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Calorimetric and Thermogravimetric Study of Competitive Clathration in the β-[Ni(NCS)$_2$(4-MePy)$_4$] Host*

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Abstract. The stoichiometry of mixed guest clathrates of [Ni(NCS)$_2$(4-methylpyridine)$_4$] (host) with methanol/4-methylpyridine and acetone/4-methylpyridine as well as the enthalpies of clathration and the thermokinetic course of the processes were investigated. Two different mechanisms of molecular inclusion are proposed: (I) simple competition for the same type of absorption sites with two methanol molecules substituting one of 4-methylpyridine in the solid inclusion compound; and (II) competitive absorption for two types of absorption sites of acetone and 4-methylpyridine. Partial molar enthalpies of clathration of the individual guests are derived and discussed. The thermokinetic course of the processes is also given. The analytical thermogravimetric procedure is described and the solid products of thermal decomposition of the clathrates and of the host complex were identified by using X-ray powder diffractometry.

Key words. Clathrate, inclusion compound, inclusion of acetone, inclusion of methanol – enthalpy of.

1. Introduction

This paper is part of the series devoted to studies of guest–lattice interactions in the clathrate inclusion compounds formed by the MX_2A_4 Werner type coordination complexes (host) with organic guest compounds. The previous papers [1–3] have concentrated on clathration of aromatic guest species: benzene and its derivatives. It has been stated that the steric guest–lattice fit is of predominant importance both from the point of view of clathration selectivity and the enthalpy of clathration. Much less is known about the clathration of aliphatic guest molecules. Allison and Barrer [4] were the first to tackle this problem, and they used the term 'organic zeolite' to describe the absorption behaviour of the β-MX_2A_4 porous phases. The experimental technique applied in the work cited, i.e. absorption from the gas

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phase, allowed the study of inclusion phenomena at rather low guest/host molar ratios. In a series of chromatographic studies on the sorbents derived from [$Ni(NCS)_2$(4-methylpyridine)$_4$] [5–7] the importance of clathration of aliphatic solvents has been pointed out; particularly the significant competition of the solvent molecules for the absorption sites in the solid. This is especially significant when the solvent is in great excess as compared to the solute. It has also been suggested [8] that some solvents, such as acetone or ethanol, are absorbed in strongly non-stoichiometric amounts despite their high concentrations in the liquid equilibrated with the inclusion compound.

The guest–lattice interactions in these compounds are of interest for at least two reasons. First, from a practical viewpoint, since clathration of the guest compounds which are solid substances may conveniently be performed from solution phases and the possible interference from clathration of the solvent may be important. A suitable example of this may be clathrate chromatography [6]. Second, since clathration of molecules smaller than aromatic hydrocarbons and their derivatives may give rise to the formation of qualitatively different clathrate structures.

Methanol and acetone were chosen as suitable guests for the present study; the two behave differently in clathration equilibria, as has been shown in chromatographic studies [6, 8].

2. Experimental

Thermal decomposition was studied by using a Daini-Seikosha SSC/560GH thermoanalyzer. X-Ray powder diffraction spectra were recorded by using a Rigaku–Denki powder diffractometer (CuK_α). The aliphatic guest molecules are very volatile, and it was therefore important to choose an appropriate analytical technique to determine the host/guest ratio of the aliphatic guest in the solid clathrate. This must be carried out *without* removing it from the mother liquor with which it is in equilibrium. Two procedures have been applied: one for macrocrystalline samples of crystal size of the order 1–2 mm (a), and (b) for microcrystalline samples. In (a) one or two single crystals were taken with some excess of the respective mother solution and submitted to a stepwise thermogravimetric analysis. In the first step an isothermal weight loss was measured at 25°C and at a controlled air flow rate. Within this step, which lasts from 30 to 60 minutes according to the rate of desorption of the guest from the solid, two processes occur: evaporation of the excess of the liquid and desorption of a part of the guest content in the solid clathrate.

