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THERMOKINETIC STUDIES OF PORPHYRIN COMPLEXATION IN NON-AQUEOUS SOLUTIONS BY HEAT CONDUCTION MICROCALORIMETRY

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Abstract

Porphyrins are known as unique ligands forming some of the most stable complexes with various metal ions. In this work the thermokinetic investigations of complex formation of tetraphenylporphyrins with copper(II) acetate were carried out in two anhydrous organic solvents: acetic acid and DMF at 25°C. Measurements were performed in a heat conduction microcalorimeter [7] adapted for non-aqueous solvents. Total heat effects and thermokinetics were determined. The results were discussed together with spectrophotometric data.

Taking into account the high stability of metalloporphyrin complexes, the heat of their formation is rather small (in the case of acetic acid ΔQ=32.7±1.2 kJ mol^{-1}, for DMF ΔQ= 26.2±1.3 kJ mol^{-1}). Such result can suggest that: 1) the stability of complexes is influenced strongly by an entropy factor, 2) the complexation involves breaking of the NH-bond in the porphyrin coordination centre, accompanied by high consumption of energy.

Keywords: complexation, copper(II) complexes, tetraphenylporphyrin, thermokinetics

Introduction

Metalloporphyrins, which comprise important natural complexes such as chlorophyll, haem of the blood, and others, represent a vast specific group of intercomplex compounds. Porphyrins form some of the most stable complexes with all metals of the Periodic Table [1, 2]. Due to the fact that porphyrin molecules perform their biological and catalytic function only within metalloporphyrins, the investigation of the conditions and energetic and thermochemical characteristics of the complexation reactions of porphyrin is of great importance. This information is interesting in macrocyclic coordination chemistry as well as in the design of rational methods of synthesis of metalloporphyrins.

The main porphyrin functions are determined by the coordination properties of the porphyrin molecule and a metal. The central metal atom displaces two hy-

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drogen ions from the porphyrin ligand (Fig. 1) and finds itself practically in a symmetrical electrostatic field of four nitrogen atoms, with which it may form four equivalent or almost equivalent coordination donor–acceptor bonds. In this way complexes of 1:1 composition are formed with transition metal ions.

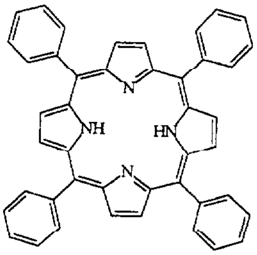

Fig. 1 Structural formula of tetraphenylporphyrin

The specific features of metalloporphyrins, as intercomplex compounds, are due not only to the tetradentate nature of the ligand, but also to its rigidity. The rigidity is determined by (i) the planar structure of the large ring of the porphyrin molecule, and (ii) the unique conjugation, which is due to the strong π-electron interaction over the macroring and (iii) the favourable structure of the coordination centre. The latter consists of four nitrogen atoms, on account of which most metal ions easily enter the space, coming into close contact with the nitrogen atoms.

Much attention has been given to the investigation of the complexation reactions of porphyrin with various metal salts by spectrophotometric methods [2–4]. They allowed to establish the regularities of porphyrin complexation in pure and mixed solvents and to determine reaction energetics, to establish the mechanism of formation of metalloporphyrins [2]. However, this method of investigation does not permit determination of the thermochemical characteristics of the reaction and to assess the total heat effect of metalloporphyrin complexation. Therefore, we have undertaken the thermokinetic investigation of the complex formation of tetraphenylporphyrins with copper(II) acetate in anhydrous organic solvents by means of a quasi-isothermal microcalorimetric method.

Experimental

The peculiarity of porphyrin is that these compounds are practically insoluble in water and have limited solubility in organic solvents. This fact allows to investigate porphyrins in the low concentration region only and requires sensitive instruments for following the formation of metalloporphyrins. No general method is available for the insertion of all metal ions. Anhydrous acetic acid and dimethylformamide (DMF) were applied as the most convenient media for metalloporphyrin complexation with transition metal ions [5].

