ELSEVIER

Thermochimica Acta 311 (1998) 163–171

thermochimica acta

# Thermophysical and structural properties of crystalline solvates of tetraphenylporphyrin and their zinc, copper and cadmium metallo-complexes

German L. Perlovich[ab], Wojciech Zielenkiewicz[a,*], Zbigniew Kaszkur[a], Eva Utzig[a], Oleg A. Golubchikov[b]

[a] *Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/55, 01-224 Warsaw, Poland*
[b] *Institute of Non-Aqueous Solution Chemistry, Russian Academy of Sciences, 153045 Ivanovo, Russian Federation*

Received 25 July 1997; received in revised form 21 November 1997; accepted 2 December 1997

## Abstract

The results of a thermochemical and structural investigation of the process of desolvation of crystalline solvates of tetraphenylporphyrin $H_2$TPP with *o*-, *m*-xylene; zinc(II) tetraphenylporphyrin ZnTPP with benzene, toluene, *o*-, *m*-, *p*-xylene; cadmium(II) tetraphenylporphyrin CdTPP and copper(II) tetraphenylporphyrin CuTPP with *o*-, *m*-xylene are reported. Thermogravimetry and differential scanning calorimetry were used to determine the stoichiometry of crystalline solvates, the energy of activation and the heat effect of the desolvation process. The lattice parameters of the unsolvated crystalline CdTPP, ZnTPP and crystalline solvates of ZnTPP with *p*-xylene and CuTPP with *m*-xylene were determined using the X-ray powder diffraction method and the algorithm of Ito. The stoichiometry 1:1 for crystalline solvates [ZnTPP+(*p*-xylene)$_1$] and [CuTPP+(*m*-xylene)$_1$] was observed. The values of free volume per solvent molecules $V^{\text{free}}$ defined as the difference between volume of unit cell of crystalline solvate and the sum of the volume of a unit cell of unsolvated phase of an investigated compound and Van der Waals volume of solvent molecules were calculated. The packing coefficients $K_{\text{chan}}$ of the solvent molecules located in channels of the porphyrin matrix were also calculated. For ZnTPP crystalline solvates, we found the correlations between heat of desolvation and free volume per guest molecules of unit cell, as well as between the coefficient of channel packing and the temperature for which the half-lifetime of desolvation phase is equal to 60 min. A linear kinetic compensation effect for the crystalline solvates studied was found.

*Keywords:* Coefficient of packing; Crystalline solvate; Desolvation; Porphyrin sponges; Tetraphenylporphyrin; Tetraphenylporphyrin metallo-complexes; Thermal behaviour; X-ray

## 1. Introduction

Porphyrins are cyclic aromatic polyamines based on a macrocycle skeleton containing 16 atoms. The interest in this type of compound arises from their unique molecular structure. Investigations of structural properties of porphyrin sponges have advanced appreciably in recent years [1–4], as a result of advanced developed techniques available of growing organic crystals with programmable lattice architecture. The crystalline solvates contain three-dimensional channels occupied by solvent molecules (Fig. 1). Sizes of

---

*Corresponding author. Fax: 48 22 6325 276.

*PII* S0040-6031(97)00472-3

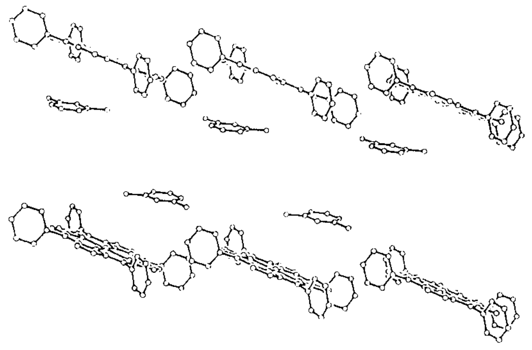

Fig. 1. A section parallel of the b and c axes for porphyrin sponges [1–4].

the channels may vary depending on the parameters of the crystal growing process and the geometry of guest molecules (the topological structure of porphyrin matrix does not change). Observation of the desolvation process suggests the possibility of removing a definite number of solvent molecules from the channels and therefore to control stoichiometry and the packing density of the channels as well as orientation of the guest molecules in the channels. The objective of this work is to find correlations between energetic and structural properties which characterize the evolution of selected crystalline phases. Presented further are the results of systematic thermophysical and structural investigations undertaken on the crystalline solvates based on tetraphenylporphyrin and its zinc(II), cadmium(II), and copper(II) metallo-complexes. The work is a continuation of our previous study [9] enlarging our knowledge by investigations of new groups of crystalline solvates.

## 2. Materials and methods

The free-base tetraphenylporphyrin $H_2TPP$ and four-coordinate metallo-complexes tetraphenylporphyrin MTPP (where M=Cu, Zn and Cd) were synthesized according to known methods [5,6]. All the compounds were thoroughly purified by repeated preparative chromatography (using a mixture of chloroform–benzene) and repeated recrystallization procedures. The final stages of purification were effected by carefully controlled sublimation techniques using a flow of inert gas ($N_2$) [7]. The absorption spectra of these substances were found to conform to the literature data.

Benzene, toluene, *o*-, *m*-, *p*-xylene (Fluka) were dried by boiling with anhydrous $CaCl_2$ for 3 h. These solvents were twice distilled and stored in a protected (moisture-free) container.

All crystalline solvates were grown by slow evaporation of saturated solutions of the compounds followed by drying at room temperature. We did not succeed in preparing the crystalline solvates of $H_2TPP$ from benzene, toluene and *p*-xylene solutions. Nevertheless, the X-ray data for $[H_2TPP+(p\text{-xylene})_1]$ are reported in the literature [1]. We believe that this phase is stable in saturated solution but in an air atmosphere at 298 K it quickly decomposes to the unsolvated state. Crystalline solvates CdTPP obtained from solution were very unstable and therefore the TG measurements were performed immediately after the preparation.

X-Ray measurements were made using the Rigaku–Denki powder diffractometer, $CuK_\alpha$ radiation ($\lambda$=1.5418), and Bragg–Brentano geometry. The powder diffraction pattern was scanned in steps of 0.05° ($2\theta$) up to 50° and a fixed counting time (10 s) was employed. The calculation of the unit cell parameters and the identification of reflection planes were performed using the Ito algorithm [8].