When plotting the weight loss on a logarithmic scale against time the two components (i.e. drying and desorption) can be separated, as illustrated in Figure 1a, and the original guest content in the solid can be determined through extrapolation to time = 0 (a linear extrapolation was used on the basis of the previous study [10]). After the first isothermal step, a thermal decomposition of the solid was started by heating up to 250°C. A typical thermogravimetric curve is represented in Figure 1b. The solid products obtained in each of the steps indicated in Figure 1 have been identified through comparison of their X-ray powder patterns with those obtained for the solids prepared by wet methods [9]. As can be seen from the data reported in Figure 2 it seems each product is an individual phase rather than a

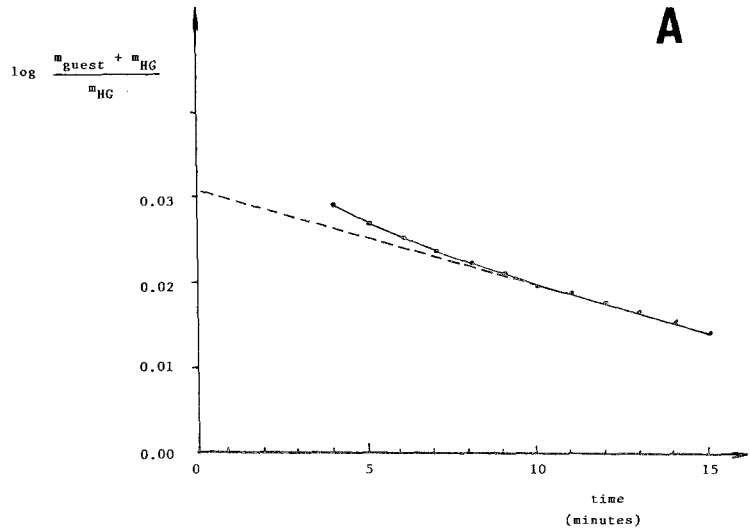
A
log $\frac{m_{guest} + m_{HG}}{m_{HG}}$
0.03
0.02
0.01
0.00
0
5
10
15
time
(minutes)

Fig. 1A.

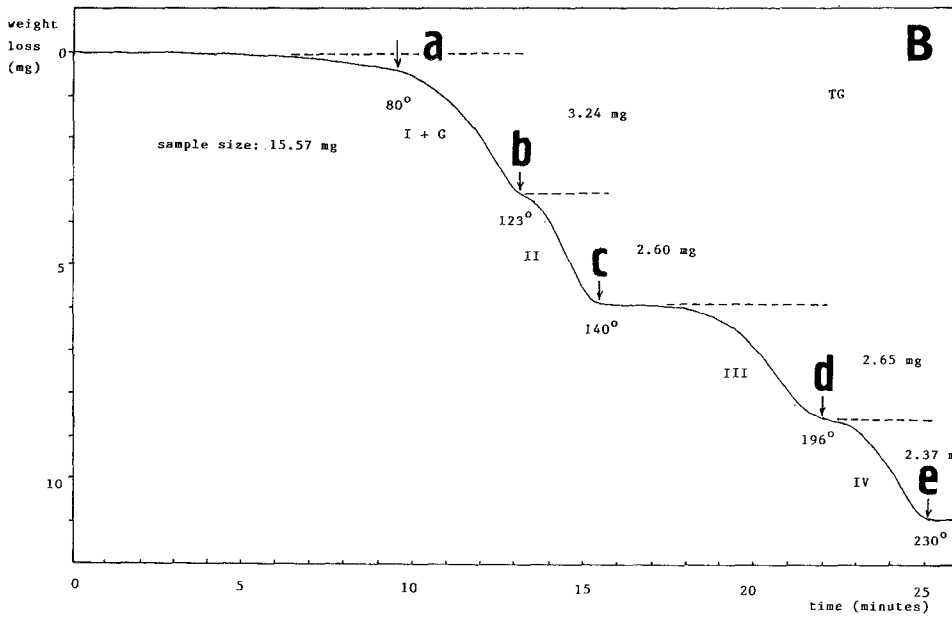
weight
loss
(mg)
0
5
10
B
a
b
c
d
e
80°
I + G
3.24 mg
TG
sample size: 15.57 mg
123°
II
2.60 mg
140°
III
2.65 mg
196°
2.37 mg
IV
230°
0
5
10
15
20
25
time (minutes)

Fig. 1B.

