothermic effect was indeed observed when using the solid clathrate taken out from the most concentrated *p*-DBB solution in *p*-xylene. The heat measured in the DSC experiments was used to calculate the extra amount of *p*-DBB (heat of fusion 20.3 kJ/mol). Fortunately, the TGA curves themselves also give quantitative evidence of the extra (non-clathrated) amount of *p*-DBB in the sample, as may be seen from Figure 2b. The preliminary step of decomposition is well separated from the decomposition of the clathrate. The data on composition of the clathrates given in the next paragraph are derived from four independent determinations, and the TGA and DSC curves were in perfect accordance (only the preliminary steps were analyzed by using both techniques).

3. Results and Discussion

The results on the selectivity of inclusion of *p*-xylene/*p*-DBB mixtures as well as the respective enthalpies of inclusion are summarized in Table I and illustrated in Figure 2.

The plot in Figure 2a representing the selectivity of clathration was prepared in accordance with the concept of Smith *et al.* [4], i.e. the mole ratio of the two guests in the liquid phase, R_L , is plotted against the mole ratio in the coexisting solid phase, R_S (on the logarithmic scale). There appears to be a linear relation, within the error limits, between $\ln R_L$ and $\ln R_S$, and, as it may easily be concluded from the illustration, *p*-dibromobenzene is absorbed preferentially over *p*-xylene. The straight line in Figure 2a may be represented in the form:

$$\ln R_S = m \ln R_L + b \quad (2)$$

where $m = 1.72$ and $b = -2.8$. When compared to the recently reported [4] studies on clathration of the following series of guests: bromotoluene – *p*-xylene – chlorotoluene – dichlorobenzene – fluorotoluene – ethylbenzene – toluene –

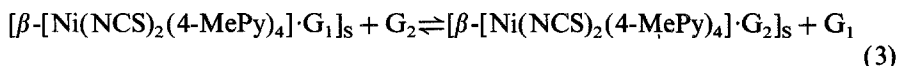
benzene (the series on p. 420 in Reference [4]), it is clear that *p*-dibromobenzene should be placed at the top of the series, as the most selectively clathrated by $[\text{Ni}(\text{NCS})_2(4\text{-MePy})_4]$.

It is worth noting here that *p*-DBB fits also the correlation between the selectivity of inclusion and the 'van der Waals length' of guest molecules. The *p*-DBB molecule is longer than any of the series cited above, as expected for the one that is most selectively absorbed [4]. This type of correlation seems rather interesting despite its obscure theoretical background. Selectivity of inclusion may be related, as shown by Smith *et al.* [4], to the length of the guest molecule. The same type of correlation has been found in studies of competitive clathration of isomers of

Table I. Clathration enthalpy and distribution of the guests *p*-xylene/*p*-dibromobenzene between liquid and solid phases

	<i>p</i> -xylene content (mole per mole of guest) in:		$-\Delta H_{\text{clathr}}$ clathration enthalpy kJ/mol
	liquid	enclathrated mixture	
1	1.00	1.00	31.4
2	0.94	0.87	31.1
3	0.89	0.66	30.6
4	0.80	0.32	29.6
5	0.68	0.23	29.0

xylene. The quantity $\ln K_r$, where K_r is the equilibrium constant of the substitution process:



plotted against the average length of the guest molecule (weighted average of the length of the guest molecules; the weight being identical with the molar content of the guest in the enclathrated guest mixture) produce a linear relation, which is a common line for the systems: *p*-/*m*- and *p*-/*o*-xylene.

It should be noted here that

$$K_r = \frac{[\text{G}_1]_L[\text{G}_2]_S}{[\text{G}_1]_S[\text{G}_2]_L} = \left(\frac{[\text{G}_1]_L}{[\text{G}_2]_L}\right) / \left(\frac{[\text{G}_1]_S}{[\text{G}_2]_S}\right) = R_L/R_S \quad (4)$$

and thus, in the terms used by Smith *et al.*,

$$\ln K_r = \ln R_L - \ln R_S. \quad (5)$$

Then if the experimental results on selectivity are given in the form $\ln R_S = m \ln R_L + b$ and $m \neq 1$, the result is equivalent to the statement that the K_r 'constant' is not constant, but concentration dependent.