The following parameters were calculated: the change of the unit cell volume of the crystalline solvate during process of desolvation $\Delta V$; the free volume per guest molecules $V^{\text{free}}$; coefficients of crystalline solvate packing $K_{\text{cryst}}$; and coefficients of packing of guest molecules in channels of porphyrin matrix $K_{\text{chan}}$.

The free volume per solvent molecules $V^{\text{free}}$ defined as a difference between the volume of the unit cell of the crystalline solvate $V(Z[\text{MTPP}+(\text{solvent})_n])$ and the sum of the volume of unit cell of the unsolvated phase $V(Z[\text{MTPP}])$ of the compound and the Van der Waals volume of the solvent $V_{\text{solvent}}$ located in the channels of porphyrin matrix were calculated according to the relations (1)–(2):

$$[\text{MTPP} + (\text{solvent})_n] \rightarrow [\text{MTPP}] + n\,\text{solvent} \tag{1}$$

$$\Delta V = V(Z[\text{MTPP}+(\text{solvent})_n]) - V(Z[\text{MTPP}])$$

$$V^{\text{free}} = \Delta V - ZnV_{\text{solvent}} \tag{2}$$

where $Z$ is the number of structure units of crystalline solvate in a unit cell; $n$ is the number of molecules of a solvent.

The packing coefficient of crystalline solvate was calculated according to the relation:

$$K_{\mathrm{cryst}} = (Z(nV_{\mathrm{solvent}} + V_{\mathrm{host}}))/ V(Z[\mathrm{MTPP} + (\mathrm{solvent})_n]) \quad (3)$$

where $V_{\mathrm{host}}$ is the Van der Waals volume of porphyrin molecule.

The packing coefficient of a channel was calculated according to the relation:

$$K_{\mathrm{chan}} = (ZnV_{\mathrm{solvent}})/\Delta V \quad (4)$$

The thermal properties of crystalline compounds were investigated in the range 298–623 K using a Du Pont Thermal Analysis System 2100, equipped with DSC 910 and TG 951 cells. The DSC device was calibrated using an indium sample and the TG cell was calibrated using of calcium oxalate monohydrate as described previously [9]. The relative error in thermal measurements was 1%. The DSC runs were performed at a scan rate of $10\ \mathrm{K\ min^{-1}}$ in an atmosphere of flowing dry argon ($100\ \mathrm{ml\ min^{-1}}$) using open standard aluminium sample pans. On the basis of the TG curves obtained for various heating rates (0.5, 1, 2, 5, 10 and $20\ \mathrm{K\ min^{-1}}$), the activation energy of the thermal processes $E_a$, the frequency or pre-exponential factor $A$, and the temperature, for which half-lifetime $t_{1/2}$, of desolvation phase is equal to 60 min, were calculated according to the model described in [10,11]:

$$\mathrm{d}\alpha/\mathrm{d}t = f(\alpha)[A\exp(-E_a/RT)] \quad (5)$$

where $\alpha$ is the fractional extent of reaction.

Assume, that $A, f(\alpha)$ and $E$ are independent of $T$ and that $A$ and $E$ are independent of $\alpha$.

The TG Decomposition Kinetics Data Analysis Program, Version 4.0 Du Pont Analyst 2000/2100, was applied for these calculations.

In this work we do not attempt to describe the desolvation kinetic of the crystalline solvates using more complicated models. These problems will be an object of our subsequent investigations.

## 3. Results and discussion

The results of thermogravimetric and DSC investigations are given in Tables 1–3. The enthalpy effects of the desolvation process noted on the DSC curves are endothermic.

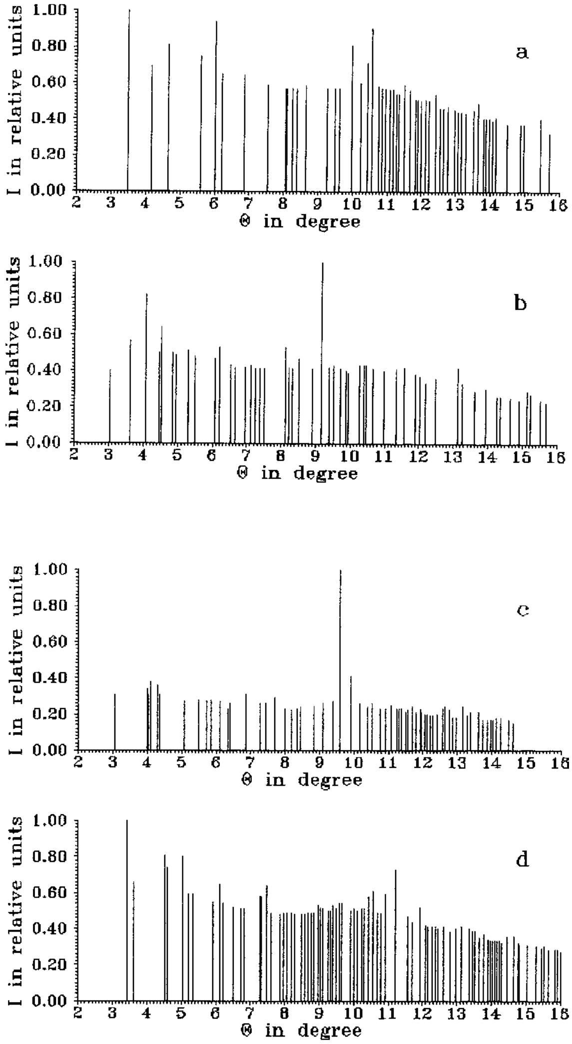

Fig. 2. The powder X-ray diffraction diagrams obtained for [ZnTPP] (a); [ZnTPP+($p$-xylene)$_1$] (b); [CuTPP+($m$-xylene)$_1$] (c) [CdTPP] (d).

