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THERMOCHEMICAL CHARACTERISTICS OF THE NEAR SURROUNDINGS OF TETRAPHENYLPORPHIN IN BENZENE, PYRIDINE AND CARBON TETRACHLORIDE *

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ABSTRACT

A new approach which allows the solvation surroundings of macrocyclic molecules to be simulated is proposed on the basis of thermogravimetric data. For the first time the compositions are determined of saturated solvates of tetraphenylporphin (H_2TPP) with benzene, pyridine and carbon tetrachloride: $H_2TPP \cdot 16C_6H_6$, $H_2TPP \cdot 18C_5H_5N$ and $H_2TPP \cdot 16CCl_4$. The energetic parameters of the interparticle interactions in the near solvation surroundings of H_2TPP are characterized. A method is proposed for the evaluation of the change in enthalpies of solvation of macrocyclic molecules based on the values of the heats of evaporation.

INTRODUCTION

No method has succeeded in determining the composition of the solvation surroundings of macrocyclic molecules in solution and a complete set of the energetic parameters of interparticle interactions within a solvate. The difficulties of resolving this task are connected with (a) the necessity of conducting the investigations mainly against the background of "inert" solvents, the influence of which on the solute needs verification (spectroscopic investigations of the processes of axial coordination), (b) unresolved questions of the standardization of thermodynamic values and the absence of data on the reactivities of the solution components (determination of the stability constants of complexes), (c) dealing with total thermodynamic values and physico-chemical characteristics (thermochemistry, volumetry) as well as with (d) insufficient sensitivity of the methods to solvate structures at available concentrations of substances in solution (structural methods). The last obstacle is partially overcome when studying crystalline solvate com-

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plexes separated from solution. In particular, such an approach was realized when studying the stereochemistry of the solvates of porphyrins by the Röntgenostructural method [1].

Tetraphenylporphin (H_2TPP) was chosen as the subject of the investigations. Its crystalline structure is characterized by parallel packing of preferentially planar macrocycles, considerable angles (61–63°) and slopes (9.1°) of the phenyl side groups [2] relative to the molecular plane. The closest distances between side and central groups of the neighbouring molecules are 3.6–3.8 Å. Such packing of the molecules results in the formation of cavities of substantial volume within the crystalline structure; this creates favourable steric conditions for the interstition of solvent particles and for their interaction with any fragment of the porphyrin molecule which is known to be involved in the solvation of metal porphyrins with toluene, chloroform, dichlorethane, etc. [1]. It has been established that the solvent molecules are situated symmetrically within an elementary cell of the crystalline structure with clear stoichiometry relative to porphyrin.

Proceeding from the data above it seems reasonable to study the solvation interactions of tetraphenylporphin as an example of crystallosolvates. The thermogravimetric method offers considerable possibilities in this respect.

EXPERIMENTAL

The investigations dealt with saturated solvates of H_2TPP with benzene, carbon tetrachloride and pyridine which were separated by crystallization from concentrated solutions and in equilibrium with it. All the substances were classified as "especially pure" and "spectrally pure". Purification, dehydration and quality control of the substances were conducted according to known techniques [3,4].

Thermogravimetric investigations were conducted on a derivatograph 1000 D (MOM, Hungary), which allowed, under the experimental conditions used, the simultaneous registration of the change in temperature of a sample with ±0.5 K precision (T curve), the change in mass of a sample with ±0.2 mg precision (TG curve), the relative value of the velocity of the change in mass with ±0.25 mm precision (DTG curve) and the differential thermal analysis curve (DTA curve). The temperature range investigated was 293–393 K. Electronic absorption spectra of the thermolysis products over the temperature interval noted showed no traces of the thermal destruction of porphyrin, and consequently the mass changes of the solvates noted are related only to removal of solvent. The velocity of heating of the samples under non-isothermal conditions was 0.6 K min^{-1}. To compare the results, investigations of the processes of solvate destruction in an isothermal regime were performed at 303 K.