K_r is the concentration constant. If we introduce the thermodynamic equilibrium constant K of the process given by Equation (3) then it may be written

$$K = K_r(a_2^S a_1^L / a_2^L a_1^S)$$

where a_1^S , a_2^S , a_1^L and a_2^L stand for activity coefficients of the guest components 1 and 2 in the liquid (L) and solid (S) phases, respectively. If we denote the activity term $a_2^S a_1^L / a_2^L a_1^S$ as A , then

$$K = K_r A \quad \text{or} \quad K_r = K/A.$$

By introducing this expression into Equation (5) we obtain

$$\ln R_S = \ln R_L - \ln(K/A)$$

$$\ln R_S = \ln R_L + \ln A - \ln K$$

and, finally,

$$\ln R_S = \ln R_L A - \ln K. \quad (6)$$

When comparing this to the experimental correlation of the type $\ln R_S = m \ln R_L + b$, then

$$b = -\ln K \quad \text{and} \quad A = R_L^{(m-1)}. \quad (7)$$

It seems interesting that the correlation constant b may be used as a direct measure of the thermodynamic constant of clathration equilibria; the only condition being a 1:1 substitution mechanism according to Equation (3).

As shown in Figure 2b, the enthalpy of clathration of the mixture is, within experimental error, linearly dependent on the *p*-xylene/*p*-dibromobenzene molar ratio in the enclathrated mixture. This may suggest that, within the limits of error, the partial molar enthalpies of inclusion of *p*-xylene and *p*-dibromobenzene are independent of the *p*-xylene/*p*-dibromobenzene molar ratio. This result is different from the respective relationships found for the mixtures of xylene isomers, where the partial molar enthalpies of clathration of individual components are functions of their content in the solid clathrate [1]. This may lead to the conclusion that substitution of *p*-xylene molecules with *p*-dibromobenzene molecules is not associated with any significant change of the geometry of the cavities in the host lattice, and that the guest-guest interactions in the clathrate lattice are negligible, at least from the thermochemical standpoint. The heat of dissolution of *p*-DBB in *p*-xylene is 17.5 ± 0.1 kJ/mol and is independent of the composition of the mixture [7] thus having no influence upon the determined relationship between clathration enthalpy and composition of the guest mixture.

The result given by Equation (7) may be used for estimating the standard Gibbs free energy of the exchange process of Equation (3) (displacement of *p*-xylene by

Table II. Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) of guest exchange processes according to reaction (3), and clathration enthalpy (ΔH_{clathr}) of the second guest in the guest pairs

Guest pair	ΔG^0 (J/mol)	ΔH^0 (J/mol)	ΔS^0 (J/mol deg)	$-\Delta H_{\text{clathr}}$ (J/mol)
1. <i>p</i> -xylene/ <i>p</i> -dibromobenzene	-6960	2900	33.0	28500
2. <i>p</i> -xylene/ethylbenzene	3320	-800	-13.5	32200
3. <i>p</i> -xylene/toluene	4260	7700	11.5	23700
4. <i>p</i> -xylene/4-methylpyridine	5200	11300	20.5	20100
5. <i>p</i> -xylene/benzene	6350	11300	16.6	20100
6. <i>p</i> -xylene/ <i>o</i> -xylene	6940	12200	17.7	19200
7. <i>p</i> -xylene/ <i>m</i> -xylene	7930	12400	15.0	19000

Note: ΔG^0 derived by using equations: $\Delta G^0 = -RT \ln K$ and $-\ln K = b$ (b from selectivity data, cf. text); the numeric data used being reported in: present study (No. 1), Ref. [4] (Nos. 4 and 5), Ref. [1] (Nos. 6 and 7) and Ref. [9] (Nos. 2 and 3). Enthalpy data taken from: 1 present study, 2 Ref. [9], 3 Ref. [6], 4 Ref. [10], 5 through 7 Ref. [6]. The standard state for each guest is that guest in the 1:1 inclusion compound in equilibrium with the pure liquid guest at 298 K (metastable liquid form in the case of *p*-DBB).

the other guest) and, where the clathration enthalpy data are available, to estimate the standard entropy change associated with reaction (3). The results of the respective calculations are given in Table II. It is interesting to note that both enthalpy and entropy driven selectivities result from these data. The first two examples in Table II, i.e. the selectivity for *p*-DBB against *p*-xylene and that for *p*-xylene against ethylbenzene provide purely entropy driven selectivity. The selectivity in the other five systems, with more clathration of *p*-xylene than other components of the guest pairs, is enthalpy driven.

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