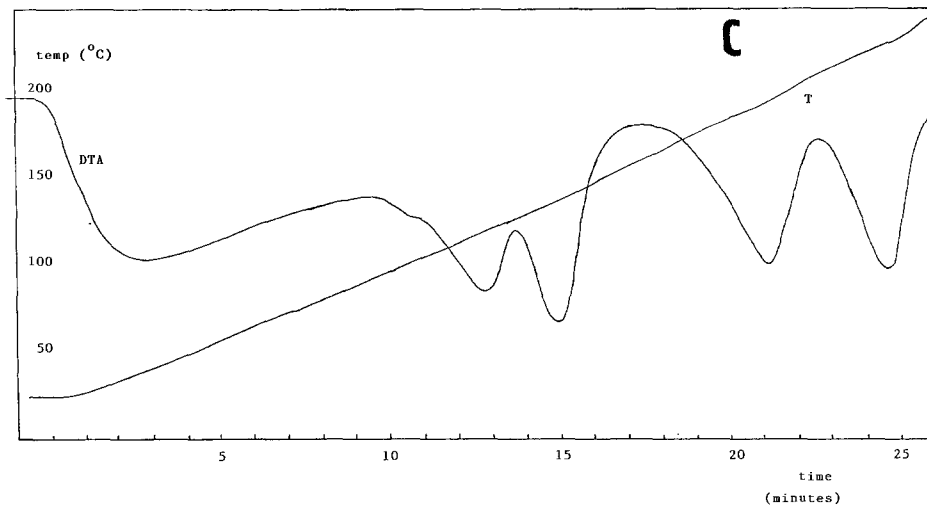

Fig. 1C.

Fig. 1. The course of: (A) drying of clathrate crystals at 25°C (given on a log scale), followed by (B) thermal decomposition (gravimetric curve) of the β-[Ni(NCS)$_2$(4-methylpyridine)$_4$] · G clathrate. Notation I through IV refers to the removal of 4-MePy ligands 1 through 4; the letters 'a' through 'e' denote the solid products of decomposition. In (C), the DTA and T curves of the same experiment are given. The scale of the ordinate (up: exothermic; down: endothermic) is arbitrary.

mixture of substrate and the product of thermal decomposition. Thus it is not very $1.074 \times 15.57 - 15.57 = 1.15$ mg, or 1.34 mole of CH_3OH per mole of the host, if clear why steps III and IV are not exactly equal on the weight scale. However, the sum of the weight losses in steps III and IV is completely independent of the detailed thermogravimetric procedure and thus may conveniently be used for stoichiometric calculations. Then the difference between the weight losses in steps (I + G and II) and III through IV is indicative of the guest content in the solid after the isothermal step 0. Taking into account the very significant difference of desorption rates of small aliphatic and larger aromatic guest molecules [10] one may assume the guest desorption in the preliminary isothermal step is the aliphatic one only. The analytical calculations in the example given in Figure 1 were the following:

- the average weight loss in steps III and IV, i.e. $(2.65 + 2.37)/2 = 2.51$ mg, was assumed as 1/4 of the content of coordinated 4-MePy in the sample;
- the content of [Ni(NCS)$_2$(4-MePy)$_4$] in the sample was calculated by multiplying the ratio of molar weights of [Ni(NCS)$_2$(4-MePy)$_4$] and 4-MePy (547.2/93.13) by 2.51;
- the difference in weight loss between [(I + G) + II] and (III + IV) was ascribed to the content of nonvolatile guest (G) in the sample (0.82 mg, or 0.33 mole of 4-MePy per mole of the host if G = 4-MePy);
- the sum of the content of [Ni(NCS)$_2$(4-MePy)$_4$] and G, calculated as above, was taken as the sample size at the beginning of the thermal decomposition; the value being necessary for calculations to be done in the preliminary (isothermic) step;
- the extrapolated value of the ratio $[(m_{guest} + m_{HG})/m_{HG}]$ (equal to 1.074, Fig. 1a)