The X-ray data for unsolvated phases of [ZnTPP], [CdTPP] and for crystalline solvates [ZnTPP+($p$-xylene)$_1$], [CuTPP+($m$-xylene)$_1$] were measured by powder diffraction. Fig. 2 shows the X-ray diagrams obtained for the compounds investigated. The results of identification of the reflection planes of the first 20 peaks are given in Tables 4. Table 5 reviews the unit cells parameters of the crystalline phases. The X-ray

Table 1
The results of the thermogravimetric experiments for the reaction of desolvation at different heating rates, ($\beta$ in K min$^{-1}$). The temperatures of start, $T_s$ in K, and finish, $T_f$ in K; the stoichiometry of crystalline solvate (host:guest), S

| $\beta$ | ZnTPP | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Benzene | | Toluene | | *m*-xylene | | *o*-xylene | | *p*-xylene | |
| | $T_s$ | $T_f$ | $T_s$ | $T_f$ | $T_s$ | $T_f$ | $T_s$ | $T_f$ | $T_s$ | $T_f$ |
| 0.5 | — | — | 305.3 | 332.6 | 317.6 | 350.1 | 318.6 | 363.2 | — | — |
| 1 | 310.3 | 357.8 | 307.0 | 345.5 | 320.3 | 355.8 | 320.1 | 378.2 | 345.9 | 408.8 |
| 2 | 314.0 | 368.7 | 309.7 | 351.2 | 324.8 | 359.0 | 325.8 | 396.8 | 351.1 | 415.1 |
| 5 | 314.8 | 373.8 | 311.2 | 360.7 | 328.9 | 368.1 | 327.4 | 408.3 | 367.7 | 429.6 |
| 10 | 324.7 | 383.8 | 313.2 | 372.7 | 331.3 | 377.5 | 331.8 | 414.4 | 370.9 | 441.9 |
| 20 | 324.7 | 393.4 | 314.2 | 385.4 | 336.9 | 395.1 | 333.2 | 431.7 | 382.2 | 458.1 |
| S | 1:2 | | 1:2 | | 1:2 | | 1:2 | | 1:1 | |

| | $H_2$TPP | | | | CdTPP | | | |
|---|---|---|---|---|---|---|---|---|
| | *m*-xylene | | *o*-xylene | | *m*-xylene | | *o*-xylene | |
| | $T_s$ | $T_f$ | $T_s$ | $T_f$ | $T_s$ | $T_f$ | $T_s$ | $T_f$ |
| 0.5 | — | — | 297.4 | 325.5 | 296.2 | 311.6 | — | — |
| 1 | 317.9 | 366.4 | 297.9 | 358.8 | 296.2 | 315.2 | 296.2 | 327.6 |
| 2 | 325.7 | 370.3 | 298.5 | 365.9 | 296.2 | 320.7 | 296.2 | 336.9 |
| 5 | 329.7 | 374.3 | 299.0 | 375.0 | 296.2 | 333.0 | 296.4 | 342.7 |
| 10 | 337.3 | 380.9 | 299.2 | 387.0 | 297.2 | 343.3 | 296.5 | 366.2 |
| 20 | 336.4 | 330.0 | 299.7 | 397.4 | 297.5 | 368.6 | 297.2 | 373.7 |
| S | 1:2 | | 1:2 | | 1:2 | | | 1:2 |

Table 2
The results of the thermogravimetric experiments for the reaction of desolvation at different heating rates, ($\beta$ in K min$^{-1}$). The temperatures of start, $T_s$ in K, and finish, $T_f$ in K; $\Delta_m$ in %; AML – the average mass losses (%); the stoichiometry of reaction, SR; the stoichiometry of crystalline solvate (host:guest), S

| $\beta$ | CuTPP+(*m*-xylene) | | | | CuTPP+(*o*-xylene) | | | |
|---|---|---|---|---|---|---|---|---|
| | First stage | | Second stage | | First stage | | Second stage | |
| | $T_s/T_f$ | $\Delta_m$ | $T_s/T_f$ | $\Delta_m$ | $T_s/T_f$ | $\Delta_m$ | $T_s/T_f$ | $\Delta_m$ |
| 1 | 322.9/355.7 | 8.1 | 355.4/452.4 | 4.7 | — | — | — | — |
| 2 | 327.9/361.9 | 8.1 | 363.3/452.0 | 4.8 | 303.2/438.8 | 18.1 | 438.8/503.2 | 2.9 |
| 5 | 329.8/365.1 | 7.9 | 364.7/453.2 | 4.9 | 303.2/446.2 | 18.2 | 446.2/522.2 | 3.1 |
| 10 | 330.8/369.7 | 7.9 | 370.2/514.2 | 5.1 | 303.2/473.2 | 18.3 | 473.2/540.2 | 3.0 |
| 20 | 336.0/379.9 | 8.3 | 378.9/559.2 | 5.1 | — | — | — | — |
| AML | | 8.1 | | 4.9 | | 18.2 | | 3.0 |
| SR | (5:5)→(5:2) | | (5:2)→(5:0) | | (20:20)→(20:3) | | (20:3)→(20:0) | |
| S | 1:1 | | | | 1:2 | | | |

literature data for the crystalline phases studied by us [1–4,12,13,15,18] (Table 6) and the data obtained here for the unknown phases were used for calculations of the $\Delta V$, $V^{\text{free}}$, $K_{\text{cryst}}$ and $K_{\text{chan}}$ values (Table 7).

