ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 6, pp. 1268–1272. © Pleiades Publishing, Ltd., 2008.
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Thermodynamics of Formation of Porphyrin Sponge in the Etioporphyrin III–Methanol System

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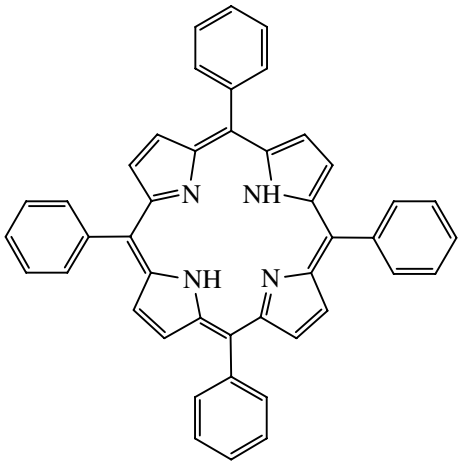
Received October 18, 2007

Abstract—The processes of dissolution and formation of porphyrin sponge in the etioporphyrin III (H_2P)–methanol system at 298–318 K were studied by methods of isothermal saturation and quantitative vacuum sublimation. Recrystallization of H_2P from methanol yields the porphyrin sponge $H_2P{\cdot}3CH_3OH$ as the equilibrium bottom phase. In the course of separation from the solution, the porphyrin sponge transforms into another polymorphous modification characterized by higher energy of stabilization with solvent molecules. In addition, a third desolvated phase, dissolving in methanol considerably more rapidly, is formed on the surface of air-dry $H_2P{\cdot}3CH_3OH$ crystals. The thermodynamic functions of the equilibrium between the porphyrin sponge and saturated H_2P solution were determined..

DOI: 10.1134/S1070363208060297

More than 200 crystal solvates of metal tetraphenylporphyrins, termed porphyrin sponges, were examined by the end of XX century by single crystal X-ray diffraction [1–6]. It was shown in these studies that *meso*-tetraphenylporphine (**I**) molecules are universal blocks for construction of clathrate crystal lattices.

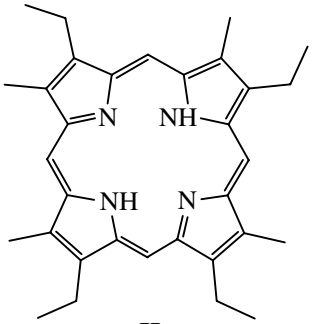


I

meso-Tetraphenylporphine

Rigid and highly symmetrical molecules of **I** cannot be efficiently packed in the three-dimensional space. Intercalation of solvent molecules into the porphyrin matrix allows more efficient crystal packing to be attained. The architecture of a porphyrin sponge corresponds to the layered planar packing of host molecules, penetrated by three-dimensional channels filled by guest molecules. Depending on the solvent, the energy of stabilization of the crystal lattice by guest molecules relative to the nonsolvated phase can reach tens kJ mol^{-1}. Porphyrin sponges are formed as an equilibrium bottom phase by simple recrystallization of porphyrins from guest solvents. Along with crystal solvates of metal tetraphenylporphyrins, crystal solvates of the free porphyrin ligand with m-xylene and benzaldehyde were obtained. This fact made us to cast a new glance on the results of numerous studies concerning thermodynamics of solution of porphyrins [7]. In our previous paper [8] we suggested and tested an approach to studying the composition and thermodynamics of formation of porphyrin sponges with guest solvents. We found that crystalline samples of I, recrystallized from chloroform and methanol, are crystal solvates $\mathbf{I}{\cdot}CH_3Cl$ and $\mathbf{I}{\cdot}3CH_3OH$. In this study we examined the kinetics of formation of porphyrin sponge in the etioporphyrin III–methanol system in the range 298–318 K by methods of isothermal saturation and quantitative vacuum sublimation.

In the first step, compound **II** isolated from chloroform was recrystallized from methanol.