Tetraphenylporphin (H_2TPP) was synthesized by the Treibs method [6] and was chromatographed twice on Al_2O_3 of the second degree of activity, with chloroform as the eluent, and it was recrystallized from a mixture of chloroform and hexane. Analytically pure copper(II) acetate ($Cu(OAc)_2$) was recrystallized from aqueous acetic acid and dehydrated at 140°C. Chemically pure acetic acid was dehydrated by boiling with a calculated quantity of acetic anhydride (for 20 h), and then distilled off. The residual water content, determined by Karl Fischer titration, was not greater than 0.02% in the solvent.

The calorimetric measurements were carried out in a heat conduction microcalorimeter with tantalum reaction vessel [7], modified for the studies of complexation reactions in non-aqueous solvents. The experiments were performed at 25°C.

In each experiment the defined volume of salt solution of concentration C_s was injected into the calorimetric vessel containing a known volume of porphyrin solution of concentration C_p. The calorimetric signal $\Theta(t)$ was recorded as a function of the time by means of the computerized data acquisition system. Each experiment was made at least in duplicate and repeatability was satisfactory. Total heat effects as a function of the time $Q(t)$, and the thermokinetic curves $W(t)=\mathrm{d}Q(t)/\mathrm{d}t$ were computed using a numerical optimization method. The resulting values of the heat changes ΔQ were corrected for the heats of dilution of the salt solution, determined in separate runs.

Spectroscopic investigations of the complexation were performed using a Specord M-400 spectrophotometer. The experiments were carried out in a hermetically sealed quartz vessel placed in a thermostatic chamber. The temperature was monitored over the course of the experiments with an accuracy of 0.05°C.

Results and discussion

Previous investigations of the formation kinetics of metalloporphyrins by spectrophotometric methods testify that the complexation reaction of tetraphenylporphyrin with copper(II) acetate in organic solvents may be written as

$$Cu(OAc)_2(Solv)_4+H_2TPP(Solv)_n \rightarrow CuTPP(Solv)_m+2HOAc+(n+4-m)Solv \quad (1)$$

Reaction (1) has simple stoichiometry and measurable reaction rate. Therefore this reaction is a convenient model for the investigation of the thermokinetics of porphyrin complexation.

As porphyrins have a powerful chromophore system, there are four visible bands in neutral solvents. Simple square planar chelates of porphyrins with divalent metal ions have two visible bands. Thus a metalloporphyrin formation produces a pronounced change in absorption electronic spectra. Therefore spectroscopic methods can be widely applied for the investigation of various processes with participation of porphyrins.

In acetic acid the tetraphenylporphyrin is specifically solvated on the coordination centre by two acetic acid molecules at the expense of $CH_3COOH\cdot\cdot\cdot N<$hydrogen bonding type. This solvatocomplex has characteristic absorption electronic spectra with intensive absorption maxima at 655 nm. Figure 2 shows the spectral change during the complexation reaction of porphyrin acetic acid. The gradual spectral change and the isosbestic points retained during the whole time of the reaction show that copper(II)-tetraphenylporphyrin complexes of 1:1 composition are formed.

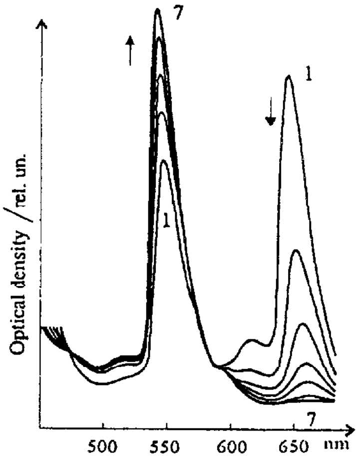

Fig. 2 Spectroscopic changes during the formation process of Cu-tetraphenylporphyrin in acetic acid at 25°C; τ=0 (1); τ=10 min (7)

In dimethylformamide H_2TPP does not form solvatocomplexes similar to those formed with acetic acid. However, the spectral changes during porphyrin complexation in DMF, similarly as in acetic acid, prove the formation of complexes with 1:1 composition.

Copper(II) acetate exists in non-aqueous solvents in monomer-dimer equilibrium in acetic acid [8] and DMF [9]:

$$2M(OAc)_2 \leftrightarrow M_2(OAc)_4 \qquad (2)$$

The order of reaction (1), being equal to one and a half (Table 2), can be explained on the assumption that the reaction of monomeric species of $Cu(Ac)_2$ with porphyrins is a rate determining step. The rate constant (k_v) of complexation involving monomeric species was calculated on the basis of the equilibrium data in the solvents [4, 9].

