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THERMOGRAVIMETRY OF π–π COMPLEXES OF ZINC(II) TETRA-*TERT*-BUTYLPHTHALOCYANINE WITH AROMATIC MOLECULES

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Physical-chemical characteristics of molecular complexes of Zn(II)tetra-*tert*-butylphthalocyanine (Zn(*tert*-Bu)$_4$Pc) with aromatic solvents were obtained. The results show that polarization parameters of the interacting molecules play an important role in stabilization of the phthalocyanine π–π complexes. Dispersion forces are the major factor governing the π–π complex formation of Zn(*tert*-Bu)$_4$Pc with aromatic molecules. The metallophthalocyanine may be applicable as efficient analytical reagent for separation of isomeric forms of aromatic molecules.

Keywords: π–π *interaction, molecular complexes, thermogavimetric analysis, zinc(II)phthalocyanine*

Introduction

π–π interactions are very important in biological systems. π–π interactions play a crucial role in controlling the crystal packing of organic molecules, in determining the conformation of nucleic acids and proteins [1] and stabilization of double helix structure of DNA [2] as well as geometry and energy of complex formation of drugs with DNA [3]. Moreover, this specific binding mode is widely spread in supramolecular [4] and analytical chemistry [5–7].

Metallophthalocyanines have extensive aromatic π–π system containing heteroatoms. Therefore they should form a priori π–π complexes with aromatic ligands. This fact is very important because some methods of synthesis of the metallophthalocyanines use high boiling solvents as media [8, 9]. An information about energy and thermal stability of the molecular phthalocyanine complexes with aromatic solvents allows to choose appropriate solvent because in the case of formation of stable π–π complexes of metallophthalocyanine with the solvent molecules, a yield of the product should increase.

The aim of the present work to study the physical-chemical characteristics (composition, temperature of decomposition and energy stability) of Zn(*tert*-Bu)$_4$Pc π–π complexes with some aromatic molecules having different nature, number and mutual arrangement of substitutes. Zn(*tert*-Bu)$_4$Pc is a typical coordinationally unsaturated metallophthalocyanine.

Experimental

Materials

Zinc(II) tetra-*tert*-butylphthalocyanine was synthesized and purified as described previously [10]. The purity of Zn(*tert*-Bu)$_4$Pc was checked according to electron absorption spectra in dimethylformamide which demonstrated good agreement with literature data [10]. The spectra were recorded on Specord M-40 spectrometer. Toluene, *o*-xylene, *p*-xylene, *tert*-butyl benzene, chlorobenzene, *o*-dichlorobenzene, nitrobenzene (high purity grade) were purified according to known procedures [11], treated by 4 Å molecular sieves and then distilled. The purity of the solvents was checked by chromatography. It was 99.98%. The content of water in the reagents was determined by Fisher method. It was not greater than 0.02% for all solvents used.

The crystallosolvates of Zn(*tert*-Bu)$_4$Pc with organic solvents were prepared by slow crystallization from saturated solutions at 298–300 K as for DSC and X-ray diffraction analysis.

Equipment and methods

Thermogravimetric measurements were made with thermoanalytical set [12] designed to record four curves: changing temperature *T*, changing mass of a heated sample with time (TG), rate of the mass change (DTG), and derivative thermal analysis (DTA) curve. Samples of the crystallosolvates of

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100–150 mg were placed in a platinum crucible and heated at a heating rate of 0.6°C min^{-1}.

The functional dependence of the vaporization rate and the pressure of the saturated vapor of a solvent, which are sensitive to differences in the state of molecules vaporized [13, 14], served as a theoretical basis for thermogravimetric analysis. At minimal heating rate assumption of quasi-equilibrium vaporization process is valid. Therefore, the Knudsen (1) and Clapeyron–Clausius (2) equations can be applied to the processes under study:

$$\frac{\mathrm{d}W}{\mathrm{d}\tau} = \alpha_{\mathrm{k}} S \frac{N_{\mathrm{A}}}{\sqrt{\pi RTM}} p \qquad (1)$$

$$\ln P = -\frac{\Delta_{\mathrm{evp}} H}{RT} + B \qquad (2)$$

where N_A is the Avogadro number, M is the molecular mass of vaporized substance, α_k is the accommodation coefficient, R is the universal gas constant, S is the vaporization area, p is the pressure of saturated vapor at the sample temperature T, $\mathrm{d}W/\mathrm{d}\tau$ is the mass loss rate which is proportional to the deviation of the DTG curve from the basis line, $\Delta_{evp}H$ is the change of the enthalpy of vaporization, B and C are the constants of integration. Simultaneous solution of Eqs (1) and (2) gives the following relation

$$\ln\left(\frac{\mathrm{d}W}{\mathrm{d}\tau} T^{1/2}\right) = -\frac{\Delta_{\mathrm{evp}} H}{R} \frac{10^3}{T} + C \qquad (3)$$

Equation (3) allows one to determine $\Delta_{evp}H$ values by mathematical processing of the DTG curves. Numerical DTG data were processed with an original program [12]. The error of indirect measurements was calculated by adding up its components according to the addition rules for random errors; in this study, their distribution laws were considered via entropy coefficients as recommended in [15].