II

Etioporphyrin III

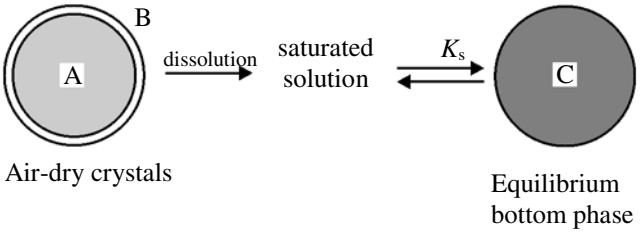


Fig. 1. Scheme of transformations of the porphyrin sponge **II**·3CH_3OH in methanol.

According to [9], the solubility of **II** in methanol K_s^{298} is 2.7×10^{-5} M. Because of low solubility of **II**, it was recrystallized using the Soxhlet apparatus at the boiling point of methanol (64.5°C). As in the case of **I**, initially (within the first 3 h) a small amount of the porphyrin was rapidly extracted, after which the dissolution drastically decelerated. This fact suggests that the samples of **II** are a porphyrin sponge stabilized by chloroform molecules [8, 10].

Air-dry samples of compound **II** precipitated from methanol were analyzed by quantitative vacuum sublimation. The weight loss observed, 15%, exactly corresponds to the crystal solvate composition **II**·3CH_3OH. This fact indicates that the formation of porphyrin sponges is a general phenomenon and is not a specific feature of the molecular structure of **I**. Molecules of **II** with a different, compared to **I**, system of substituents also form porphyrin sponges of similar composition, with three molecules of guest solvent per porphyrin molecule.

In the next step, we studied the dissolution and thermodynamics of formation of the crystal solvate **II**·3CH_3OH in methanol. Different weighed portions of **II**·3CH_3OH were introduced into a known volume of the solvent, and variation of the volumetric concentration of the porphyrin in time was monitored. Experiments performed at 288–318 K showed that air-dry crystals of **II**·3CH_3OH, as in the case of **I**·3CH_3OH [8, 10], consist of core–shell particles (Fig. 1).

The shell is the desolvated phase B of the dry porphyrin sponge, which formed after separation of the precipitate from the mother liquor by the loss of solvent molecules from the surface of the crystalline matrix **II**·3CH_3OH. After introducing air-dry crystals of **II**·3CH_3OH into methanol, the desolvated phase completely dissolves in 3 h, irrespective of the sample weight M_0 and temperature. The core of the porphyrin sponge **II**·3CH_3OH consists of the solvated phase A (the porphyrin sponge is impregnated with methanol). The crystal lattice of the solvated phase is stabilized by guest molecules. Therefore, its dissolution is kinetically hindered. Under the experimental conditions (5–6 h), it acts as virtually insoluble ballast, and the measured volumetric concentration of **II** is fully determined by an impurity of the desolvated phase B.

The material balance with respect to compound II in system (1) per liter of solution is given by Eq. (2), and the contents of the solvated and nonsolvated phases in the porphyrin sponge sample, by Eq. (3).

$$\mathbf{II}\cdot 3CH_3OH_{(pr)}–\mathbf{II}_{(sol)}–CH_3OH, \quad (1)$$

$$M_0 = M_{(pr)} + C, \quad (2)$$

$$M_0 = [A] + [B]. \quad (3)$$

Here M_0 is the total amount of substance **II** (mol) in the initial weighed portion of **II**·3CH_3OH per liter of solution, $M_{(pr)}$ is the amount of **II** (mol) in the precipitate per liter of solution, and C is the molar concentration of the solution.

The quantity [B] for air-dry crystals of **II**·3CH_3OH can be estimated from the dependence of the volumetric concentration of solutions C on the weight of the porphyrin sponge sample M_0. An example of such dependence is given in Table 1 and Fig. 2.