The functional dependence of the rate of evaporation and the saturated vapour pressure of the solvent, which is sensitive to the differences in the states of the molecules evaporated [5,6], was chosen as the theoretical basis for the thermogravimetric studies on solutions and solvates

$$V_{\text{evap}} = \frac{\mathrm{d}w}{\mathrm{d}\tau} = \mathrm{d}_\kappa S \frac{N_{\mathrm{A}}}{(2\pi RTM)^{1/2}} \mathrm{P} \tag{1}$$

$$\ln P = -\frac{\Delta H_{\text{evap}}}{RT} + B \tag{2}$$

The combined resolution of eqns. (1) and (2) yields

$$\ln\left(\frac{\mathrm{d}w}{\mathrm{d}\tau} T^{1/2}\right) = -\frac{\Delta H_{\text{evap}}}{R}\frac{10^3}{T} + C \tag{3}$$

where N_{A} is Avogadro's number, M is the molar mass of the substance evaporated, R is the universal gas constant, S is the evaporation area, P is the saturated vapour pressure at temperature T of the sample, $\mathrm{d}w/\mathrm{d}\tau$ is the velocity of mass decrease (proportional to the deviation of DTG signal from the zero line), ΔH is the heat of evaporation, B and C are constants, and d_κ is the accommodation coefficient.

RESULTS AND DISCUSSION

The results of processing of the thermogravimetric data according to eqn. (3) for pure solvents (C_6H_6, C_5H_5N, CCl_4) and H_2TPP solutions (with concentration 3×10^{-3} mol kg^{-1} of solvent) are compiled in Table 1. The process of solvent evaporation over the temperature range noted has two

TABLE 1

Heats of evaporation of pure solvents and tetraphenylporphin solutions (ΔH_{evap})

System	T, K	ΔH_{evap}, kJ mol^{-1}	ΔH_{evap}, kJ mol^{-1} [7,8]
C_6H_6	298–313	33.5 ± 1.1	33.85
	> 321	31.2 ± 1.4	30.5
C_6H_6–H_2TPP	298–313	33.4 ± 2.0	
	> 314	30.7 ± 2.0	
C_5H_5N	298–323	40.3 ± 1.5	40.4
	> 325	35.4 ± 1.7	35.7
C_5H_5N–H_2TPP	298–314	40.1 ± 2.0	
	> 314	35.1 ± 0.9	
CCl_4	298–311	31.2 ± 1.6	32.5
	> 311	29.9 ± 1.8	29.9

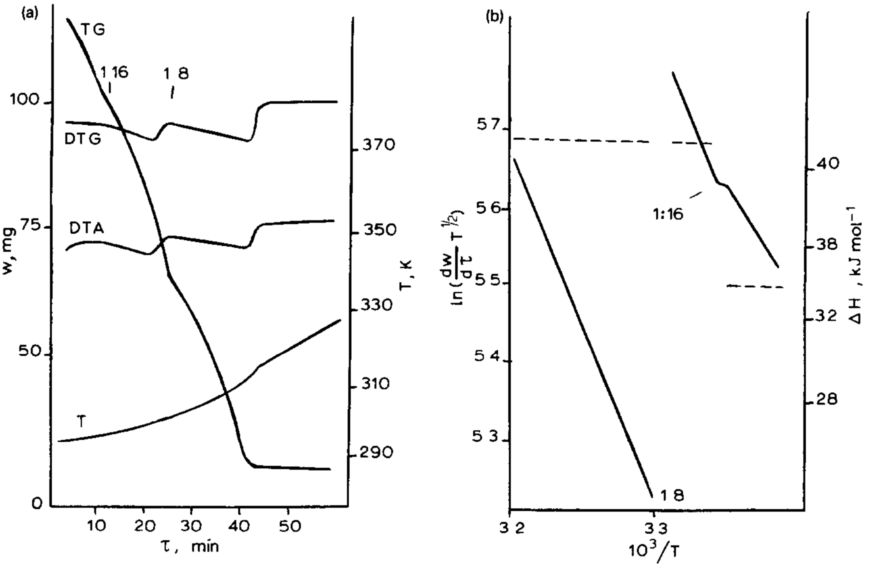

Fig. 1. (a) Derivatogram and (b) graphical resolution of eqn. (3) for a saturated H_2TPP–C_6H_6 solvate.

stages. When a certain temperature is achieved (313 K in benzene, 323 K in pyridine and 311 K in carbon tetrachloride), the heat of evaporation falls due to the increase in the kinetic energy of the solvent molecular motion. The calculation ΔH_{evap} values of pure solvents are reproduced at each stage and are within the error limits of the reference data [7,8], which testifies to correctness and efficiency of eqn. (3) and they coincide with the heats of evaporation from H_2TPP solutions. The latter fact allows us to conclude that the solute–solvent interaction extends only to the near solvation region of H_2TPP and does not influence noticeably the state of the rest of the solvent molecules.