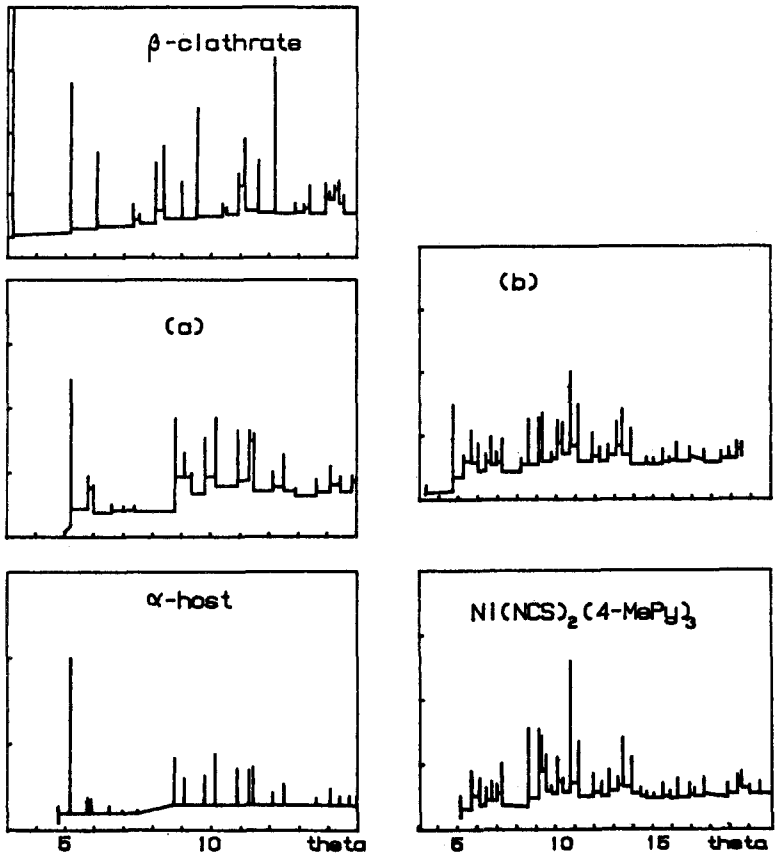

Fig. 2(a,b).

was used for calculating the content of volatile guest (m_{guest}); in the example: $1.074 \times 15.57 - 15.57 = 1.15$ mg, or 1.34 mole of CH_3OH per mole of the host, if the guest is CH_3OH).

It is, of course, rather arbitrary (and it may not be exactly true) to assume that in the first isothermic step only the volatile guest is desorbed. However, because of the very significant difference of volatility of the aliphatic guest (methanol or acetone) and the aromatic guest (4-MePy), *and* because of the low content of the latter component, the analytical errors introduced by this simplification were lower than the errors of determination of the 4-MePy content by acidimetric techniques. This is also because the overall content of 4-MePy (enclathrated + coordinated) is determined by acidimetry and the content of 4-MePy guest is the difference between $(4 + y)$ and 4; y being within the range 0.1–0.5.

In procedure (b) a slurry composed of the microcrystalline solid in its mother liquor was analyzed by a combination of pyknometry (volume of the solid in the sample), acidimetric back titration (4-MePy) and complexometric titration (Ni^{2+}).

The calorimetric procedure was analogous to that applied in our previous studies [3]. The solid sample (1 g = 1.825 mmole) of the nonclathrated α-form of the