The thermogravimetric and DSC data indicate that crystalline solvates ZnTPP with benzene, toluene, *o*-, *m*-xylene have stoichiometry (1:2), similar to those observed in the case of crystalline solvates $H_2$TPP, CdTPP with *o*-, *m*-xylene. This is in good agreement with the data obtained by X-ray investigations [1–4]. The process of desolvation of these compounds occurs in one stage with loss of all solvent molecules from the lattice:

Table 3
The activation energy, $E_a$ in kJ mol$^{-1}$; heat effect, $Q$ in kJ mol$^{-1}$; pre-exponential factor, $A=10^{\nu}$ in min$^{-1}$, of desolvation process; the temperature, $t_{1/2}$ in K, for which half-lifetime of desolvation phase is equal 60 min

| Crystalline solvates | $E_a$ | | $Q$ [a] | | $\nu$ | | $t_{1/2}$ | | $M$ [b] |
|---|---|---|---|---|---|---|---|---|---|
| | First | Second | First | Second | First | Second | First | Second | |
| ZnTPP+(benzene)$_2$ | 120±1 | — | 77.2 | — | 17.3 | — | 326 | — | 834.31 |
| ZnTPP+(toluene)$_2$ | 80±2 | — | 127 | — | 12.0 | — | 308 | — | 862.37 |
| ZnTPP+(*m*-xylene)$_2$ | 117±1 | — | 145 | — | 17.0 | — | 324 | — | 890.43 |
| ZnTPP+(*o*-xylene)$_2$ | 104±1 | — | 120 | — | 14.4 | — | 333 | — | 890.43 |
| ZnTPP+(*p*-xylene)$_1$ | 86.0±0.5 | — | 72.1 | — | 10.5 | — | 326 | — | 784.27 |
| H$_2$TPP+(*m*-xylene)$_2$ | 108±1 | — | 113.4 | — | 15.5 | — | 325 | — | 827.02 |
| H$_2$TPP+(*o*-xylene)$_2$ | 59±1 | — | 55.5 | — | 8.7 | — | 289 | — | 827.02 |
| CdTPP+(*m*-xylene)$_2$ | 91±3 | — | 71.0 | — | 15.0 | — | 285 | — | 937.46 |
| CdTPP+(*o*-xylene)$_2$ | 65±3 | — | 61.6 | — | 10.0 | — | 284 | — | 937.46 |
| CuTPP+(benzene)$_1$ [c] | 79±1 | 102±1 | 7.6 | 2.9 | 10.0 | 10.2 | 337 | 436 | 754.39 |
| CuTPP+(*m*-xylene)$_1$ | 182±2 | 68.0±0.5 | 33.6 | 6.4 | 27.0 | 7.8 | 331 | 364 | 782.45 |
| CuTPP+(*o*-xylene)$_2$ | 49±1 | 100±1 | 5.4 | 7.2 | 6.0 | 10.1 | 323 | 435 | 782.45 |

[a] The relative error in thermal measurements was 1%.
[b] Molecular mass of crystalline solvate.
[c] Ref. [9].

$$[\mathrm{MTPP} + (\mathrm{solvent})_2] \rightarrow [\mathrm{MTPP}] + 2\,\mathrm{solvent}$$

From Table 1 it follows, that ZnTPP forms numerous groups of crystalline solvates, having different solvent molecules and the same stoichiometry: [ZnTPP+(solvent)$_2$] where the solvent is benzene, toluene, *o*-, *m*-xylene. Therefore we have attempted to analyse the influence of the nature of guest molecules on the thermal behaviour of the desolvation process for this group of the compounds.

The value of $Q$ is a summarized characteristic of all heat effects occurring during desolvation. A volume of unit cell is very sensitive to all kinds of interactions of molecules in a crystal. We have attempted to find a correlation between $Q$ and $V^{\mathrm{free}}$ for [ZnTPP+(solvent)$_2$] (Fig. 3). From Fig. 3, we conclude that an increase of $V^{\mathrm{free}}$ leads to an increase of $Q$. Simultaneously it is known that the value $V^{\mathrm{free}}$ for crystalline solvates of analogous architecture is related, mainly with topology of the guest molecule and the geometrical conjugation of guest–guest and guest–host in a channel of porphyrin matrix [16]. Presumably for crystalline solvates [ZnTPP+(solvent)$_2$], the heat effect of desolvation is connected with the act of free volume activation in the crystalline lattice.

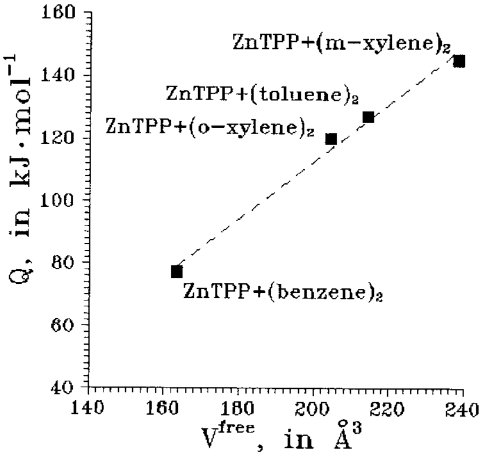

Fig. 3. The dependence of a heat effect of desolvation process, $Q$, versus a free volume per solvent molecules in an unit cell, $V^{\mathrm{free}}$, for the crystalline solvates by based ZnTPP.

The dependence of the temperature $t_{1/2}$ for which the half-lifetime for desolvation of the phase is equal to 60 min, versus the packing coefficient of channel $K_{\mathrm{chan}}$ is presented in Fig. 4. The thermal stability of the studied [ZnTPP+(solvent)$_2$] crystalline system increases with increase of the $K_{\mathrm{chan}}$. For example, the crystal ZnTPP with *o*-xylene is more thermally stable ($K_{\mathrm{chan}}$=0.698 and $t_{1/2}$=333 K), whereas ZnTPP with toluene is one of less stable ($K_{\mathrm{chan}}$=0.655 and $t_{1/2}$=308 K).

Table 4
The experimental, $(d/n)_e$ in Å, and theoretical, $(d/n)_t$ in Å, values of distance between planes of reflection; the intensity, *I* in relative units, and the indexes, (hkl), for first 20 reflections