The criterion of the solution saturation with respect to the bottom phase is the condition [B] > K_s. The quantity K_s is the constant of heterogeneous equilibrium (4) and it numerically equal to the concentration of saturated solution of (**II**) over the precipitate of the porphyrin sponge.

$$\mathbf{II}_{(sol)} \overset{K_s}{\rightleftarrows} \mathbf{II}\cdot 3CH_3OH_{(pr)}. \quad (4)$$

Table 1. Distribution of compound **II** in system (1) after stirring for 4 h at 318 K

$M_0 \times 10^{-3}$, M	$M_{(pr)} \times 10^{-3}$, M	$C \times 10^{-5}$, M
1.523	1.443	0.796
2.664	2.649	1.470
3.804	3.787	1.770
5.708	5.688	2.050
7.610	7.589	2.120
8.751	8.729	2.170
9.658	9.636	2.170

Table 2. Thermodynamic functions of solution of the solvates **II**·3CH_3OH and **I**·3CH_3OH [8] in methanol

Porphyrin sponge	T, K	$K_s \times 10^5$, M	ΔG^0, kJ mol^{-1}	ΔH^0, kJ mol^{-1}	$T\Delta S^0$, J K^{-1} mol^{-1}
	298	2.07			
II·3CH_3OH	308	2.12	26.4±0.02	1.6±0.02	–24.8±0.02
	318	2.17			
	288	7.28			
I·3CH_3OH	298	7.38	29.3±0.1	1.0±0.1	–28.3±0.1
	308	7.46			
	318	7.55			

The constant K_s determined in system (1) at 318 K is 2.17×10^{-5} M, which is close to the value obtained in [9]. The relative content of the desolvated phase B is equal to the C/M_0 ratio at $C < 2.17$ M. According to the calculation, in air-dry crystals of **II**·3CH_3OH it does not exceed 0.5%. The experimental dependences of C on the stirring time, measured on condition that [B] > K_s, are shown in Fig. 3. When [B] exceeds K_s, a new equilibrium bottom phase C, differing from the initial solvated phase A, is formed in system (1). The dynamic equilibrium between a saturated solution of **II** and phase C is characterized by fairly fast exchange and is attained within 2 h. Process (4) is fully reversible. The values of K_s obtained in the course of heating and cooling the system fully coincide.

Experiments on the recrystallization of the solvate **II**·3CH_3OH in a Soxhlet apparatus showed that phase A in system (1) also slowly dissolves and participates in the formation of phase C. Complete recrystallization of phase A at the boiling point of methanol takes about three weeks. After the completion of this period, heterogeneous system (1) passes from the steady state to an equilibrium. Phase C exists only in contact with a

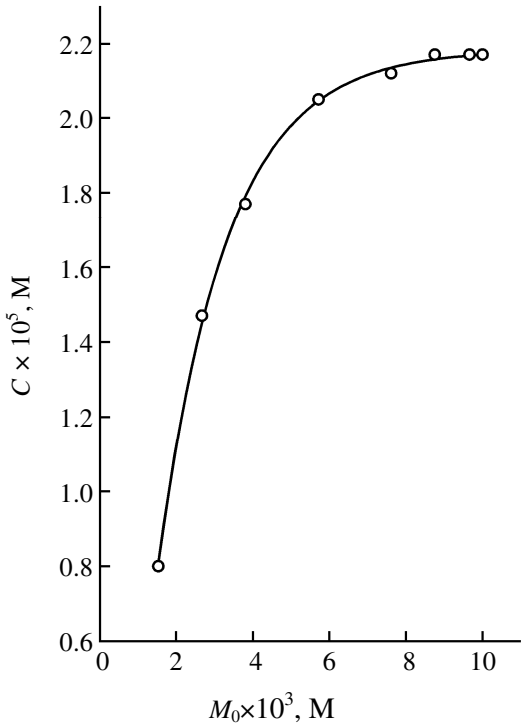


Fig. 2. Concentration of solutions of **II** as a function of the weight of the **II**·3CH_3OH sample in system (2). T 318 K, τ 4 h.