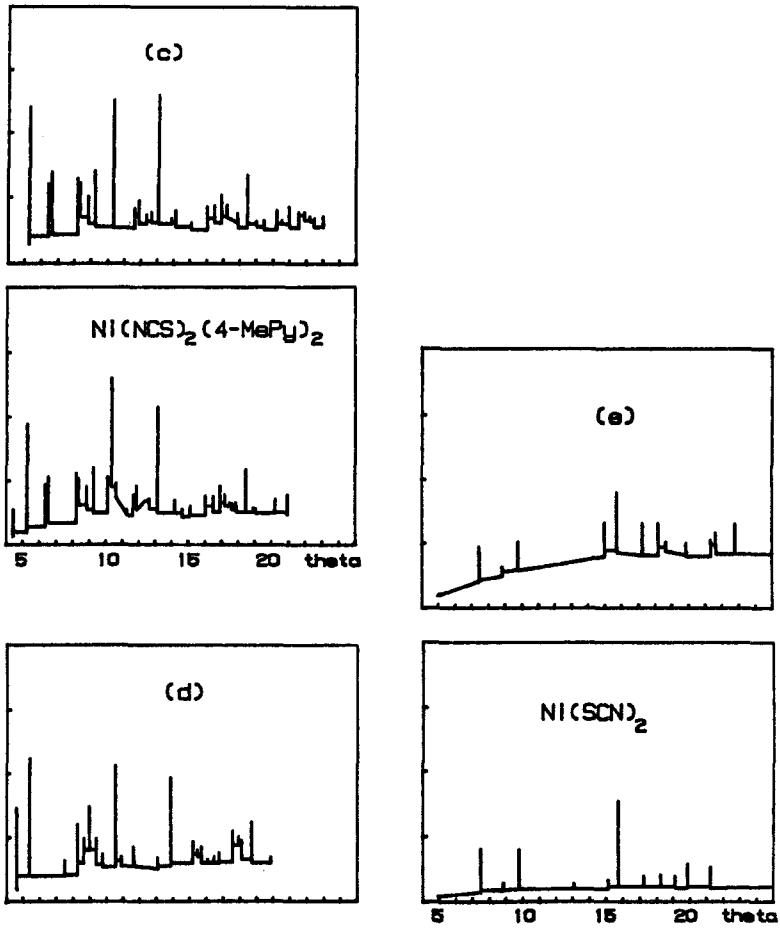

Fig. 2(c,d,e).

Fig. 2. Representation of X-ray powder diffraction data of solid products of thermal decomposition of $Ni(NCS)_2(4\text{-methylpyridine})_4 \cdot G$ clathrates and of the host complex. Letters (a) through (e) refer to the steps of thermal decomposition (cf. Figure 1) after (a) desorption of the guest at 80°C; (b) through (e) to the removal of consecutive 4-MePy ligands 1 through 4. The chemical formulae given in the diagrams refer to reference solid samples obtained by wet methods.

$[Ni(NCS)_2(4\text{-MePy})_4]$ complex was placed in a thin-walled glass ampoule and put into the calorimetric vessel containing an excess amount (15 ml) of liquid guest system. After thermal equilibrium was attained the glass ampoule was broken to start clathration and the development of the thermal power was recorded. A BMR microcalorimeter was used [11]. The thermograms were analyzed by using the *n-body* model [12] to obtain the thermokinetic course of the processes under investigation.

3. Results and Discussion

The results of chemical analysis and of calorimetric measurements are summarized in Table I. Preparation of clathrate samples containing methanol or acetone as the

Table I. Guest composition and enthalpy of clathration in the systems: [Ni(NCS)$_2$(4-methylpyridine)$_4$] · y(4-methylpyridine) · x(methanol) and [Ni(NCS)$_2$(4-methylpyridine)$_4$]·y(4-methylpyridine)·x(acetone)

Content of the guest (mole/mole of the host)		Clathration enthalpy (kJ/mol)	
		Experimental	Calculated[a]
4-MePy	methanol		
0.13 + 0.04	2.01 ± 0.1	14.47 ± 0.2	14.47
0.23 + 0.06	1.66 ± 0.1	14.66 ± 0.2	14.98
0.29 + 0.04	1.41 ± 0.1	15.05 ± 0.1	15.06
4-MePy	acetone		
0.33 + 0.03	0.25 ± 0.05	6.35 ± 0.03	6.34
0.42 + 0.03	0.16 ± 0.05	6.92 ± 0.2	6.52
0.52 + 0.02	0.21 ± 0.05	8.11 ± 0.2	8.19

[a] cf. Equation [1] and corresponding text.