| No. | $(d/n)_e$ | $(d/n)_t$ | *I* | (hkl) | $(d/n)_e$ | $(d/n)_t$ | *I* | (hkl) |
|---|---|---|---|---|---|---|---|---|
| CuTPP+(*m*-Xylene)$_1$ | | | | | CdTPP | | | |
| 1 | 14.49±0.15 | 14.49 | 0.31 | (100) | 12.94±0.15 | 12.94 | 1.00 | (100) |
| 2 | 11.06±0.15 | 11.06 | 0.34 | (010) | 12.20±0.15 | 12.20 | 0.66 | (010) |
| 3 | 10.92±0.15 | 10.93 | 0.31 | $(1\bar{1}0)$ | 9.77±0.08 | 9.77 | 0.81 | (001) |
| 4 | 10.79±0.15 | 10.79 | 0.38 | (001) | 9.61±0.08 | 9.59 | 0.74 | $(1\bar{1}0)$ |
| 5 | 10.31±0.15 | 10.31 | 0.36 | $(01\bar{1})$ | 8.79±0.08 | 8.80 | 0.80 | $(01\bar{1})$ |
| 6 | 10.11±0.15 | 10.07 | 0.31 | $(10\bar{1})$ | 8.50±0.08 | 8.52 | 0.59 | $(10\bar{1})$ |
| 7 | 8.70±0.08 | 8.74 | 0.27 | $(1\bar{1}1)$ | 8.31±0.08 | 8.30 | 0.59 | (110) |
| 8 | 8.03±0.08 | 8.10 | 0.28 | $(11\bar{1})$ | 7.48±0.08 | 7.45 | 0.55 | $(11\bar{1})$ |
| 9 | 7.73±0.08 | 7.71 | 0.27 | (101) | 7.22±0.08 | 7.23 | 0.65 | (101) |
| 10 | 7.56±0.08 | 7.56 | 0.28 | (110) | 7.11±0.08 | 7.12 | 0.54 | $(1\bar{1}1)$ |
| 11 | 7.22±0.08 | 7.25 | 0.27 | (200) | 6.81±0.08 | 6.82 | 0.52 | (011) |
| 12 | 6.99±0.08 | 6.96 | 0.23 | $(20\bar{1})$ | 6.57±0.08 | 6.59 | 0.51 | $(\bar{1}11)$ |
| 13 | 6.89±0.08 | 6.93 | 0.26 | $(\bar{1}11)$ | 6.49±0.08 | 6.47 | 0.51 | (200) |
| 14 | 6.44±0.08 | 6.44 | 0.31 | (011) | 6.095±0.02 | 6.095 | 0.58 | (020) |
| 15 | 6.09±0.08 | 6.08 | 0.26 | $(2\bar{1}1)$ | 6.09±0.02 | 6.09 | 0.58 | $(2\bar{1}0)$ |
| 16 | 5.94±0.08 | 5.94 | 0.26 | $(01\bar{2})(1\bar{2}0)$ | 5.93±0.02 | 5.89 | 0.64 | $(02\bar{1})(20\bar{1})$ |
| 17 | 5.75±0.05 | 5.76 | 0.29 | $(21\bar{1})(11\bar{2})$ | 5.82±0.02 | 5.84 | 0.49 | $(1\bar{2}0)$ |
| 18 | 5.53±0.02 | 5.53 | 0.23 | $(020)(10\bar{2})$ | 5.57±0.02 | 5.59 | 0.49 | (111) |
| 19 | 5.41±0.02 | 5.40 | 0.22 | $(020)(2\bar{2}1)$ | 5.49±0.02 | 5.44 | 0.49 | $(1\bar{2}1)$ |
| 20 | 5.33±0.02 | 5.35 | 0.23 | $(1\bar{1}2)$ | 5.40±0.02 | 5.40 | 0.49 | (210) |
| Zn(TPP)+*p*-Xylene)$_1$ | | | | | ZnTPP | | | |
| 1 | 14.59±0.15 | 14.59 | 0.40 | (100) | 12.73±0.15 | 12.73 | 1.00 | (100)(010) |
| 2 | 12.27±0.15 | 12.27 | 0.57 | (010) | 10.62±0.15 | 10.68 | 0.69 | $(1\bar{1}0)$ |
| 3 | 10.90±0.15 | 10.90 | 0.82 | (001) | 9.50±0.08 | 9.50 | 0.81 | (001) |
| 4 | 9.94±0.08 | 9.91 | 0.50 | $(1\bar{1}0)$ | 7.90±0.08 | 7.91 | 0.75 | $(110)(01\bar{1})(10\bar{1})$ |
| 5 | 9.79±0.08 | 9.79 | 0.64 | $(01\bar{1})$ | 7.35±0.08 | 7.35 | 0.94 | (011)(101) |
| 6 | 9.10±0.08 | 9.14 | 0.50 | $(10\bar{1})$ | 7.13±0.08 | 7.10 | 0.65 | $(1\bar{1}1)(\bar{1}11)$ |
| 7 | 8.96±0.08 | 8.94 | 0.49 | (110) | 6.44±0.08 | 6.50 | 0.64 | $(1\bar{2}0)(2\bar{1}0)$ |
| 8 | 8.34±0.08 | 8.37 | 0.51 | (101) | 5.86±0.05 | 5.82 | 0.59 | (111) |
| 9 | 8.05±0.08 | 8.12 | 0.48 | $(11\bar{1})$ | 5.50±0.05 | 5.48 | 0.57 | $(02\bar{1})(20\bar{1})$ |
| 10 | 7.28±0.08 | 7.30 | 0.47 | (200) | 5.47±0.05 | 5.46 | 0.57 | $(1\bar{2}1)(\bar{2}11)$ |
| 11 | 7.12±0.08 | 7.13 | 0.53 | (011) | 5.37±0.05 | 5.34 | 0.57 | $(2\bar{2}0)$ |
| 12 | 6.76±0.08 | 6.73 | 0.43 | $(\bar{1}11)$ | 5.21±0.05 | 5.26 | 0.57 | $(2\bar{1}1)(\bar{1}21)$ |
| 13 | 6.64±0.08 | 6.58 | 0.42 | $(2\bar{1}0)$ | 5.12±0.02 | 5.11 | 0.59 | (021)(210)(201) |
| 14 | 6.37±0.08 | 6.34 | 0.42 | $(20\bar{1})$ | 4.77±0.02 | 4.75 | 0.57 | (002) |
| 15 | 6.22±0.08 | 6.23 | 0.43 | $(02\bar{1})$ | 4.68±0.02 | 4.69 | 0.57 | $(12\bar{1})(21\bar{1})$ |
| 16 | 6.11±0.02 | 6.12 | 0.41 | (020)(111) | 4.61±0.02 | 4.66 | 0.57 | $(2\bar{2}1)(\bar{2}21)$ |
| 17 | 6.00±0.02 | 6.00 | 0.41 | (210) | 4.45±0.02 | 4.43 | 0.81 | $(1\bar{3}0)(3\bar{1}0)$ |
| 18 | 5.90±0.02 | 5.88 | 0.41 | $(1\bar{2}0)$ | 4.34±0.02 | 4.34 | 0.60 | $(012)(102)(1\bar{1}2)$ |
| 19 | 5.45±0.02 | 5.45 | 0.53 | $(002)(120)(\bar{2}11)$ | 4.26±0.02 | 4.25 | 0.71 | $(11\bar{2})$ |
| 20 | 5.39±0.02 | 5.37 | 0.42 | $(11\bar{2})$ | 4.22±0.02 | 4.24 | 0.90 | (030)(300) |