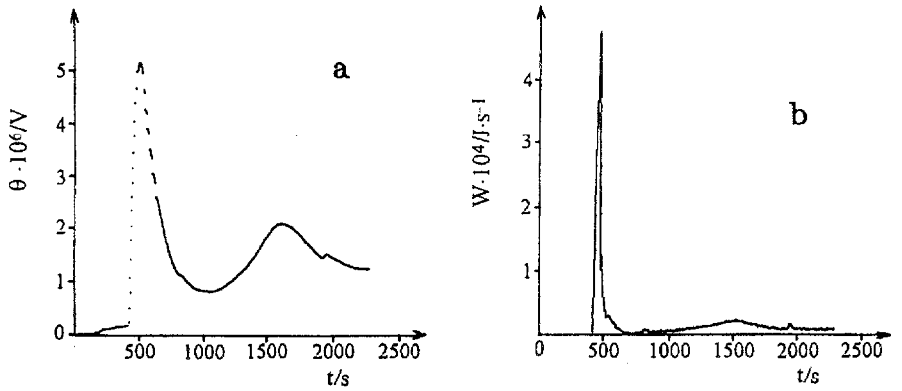

Fig. 3 Calorimetric results of tetraphenylporphyrin complexation with copper(II) acetate in acetic acid;
a – calorimetric signal $\Theta(t)$, b – thermokinetic course $W(t)$ reconstructed from $\Theta(t)$

The curves shown in Fig. 3a,b illustrate the results of calorimetric studies of Cu-tetraphenylporphyrin formation in acetic acid. Two separate peaks observed on the $\Theta(t)$ signal as well as on thermokinetic $W(t)$ runs indicate that this reaction is accompanied by two exothermal heat effects. The first peak is related to metallocomplex formation, and the second one to a slow crystallization of CuTPP from the solution. The latter peak increases with increasing concentration of H_2TPP. Its manifestation is conditioned by a lower solubility of metallocomplex in acetic acid in comparison with the solubility of H_2TPP. The effect of concentration of the reagents on the $W(t)$ courses as well as on the total heat of complex formation was studied (Table 1).

Table 1 Total heat effects of formation of Cu-tetraphenylporphyrin in anhydrous acetic acid at 25°C

$C_{H_2TPP}\cdot10^4$/	$C_{CuAc_2}\cdot10^4$/	ΔQ/	ΔH/
mol l^{-1}		mJ	kJ mol^{-1}
1.02	21.26	6.9	31.17
1.04	17.71	6.8	30.71
2.07	19.95	15.7	34.11
2.10	15.33	13.6	31.34
2.11	21.26	15.4	33.57
2.14	17.70	15.0	32.70
2.15	17.70	15.8	34.44
2.23	9.47	15.5	33.79

The thermokinetic course of formation of CuTPP in the second anhydrous solvent DMF, exhibits only one exothermal complexation effect. A comparison of the energetic quantities: ΔH, ΔE, ΔS as well as some kinetics parameters for the formation of CuTPP in the two solvents is given in Table 2.

Table 2 Energetic and kinetic quantities of formation of Cu-tetraphenylporphyrin in non-aqueous solvents at 25°C

Solvent	ΔH/ kJ mol^{-1}	Reaction order	Rate constant k_v/l s^{-1} mol^{-1}	ΔE/ kJ mol^{-1}	ΔS^*/ J mol^{-1} K^{-1}
Acetic acid	32.73±1.24	1.5	76.4±2	94.5±4.0	84
Dimethylformamide	26.25±1.32	1.5	0.20±0.01	88.3±4.0	36

In spite of the fact the metalloporphyrins belong to the most stable coordination compounds (stability constant ~10^{29}) [1], the total heat effect determined for the formation of Cu-tetraphenylporphyrin is low. This result suggests that: (i) the entropy factor plays an important role among the quantities determining the high stability of the complexes under study, (ii) the complexation involves breaking of a NH-bond in the porphyrin coordination centre, which requires a high energy.

Thus the parallel application of spectral and calorimetric methods has provided an interesting insight into the mechanism of complexation of metals by porphyrins.

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