only guest, without any admixture of 4-MePy, was apparently impossible. The solubility of the host [Ni(NCS)$_2$(4-MePy)$_4$] complex in methanolic or acetone solutions is of the order of $1-5 \times 10^{-2}$ mol/L. If not stabilized with an excess of the free 4-MePy ligand the solutions partly decompose with the passage of time, producing some less soluble three-amine [9] solid complex or even diamine products and, in the liquid phase, some excess of the free ligand is formed. In other words, the solutions which are at equilibrium with the solid clathrate contain some excess of 4-methylpyridine which itself may be clathrated by the porous β-[Ni(NCS)$_2$(4-MePy)$_4$] phase.

Since aromatic 4-MePy is usually clathrated in preference to the aliphatic solvent this process cannot be neglected in the case studied, even if the concentration of the free 4-MePy is much lower than that of the solvent. Thus, in order to derive enthalpies of clathration of the solvents studied, liquids with three different concentrations of MePy were used in each system, so that the enthalpies could be derived through extrapolation to zero concentration of MePy. The content of methanol (in moles per mole of the host) divided by two plus the content of 4-MePy is, within the limits of analytical error, equal to unity. The chemical composition of methanol clathrates obtained at different 4-MePy concentrations suggest a simple competition mechanism: two methanol molecules may substitute one 4-MePy molecule. If the enthalpy of clathration of the mixtures may be represented by the formula:

$$H = H_S y_S + H_{MePy} Y_{MePy} \quad (1)$$

where H_S and H_{MePy} stand for the partial molar enthalpy of clathration of solvent and MePy, respectively, and y_S and y_{MePy} denote their molar contents in the solid, then the respective partial molar quantities may be derived from the data given in Table I through a fitting procedure. For the methanol/4-MePy guest system the best fit corresponds to $H_{methanol} = -(5.6 \pm 0.2)$ kJ/mol and $H_{MePy} = -(24.7 \pm 1.1)$ kJ/mol although, because of the low content of MePy in the clathrate, errors in determination of the partial molar enthalpies are rather large.

The enthalpy of clathration of 4-MePy by the host from liquid 4-MePy (-20.1 kJ/mol [13]) is close to the experimental value given above. The enthalpy of mixing in the 4-MePy/methanol system does not exceed -1 kJ/mol [14] and thus, in view of the large error limits cited above, the conclusion is that the measured enthalpy of clathration of 4-MePy from methanolic solutions is comparable to that measured for the uptake from liquid 4-MePy [13].

The partial molar enthalpy of clathration of methanol given above is low, reflecting the hydrophobic nature of the cavities in the β-[Ni(NCS)$_2$(4-MePy)$_4$] 'organic zeolite'. It is usually assumed that in physical, nonspecific three-dimensional 'absorption' processes (e.g. in zeolites) the heat effects accompanying uptake of a guest from the gas phase is twice its heat of liquefaction. Thus, for methanol the expected value (absorption from a gas phase) is about -70.5 kJ/mol and about -32 kJ/mol for clathration from liquid methanol (the heat of evaporation is 35.25 kJ/mol, the heat of phase transformation of the host may be estimated as being 3.6 kJ/mol [3]). The experimental value, which is lower than that expected, may suggest that there is no hydrogen bonding between the adjacent guest molecules in the solid clathrate; the last result being in good accordance with the X-ray structure of the methanol clathrate [15]. The fitting procedure for the acetone/4-MePy guest system produced somewhat better data for 4-MePy; the partial molar enthalpies of clathration being $H_{\text{acetone}} = -(9.8 \pm 0.6)$ kJ/mol and $H_{\text{MePy}} = -(11.8 \pm 0.3)$ kJ/mol.