For the TG and DSC investigations from a *p*-xylene solution, we were able to obtain only the crystalline solvate [ZnTPP+(*p*-xylene)$_1$] (Table 1). Nevertheless, in the literature [2] there are reported results for crystalline solvates of ZnTPP with *p*-xylene of different stoichiometry: [ZnTPP+(*p*-xylene)$_2$] and [ZnTPP$_2$+(*p*-xylene)$_1$]. The [ZnTPP+(*p*-xylene)$_2$] is thermodynamically unstable and can be obtained as a kinetic product by seeding a saturated solution with crystals of [ZnTPP+(*o*-xylene)$_2$]. The [ZnTPP$_2$+

Table 5
Lattice parameters [a] for investigated compounds calculated following Ito method

| Compounds | Å | | | deg | | | Vol Å$^3$ | $Z$ |
|---|---|---|---|---|---|---|---|---|
| | $a$ | $b$ | $c$ | $\alpha$ | $\beta$ | $\gamma$ | | |
| ZnTPP | 13.32 | 13.32 | 9.54 | 93 | 93 | 107 | 1615 | 2 |
| ZnTPP+($p$-xylene)$_1$ | 12.94 | 11.48 | 14.70 | 94 | 95 | 108 | 2067 | 2 |
| CuTPP[b] | 13.97 | 12.39 | 11.56 | 110 | 102 | 108 | 1673 | 2 |
| CuTPP+(benzene)$_1$ [b] | 18.03 | 16.94 | 15.10 | 90 | 90 | 115 | 4185 | 4 |
| CuTPP+($m$-xylene)$_1$ | 15.71 | 12.84 | 12.12 | 112 | 98 | 107 | 2087 | 2 |
| CdTPP | 13.20 | 12.68 | 10.20 | 104 | 98 | 96 | 1626 | 2 |

[a] Relative accuracy: $a$, $b$, $c$ – 1%; $\alpha$, $\beta$, $\gamma$ – 2%.
[b] Ref. [9].

Table 6
Lattice parameters for investigated compounds

| Compounds | Å | | | deg | | | Vol [a] Å$^3$ | $Z$ | Space group | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| | $a$ | $b$ | $c$ | $\alpha$ | $\beta$ | $\gamma$ | | | | |
| ZnTPP | 14.8 | 17.2 | 14.6 | 90 | 90 | 90 | 3716.6 | 4 | P2$_1$2$_1$2$_1$ | [12] |
| ZnTPP | 10.382 | 12.421 | 6.443 | 98.30 | 101.15 | 96.47 | 798.1 | 1 | P$\bar{1}$ | [13] |
| ZnTPP+(benzene)$_2$ | 18.386 | 15.819 | 10.867 | 90 | 137.87 | 90 | 2120 | 2 | P2$_1$/n | [4] |
| ZnTPP+(toluene)$_2$ | 11.349 | 11.404 | 10.502 | 110.48 | 103.87 | 107.65 | 2237 | 2 | P$\bar{1}$ | [18] |
| ZnTPP+(toluene)$_2$ | 18.212 | 15.229 | 10.430 | 90 | 134.23 | 90 | (2073) | 2 | P2$_1$/n | [4] |
| ZnTPP+($m$-xylene)$_2$ | 13.465 | 21.709 | 11.174 | 64.80 | 51.98 | 72.99 | 2326 | 2 | | [1] |
| ZnTPP+($o$-xylene)$_2$ | 13.677 | 21.975 | 10.975 | 66.94 | 49.16 | 72.97 | 2292 | 2 | | [1] |
| ZnTPP+($p$-xylene)$_2$ | 13.566 | 22.435 | 11.296 | 65.06 | 46.72 | 73.40 | 2269 | 2 | | [2] |
| H$_2$TPP | 6.44 | 10.42 | 12.41 | 96.06 | 99.14 | 101.12 | 801.9 | 1 | P$\bar{1}$ | [17] |
| H$_2$TPP+($m$-xylene)$_2$ | 13.632 | 19.389 | 12.020 | 54.87 | 63.11 | 70.97 | 2308 | 2 | | [1] |
| H$_2$TPP+($p$-xylene)$_1$ | 13.667 | 17.692 | 14.470 | 60.85 | 43.34 | 80.94 | 1981 | 2 | | [1] |
| CdTPP+($m$-xylene)$_2$ | 13.563 | 21.970 | 10.995 | 65.76 | 51.55 | 72.55 | 2335 | 2 | | [2] |
| CdTPP+($o$-xylene)$_2$ | 13.807 | 22.109 | 11.085 | 66.97 | 48.52 | 73.03 | 2330 | 2 | | [2] |
| CuTPP+($m$-xylene)$_2$ | 13.528 | 19.098 | 11.984 | 53.71 | 63.87 | 70.88 | (2231) | 2 | | [2] |

[a] A volume in parentheses indicates a low-temperature structure determination.

($p$-xylene)$_1$] is directly crystallized from a saturated solution. One molecule of $p$-xylene located in the channel of crystalline lattice [ZnTPP+($p$-xylene)$_1$] has $V^{\mathrm{free}}$ approximately 1.5 times greater than in crystalline solvate with stoichiometry (1:2). Probably, the $p$-xylene molecule in relation to its largest linear dimension is located in the channel lengthwise. Analogous behaviour was observed in the case of [H$_2$TPP+($p$-xylene)$_1$] described in [1].