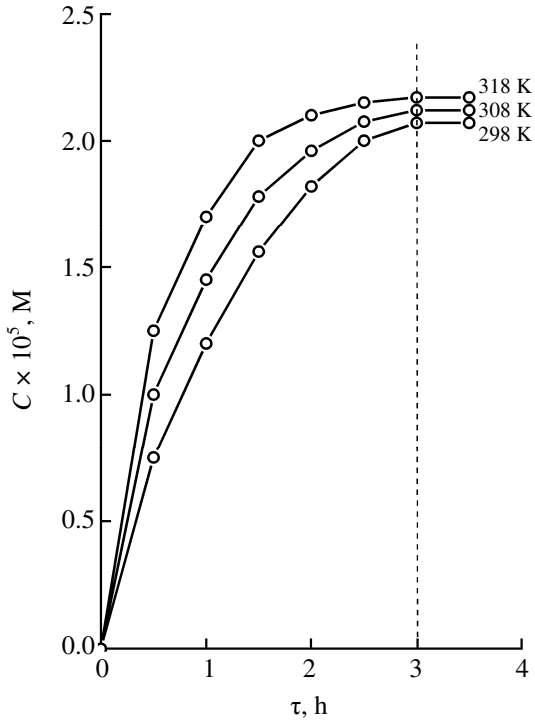


Fig. 3. Plots of C vs. τ in system (2) at M_0 8.751×10^{-3} M.

saturated methanol solution of **II**. In attempted separation from the solution, phase C transforms into A, on whose surface, in turn, phase B is formed. Phases A and C are two polymorphous modifications of which the first is characterized by the higher energy of the host–guest bond.

The values of K_s and the thermodynamic functions of solution of the solvate **II**·3CH_3OH in system (1), calculated by the van't Hoff isobar equation, are given in Table 2 together with the data obtained previously for **I**·3CH_3OH.

EXPERIMENTAL

Chemicals. Etioporphyrin III [11] was provided by Prof. A.S. Semeikin (Ivanovo State University of Chemical Technology) and was purified by chromatography on alumina (Brockmann grade II) using chloroform as eluent. The product was isolated by distilling the chloroform off on a water bath.

Methanol (chemically pure grade) was dried by distillation from magnesium methylate [12]. The residual moisture content of the distillate was determined by Fischer titration. In all the cases, it did not exceed 0.03%.

Procedure for quantitative vacuum sublimation. The methanol content of the porphyrin sponge was determined by quantitative vacuum sublimation in an installation shown in Fig. 4. A weighed portion of the porphyrin sponge was placed in the end part of cell *1*. The cell was connected to a vacuum line via stopcock *2*, and the internal volume was evacuated to a residual pressure of 10^{-4} mm Hg. Then tubular furnace *5* was switched on, and the temperature was gradually increased to 380 K. The sublimed porphyrin condensed on glass rings *3*. After the sublimation–condensation cycle was complete, the glass rings with the condensed porphyrin were removed from the cell and washed with benzene. The sublimate weight was determined spectrophotometrically from the optical density of the solution of the porphyrin in benzene, as the mean value from three replicate runs.

The stoichiometric composition of the porphyrin sponge was calculated by formula (5):

$$n = \frac{1000m(H_2AP \cdot nCH_3OH)}{Cmm(CH_3OH)V}. \qquad (5)$$

Here n is the stoichiometric content of CH_3OH molecules in the porphyrin sponge **II**·$n$$CH_3OH$;

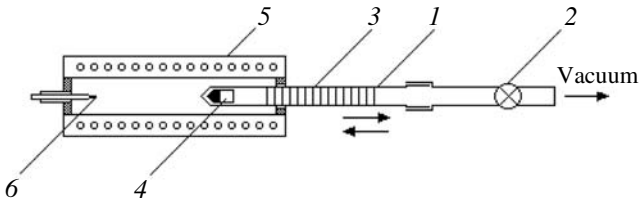


Fig. 4. Scheme of an installation for quantitative vacuum sublimation: (*1*) glass vacuum cell, (*2*) vacuum stopcock, (*3*) glass rings, (*4*) ampule with porphyrin sponge sample, (*5*) tubular furnace, and (*6*) thermocouple.