The enthalpy of clathration of 4-MePy in this system is about half of the relevant value found in the methanol/4-MePy guest system. In order to explain this difference we recall the data on composition of the acetone/4-MePy clathrates (cf. Table I). The total (acetone + MePy) guest/host molar ratio for the samples under discussion ranges from 0.58 ± 0.08 to 0.73 ± 0.07, which is closer to 0.5 than to unity. From X-ray studies [15] it is known that in the β-[Ni(NCS)$_2$(4-MePy)$_4$] phase cavities are interconnected to form a three-dimensional structure of pores. The number of interconnections is 1/2 the number of cavities and, according to de Gil and Kerr [16], the interconnecting spaces may also be considered 'cavities'. If we assume the acetone molecules locate preferentially in those cavities (call them 'type 2'), the resulting guest (acetone)/host ratio is 0.5, when no cavity is left empty. From numerous studies on the stoichiometry and structure of the [Ni(NCS)$_2$(4-MePy)$_4$] clathrates it may safely be assumed that aromatic molecules, like 4-MePy, cannot occupy the type 2 cavities and steric considerations suggest that simultaneous occupancy of the cavities of type 1 and 2 is improbable. We would then conclude that the partial molar enthalpies of clathration of acetone and 4-MePy from their liquid mixtures correspond, respectively, to inclusion of the acetone molecules in the cavities of type 2 and to inclusion of the 4-MePy molecules in the cavities of type 1; the latter process being sterically hindered by the presence of acetone in the adjacent cavities of type 2.

The thermokinetic course of the processes, as illustrated in Figure 3 shows no particular features. From the $W(t)$ curves reported in Figure 3 it may be seen that clathration is completed in one-step processes lasting about 5 (acetone/MePy) to 9 (methanol/MePy) minutes. The duration of the processes is comparable to that observed in clathration of aromatic hydrocarbons from liquid phases [2, 3]. A significant difference is that clathration of the solvents occurs in one step instead of

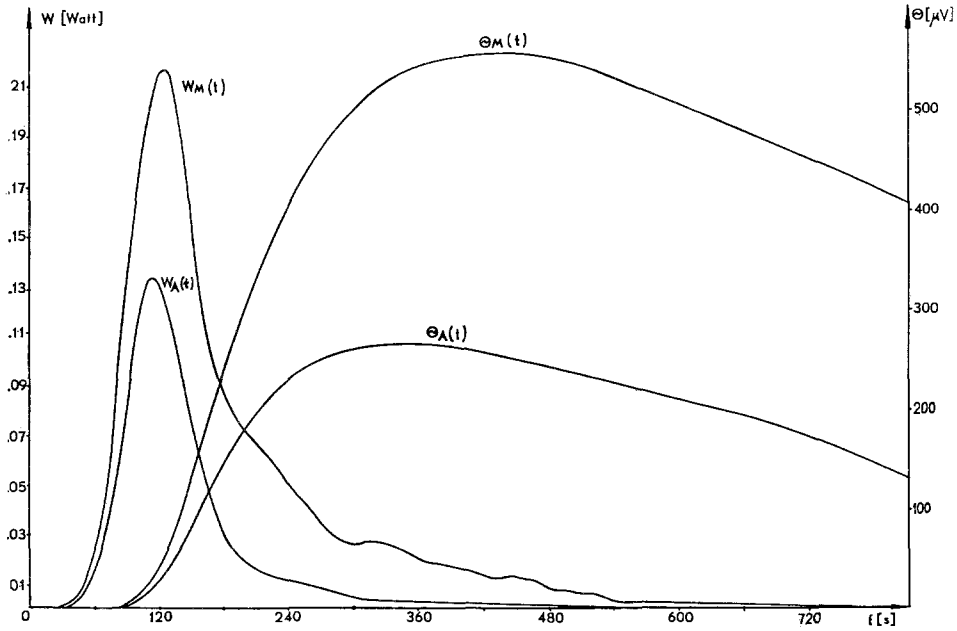

Fig. 3. The change of temperature during clathration of the MePy/methanol guest system ($\theta_M(t)$) and the Mepy/acetone system ($\theta_A(t)$) and the corresponding curves of thermal power ($W_M(t)$ and $W_A(t)$) calculated by using an *n-body* model [11].

two, as observed for benzene derivatives. This difference may perhaps be attributed to higher diffusivities of the solvent molecules in the clathrate solid phase compared to that of aromatic hydrocarbons.

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