Figure 1 shows the derivatogram and graphical processing of the thermogravimetric data for a saturated H_2TPP solvate in C_6H_6 which is in equilibrium with solution. One should expect that the bulk solvent molecules and those from the solvate surroundings of various structural fragments of porphyrin differ with respect to the energetic characteristics of the interparticle interactions. Hence, the process of removal of solvent molecules from the saturated crystallosolvate which is in equilibrium with solution (different structural fragments of solvates of a complex macrocyclic molecule included) will be multi-staged. The heats of evaporation calculated from eqn. (3) allow us to control the process of desolvation in a system and characterize the energy of solvent–solvent bonding (upon evaporation from a solvate) since ΔH_{evap} contains two contributions: major (overcoming of intermolecular interactions) and minor (work for expansion on transition into the gaseous state; up to 1–3 kJ mol^{-1}) [9]. The character of the DTG

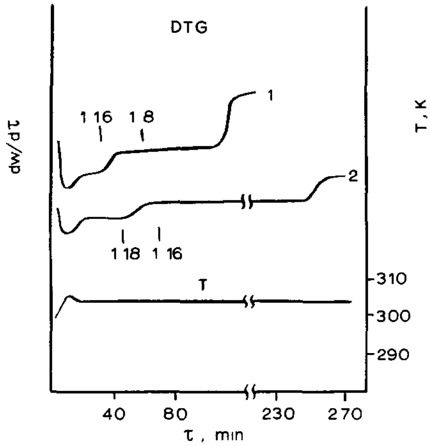

Fig. 2. Curves of the velocity of destruction of saturated solvates $H_2TPP-C_6H_6$ (1) and $H_2TPP-C_5H_5N$ (2) under isothermal conditions.

curve and the graphical dependence within the coordinates of eqn. (3) (Fig. 1) demonstrate clearly the possibility of distinguishing between separate stages of the process of solvate destruction. Mole ratios of porphyrin to solvent at the boundaries of the stages characterize the stoichiometric composition of the saturated solvates and the intermediate solvates formed during thermolysis. The solvate compositions determined under non-isothermal (Fig. 1) and isothermal (Fig. 2) conditions coincide. The values of the heats of evaporation shown by the dashed lines in Fig. 1(b) served as criteria for the identification of the process stages.

For the $H_2TPP-C_6H_6$ system, at the first stage (up to a composition 1 : 16) the ΔH_{evap} value is equal to the heat of evaporation of pure benzene (33.5 kJ mol^{-1}); this represents the removal of the molecules of solvent which are not bonded to the solvate. There are then two stages of destruction of the solvate $H_2TPP \cdot 16C_6H_6$ with the heat of evaporation of benzene molecules of 41.3 kJ mol^{-1}. One can suppose that the solvate $H_2TPP \cdot 16C_6H_6$ should be formed due to van der Waals and π–π interaction between the aromatic systems of eight C_6H_6 molecules and pyrrole fragments of macrocycles and eight C_6H_6 molecules and phenyl radicals of the H_2TPP molecule.

In the $H_2TPP-C_5H_5N$ system (Table 2), pyridine molecules not bonded with porphyrin and having $\Delta H_{evap} = 40.3$ kJ mol^{-1} are observed up to a composition of 1 : 18. Over the composition region from 1 : 16 to 1 : 0, 16 energetically equal pyridine molecules with $\Delta H_{evap} = 43.0$ kJ mol^{-1} are removed from the solvate in two stages. At compositions between 1 : 18 and 1 : 16, two C_5H_5N molecules with heats of evaporation of about 1.3 kJ mol^{-1} are removed. The absence of the temperature dependence of the velocity of the process and the extremely low ΔH_{evap} value testifies to the

TABLE 2

Heats of evaporation of solvent from solvates (ΔH_{evap}) and values of solvation enthalpy changes (ΔH_{solv})

System	Solvate composition porphyrin : solvent (moles)	ΔH_{evap}, kJ mol^{-1}	Contribution to solvation enthalpy, kJ mol^{-1}	ΔH_{solv} calculated data, kJ mol^{-1}	ΔH_{solv} [11], kJ mol^{-1}
$H_2TPP-C_6H_6$	>1:16	33.7±2.0			
	1:16–1:8	41.3±1.2	−62.4	−124.8±6.5	−125.7
	1:8–1:0	41.3±1.0	−62.4		
$H_2TPP-C_5H_5N$	>1:18	40.3±1.3			
	1:18–1:16	1.3±1.5			
	1:16–1:8	43.0±1.6	−60.8	−121.6±5.8	−127.1
	1:8–1:0	43.0±0.9	−60.8		
$H_2TPP-CCl_4$	>1:16	31.7±1.5			
	1:16–1:8	43.9±1.4	−101.6	−134.0±5.9	−129.6
	1:8–1:2	36.6±1.9	−32.4		
	1:2–1:0	1.3±1.3			