The crystalline solvates based on CuTPP were prepared only for $o$-, $m$-xylene. Their stoichiometry was (1:2) and (1:1) respectively. The crystalline [CuTPP+(benzene)$_1$] has been studied by us earlier [9]. The kinetics of desolvation is very similar for this group of crystalline solvates: (a) the process occurs in two independent stages (Table 2); (b) these stages are separated one from another on the temperature scale. It allows characterization of each stage (Table 3). The process of desolvation can be presented as follows:

$$[\mathrm{CuTPP} + (m\text{-xylene})_1] \rightarrow [\mathrm{CuTPP}] + m\text{-xylene}$$

First stage: (5:5)→(5:2)
Second stage: (5:2)→(5:0)

$$[\mathrm{CuTPP} + (\mathrm{benzene})_1] \rightarrow [\mathrm{CuTPP}] + \mathrm{benzene}$$

First stage: (5:5)→(5:3)
Second stage: (5:3)→(5:0)

It can be seen, that for crystalline solvate with $m$-xylene, the major part of the solvent molecules leave the crystal lattice during the first stage of desolvation, whereas for [CuTPP+(benzene)$_1$], this occurs during the second stage.

Table 7
Unit cell volume of starting, $V_1$, and final, $V_2$, crystal structure and the volume loss during desolvation, $\Delta V$; free volume per guest molecules, $V^{\text{free}}$; packing coefficient of guest molecules in channels of porphyrin matrix, $K_{\text{chan}}$; packing coefficient of molecules in unit cell of crystalline solvate, $K_{\text{cryst}}$

| Reactions of desolvation | Å$^3$ | | | | $K_{\text{chan}}$ | $K_{\text{cryst}}$ |
|---|---|---|---|---|---|---|
| | $V_1$ | $V_2$ | $\Delta V$ | $V^{\text{free}}$ | | |
| [ZnTPP+(benzene)$_2$]→[ZnTPP] | 2120 [a] | 1615 [b] | 505 | 163 | 0.676 | 0.729 |
| [ZnTPP+(toluene)$_2$]→[ZnTPP] | 2237 [c] | 1615 [b] | 622 | 215 | 0.655 | 0.720 |
| [ZnTPP+(*m*-xylene)$_2$]→[ZnTPP] | 2326 [d] | 1615 [b] | 711 | 238 | 0.665 | 0.721 |
| [ZnTPP+(*o*-xylene)$_2$]→[ZnTPP] | 2292 [a] | 1615 [b] | 677 | 204 | 0.698 | 0.732 |
| [ZnTPP+(*p*-xylene)$_1$]→[ZnTPP] | 2067 [b] | 1615 [b] | 452 | 216 | 0.523 | 0.697 |
| [$H_2$TPP+(*m*-xylene)$_2$]→[H2TPP] | 2308 [d] | 1604 [g] | 704 | 231 | 0.672 | 0.707 |
| [CdTPP+(*m*-xylene)$_2$]→[CdTPP] | 2335 [e] | 1626 [b] | 709 | 236 | 0.667 | 0.719 |
| [CdTPP+(*o*-xylene)$_2$]→[CdTPP] | 2330 [e] | 1626 [b] | 704 | 231 | 0.672 | 0.721 |
| [CuTPP+(benzene)$_1$]→[CuTPP] | 2093 [f] | 1673 [f] | 420 | 249 | 0.407 | 0.656 |
| [CuTPP+(*m*-xylene)$_1$]→[CuTPP] | 2087 [b] | 1673 [f] | 414 | 178 | 0.571 | 0.689 |

[a] Ref. [4].
[b] This work.
[c] Ref. [18].
[d] Ref. [1].
[e] Ref. [2].
[f] Ref. [9].
[g] Ref. [17]

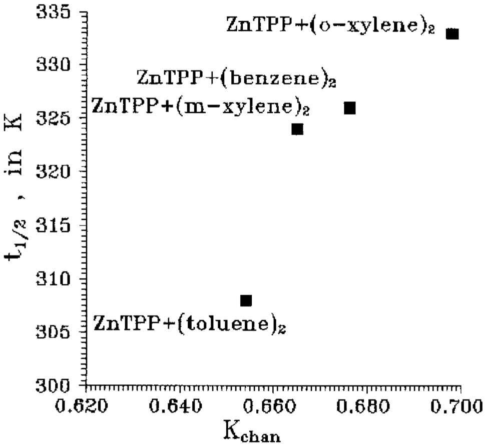

Fig. 4. The dependence of a temperature for which half-lifetime of desolvation phase equals to 60 min, $t_{1/2}$, versus a coefficient of packing guest molecules in channels of porphyrin matrix, $K_{\text{chan}}$, for the crystalline solvates by based ZnTPP.

An influence of the nature of porphyrin molecule (host) of crystalline solvate on energetics of the desolvation process was analysed as an example of crystal matrixes, which have the same solvate (guest) molecules but different host molecules: [MTPP+(*m*-xylene)$_2$] and [MTPP+(*o*-xylene)$_2$], where M=$H_2$; Zn; Cd; Cu.

We observed that for the crystalline solvates with similar values of the coefficient $K_{\text{chan}}$, there is a certain regularity in absolute values of heat of desolvation for different compounds with *o*-, *m*-xylene:

$$\begin{aligned}&[\text{ZnTPP} + (m\text{-xylene})_2]\\ &\quad > [\text{H}_2\text{TPP} + (m\text{-xylene})_2]\\ &\quad > [\text{CdTPP} + (m\text{-xylene})_2]\end{aligned}$$

$$\begin{aligned}&[\text{ZnTPP} + (o\text{-xylene})_2]\\ &\quad > [\text{CdTPP} + (o\text{-xylene})_2]\end{aligned}$$

The examination of the data in Table 3 indicates that the total heat effect of solvation $Q$ is different for different host molecules. We assumed that $Q$ depends on nonspecific guest–host interactions.

As a measure of these interactions, we have chosen values of partial molar volumes of the host $\overline{V}_2^0$ in benzene solutions. Then, the relation between $Q$ and $\overline{V}_2^0$ was derived (Fig. 5). It was found, that interactions with the solvent molecules are stronger in the case of ZnTPP molecules than for $H_2$TPP, CdTPP and CuTPP. It is very likely due to the more favorable redistribution of electron density between metal atom and the porphyrin macrocycle.