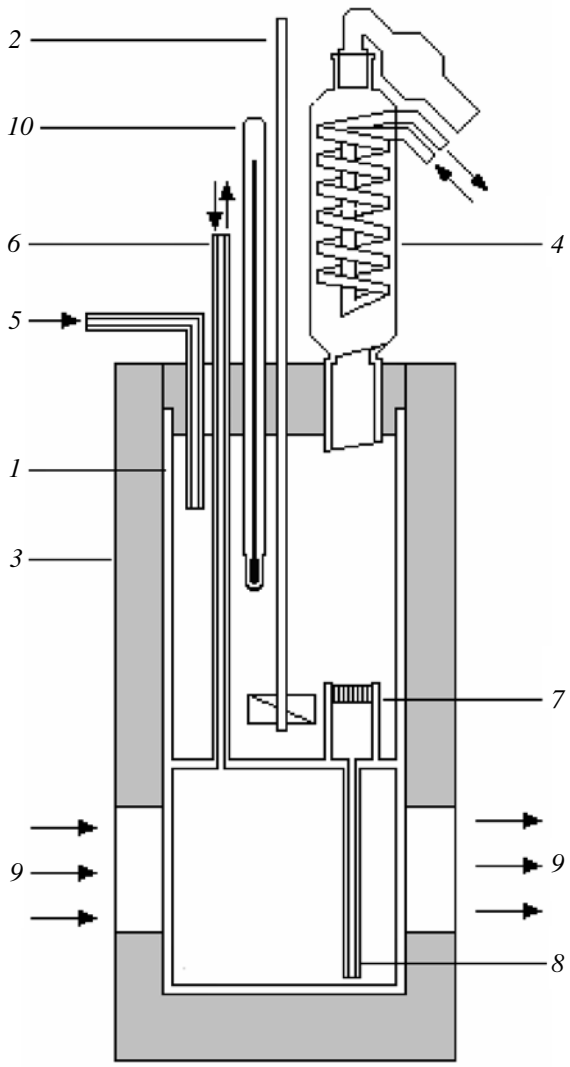


Fig. 5. Scheme of the measuring cell: (*1*) glass cell, (*2*) power-driven stirrer, (*3*) thermostat, (*4*) reflux condenser with a calcium chloride tube, (*5*) capillary for feeding dry nitrogen, (*6*) capillary for measuring pressure in the optical compartment of the cell, (*7*) glass frit, (*8*) filter capillary, (*9*) optical windows, and (*10*) mercury thermometer.

$m(H_2AP)$ and $mm(CH_3OH)$ the molecular weights of **II** and CH_3OH, g; $m(H_2AP{\cdot}nCH_3OH)O$ is the weight of the sample of crystalline $H_2AP{\cdot}nCH_3OH$, g; C is the molar concentration of the benzene solution of sublimed H_2AP; and V is the volume of the benzene solution of **II**.

Isothermal saturation procedure. The formation and transformations of the porphyrin sponge **II**·$3CH_3OH$ in methanol were studied by isothermal saturation method with spectrophotometric monitoring of the solution concentrations in the measuring cell shown in Fig. 5. The upper compartment of cell *1* was charged with 60 ml of methanol, stirrer *2* and thermostat *3* were switched on, and the supply of cold water through reflux condenser *4* and of dry inert gas through capillary *5* (to isolate the solution from the ambient atmosphere) were started. After the required temperature was attained in the lower optical compartment of the cell, rarefaction was created through capillary *6*, which led to filling of the optical compartment with the solution through filtering element *7*. The electronic absorption spectrum of the solvent was recorded in the range from 400 to 750 nm. Then, by applying a pressure, the solvent was transferred through capillary *8* to the upper compartment of the cell and a weighed portion of the solvate II·$3CH_3OH$ was added. At 30-min intervals, a part of the solution was filtered to the lower compartment and, after recording the electronic absorption spectrum, transferred back by applying a pressure. The concentrations of methanol solutions of **II**, measured at T 288 and 318 K, were converted to 298 K by Eq. (6):

$$C_{298\,K} = C_T \frac{A_{298\,K}}{A_T}, \quad (6)$$

where A is the optical density at the corresponding temperature.

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