inhibition of diffusion and the sharp increase in the velocity of the process of solvate destruction at the stage given [10]. One can suppose that the appearance at this stage of the process of the desolvation of crystallosolvate should be related to the existence of the extremely weak interaction of two electron-donating molecules of C_5H_5N with the hydrogen atoms of the reaction centre of H_2TPP. In solution, against the background of the substantially higher energies of pyridine–pyridine interactions ($\Delta H_{evap} = 40.3$ kJ mol^{-1}), the weak interaction of the H_2TPP reaction centre with pyridine ($\Delta H_{evap} = 1.3$ kJ mol^{-1}) does not result in the formation of stable bonds and will not influence noticeably the properties of solutions. This is also confirmed by the thermochemical method [11].

In carbon tetrachloride, the existence was discovered of the $H_2TPP \cdot 16CCl_4$ solvate (Table 2) with eight ($\Delta H_{evap} = 43.9$ kJ mol^{-1}) and six ($\Delta H_{evap} = 36.6$ kJ mol^{-1}) CCl_4 molecules forming the main part of the comparatively firmly bonded solvate surroundings of the H_2TPP molecule (for pure CCl_4, $\Delta H_{evap} = 31.2$ kJ mol^{-1}). The solvate also includes two weakly bonded CCl_4 molecules ($\Delta H_{evap} = 1.3$ kJ mol^{-1}) which, due to sufficient polarity of the C–Cl bond, are oriented relative to the reaction centre and "blocked" inside the solvation shell. (During the process of destruction, they are the last to be removed at compositions of 1 : 2–1 : 0).

The values of the enthalpy changes on the solvation of porphyrins can be evaluated on the basis of the calculated values of the heats of evaporation. It is common knowledge that the enthalpy change during solvation is a summary thermodynamic characteristic [12] which includes the energetic contribution from solute–solvent interaction, energy for the destruction of solvent–solvent bonds during the formation of a solvate and also the energy of solute–solute interaction, although the latter can be neglected for a standard state of solution. Thus, the difference between the values of the heat of evaporation from solvate ($\Delta H^{\mathrm{S}}_{\mathrm{evap}}$), characterizing the energy of porphyrin–solvent bond per mole of solvent, and the heat of evaporation from pure solvent ($\Delta H^{\mathrm{O}}_{\mathrm{evap}}$), characterizing the energy of destruction of intermolecular bonds in one mole of solvent, recalculated for one mole of porphyrin, will characterize the enthalpy change during the solvation of porphyrin

$$\Delta H_{\mathrm{solv}} = \sum \left[n_{\iota} \left(\Delta H^{\mathrm{O}}_{\mathrm{evap}} - \Delta H^{\mathrm{S}}_{\mathrm{evap}} \right) \right] \tag{4}$$

where n_{ι} is the number of solvent molecules in a solvate with the same energetic characteristics and $\Delta H^{\mathrm{O}}_{\mathrm{evap}}$ and $\Delta H^{\mathrm{S}}_{\mathrm{evap}}$ are the heats of evaporation of solvent molecules from pure solvent and from solvate, respectively, determined at the same temperature.

The values of the heats of solvation calculated from eqn. (4) take the temperature dependence of ΔH_{solv} into account incompletely. The results of the calculations of the heats of solvation from eqn. (4) from the thermogravimetric data are represented in Table 2 and agree well with the thermochemical data [11]. This confirms the reliability and efficiency of the method proposed. Close values of the energetic characteristics of the interaction of the basic part of solvent molecules in the formation of solvates of tetraphenylporphin in benzene, pyridine and carbon tetrachloride testify to the preservation of the universal mechanism of solvation of H_2TPP by both non-polar and electron-donating solvents. The absence of strong inter-particle interactions and even distribution of the energetically equal solvent molecules (which is confirmed by the even solvation numbers) determines the symmetry of the H_2TPP solvation shell; this in its turn determines the absence of the shift in the position of the first absorption band in the electronic spectra (649–650 nm) of H_2TPP solutions in most solvents having no proton-donating properties [4]. Small differences in the energetics of porphyrin–solvent and solvent–solvent interactions, which were revealed as the result of the investigations (Tables 1 and 2), determine low solubility of porphyrins and do not influence noticeably the state of solvent molecules that are not included in the solvate.

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