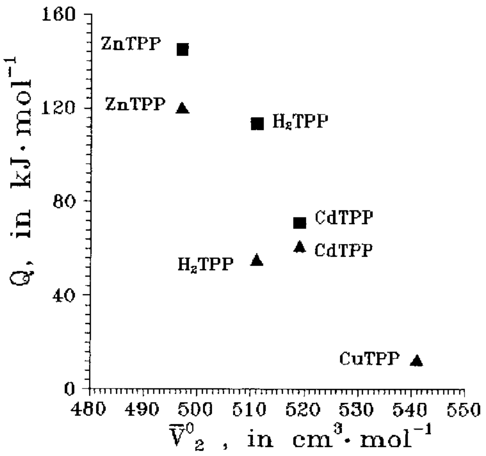

Fig. 5. The dependence of a heat effect of desolvation process, $Q$, versus a MTPP partial molar volume, $\overline{V}_2^0$, in benzene. ■ – [MTPP+($m$-xylene)$_2$]; ▲ – [MTPP+($o$-xylene)$_2$].

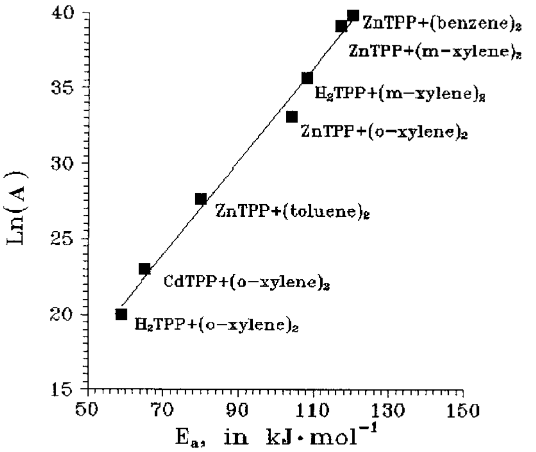

Fig. 6. The dependence of Ln($A$) versus an energy of activation, $E_a$, of a crystalline solvates [MTPP+(solvent)$_2$].

The dependences of Ln($A$) versus energy of activation of crystalline solvates: [MTPP+(solvent)$_2$], where M=H$_2$; Zn; Cd are presented in Fig. 6. As can be seen from these figures, the relation can be approximated as a straight line (linear kinetic compensation effect) [14]:

$$\mathrm{Ln}(A) = (2.2 \pm 1.3) + (0.31 \pm 0.01)E_a \qquad (6)$$

$$s = 0.814 \quad r = 0.995 \quad n = 7$$

The observed behaviour of the kinetical parameters suggests an identical mechanism of the desolvation process of the investigated crystalline solvates with stoichiometry 1:2.

## 4. Conclusion

The presented experimental results lead to the conclusion that the thermal stability of crystalline solvates [ZnTPP+(solvent)$_n$] is connected with such structural parameter as the packing coefficient $K_{\mathrm{chan}}$ of the solvent molecules located in the channels of the porphyrin matrix. The heat effect $Q$ of desolvation process of investigated compounds is sensitive to: (a) the value of free volume per solvent (guest) molecule $V^{\mathrm{free}}$; (b) the nature of the metal atom of MTPP (host); (c) the nature of the solvent (guest) molecule.

## References

[1] M.P. Byrn, C.I. Curtis, S.I. Khan, P.A. Sawin, R. Tsurumi, C.E. Strouse, J. Am. Chem. Soc. 112 (1990) 1865.
[2] M.P. Byrn, C.E. Strouse, J. Am. Chem. Soc. 113 (1991) 2501.
[3] M.P. Byrn, C.I. Curtis, I. Goldberg, Y. Hsion, S.I. Khan, P.A. Sawin, S.K. Tendick, C.E. Strouse, J. Am. Chem. Soc. 113 (1991) 6549.
[4] M.P. Byrn, C.I. Curtis, Y. Hsiou, S.I. Khan, P.A. Sawin, S.K. Tendick, A. Terzis, C.E. Strouse, J. Am. Chem. Soc. 115 (1993) 9480.
[5] A.D. Adler, F.R. Longo, J.D. Finarelli, J. Goldmacher, Y. Assour, L. Korsakoff, J. Org. Chem. 32 (1967) 476.
[6] J.A. Mullins, A.D. Adler, R.M. Hochstrasser, J. Chem. Phys. 43 (1965) 2548.
[7] O.A. Golubchikov, G.L. Perlovich, B.K. Naneishvili, Zh. Fiz. Khim. (Russian) 68 (1994) 2122.
[8] A.A. Rusakov, X-Ray of metals, Atomizdat, 1977, p. 207.
[9] G.L. Perlovich, W. Zielenkiewicz, E. Utzig, Z. Kaszkur, O.A. Golubchikov, Thermochim. Acta 279 (1996) 121.
[10] C.D. Doyle, J. Appl. Polym. Sci. 6 (1962) 639.
[11] J.H. Flynn, L.A. Wall, Polym. Lett. 4 (1966) 323.
[12] E.B. Fleischer, C.K. Miller, L.E. Webb, J. Am. Chem. Soc. 86 (1964) 2342.
[13] W.R. Scheidt, J.U. Mondal, C.W. Eigenbrot, A. Adler, L.J. Radonovich, J.L. Hoard, Inorg. Chem. 25 (1986) 795.
[14] J. Szako, J. Therm. Anal. 9 (1976) 101.
[15] W. Zielenkiewicz, G.L. Perlovich, G.E. Nikitina, A.S. Semeykin, J. Solution Chem. 25 (1996) 135.
[16] A. Gavezzotti, J. Am. Chem. Soc. 105 (1983) 5220.
[17] S.J. Silvers, A.J. Tulinsky, J. Am. Chem. Soc. 89 (1967) 3331.
[18] W.R. Scheidt, M.E. Kastner, K. Hatano, Inorg. Chem. 17 (1978) 706.