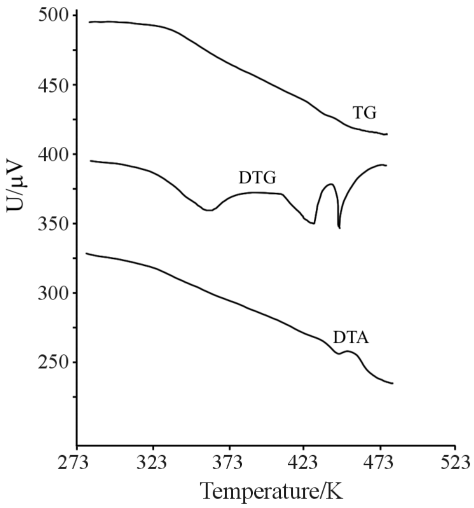

Fig. 1 TG, DTG and DTA curves of the crystallosolvate of Zn(*tert*-Bu)$_4$Pc with chlorobenzene

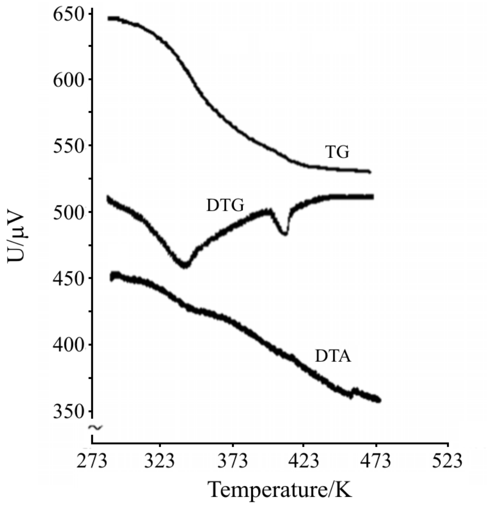

Fig. 2 TG, DTG and DTA curves of the crystallosolvate of Zn(*tert*-Zu)$_4$Pc with *tert*-butyl benzene

Results and discussion

Curves of the crystallosolvates of Zn(*tert*-Bu)$_4$Pc with all organic solvents under study are typical (Figs 1 and 2) and have several steps. Each step is characterized by a given temperature range, Zn(*tert*-Bu)$_4$Pc: solvent mole ratio, and the $\Delta_{evp}H$ value. It is known that $\Delta_{evp}H$ consists of two contributions: (*i*) the energies of solvent-solvent (evaporation of solvent molecules unbound with crystallosolvate) and solvent-solute interactions (evaporation of solvent from crystallosolvate); (*ii*) the work of expansion at transition of the solvent to the gas phase [13, 14]. The last contribution is negligible (1–3 kJ mol^{-1}). Hence, in the first approximation, the $\Delta_{evp}H$ values can be considered as characteristics of energy stability of molecular π–π complexes.

The first steps of the obtained curves are characterized by comparatively low temperatures and the values are very close to that for pure solvents [16]. This may be explained by removal of the solvent molecules bonded with Zn(*tert*-Bu)$_4$Pc due to universal interactions. The second steps at higher temperatures are characterized by a significantly greater $\Delta_{evp}H$ than for pure solvents. The specific molecular complexes are destroyed in these steps (Figs 1 and 2). The complexes have a definite stoichiometry and high energetic stability. It may be concluded that these are not inclusion complexes.

A comparison of the obtained results (Table 1) with literature data for Zn(*tert*-Bu)$_4$Pc – benzene [17] shows that an appearance of substitutes in small aromatic molecule promotes π–π complex formation. The energetic and thermal stability of Zn(*tert*-Bu)$_4$Pc π–π complexes increases in the following order:

benzene<toluene<*tert*-butyl benzene<
chlorobenzene<nitrobenzene

It is interesting to note that van der Waals volumes also increase in this order (Table 1). It is likely that substitutes in aromatic molecules hinder coplanar interaction with the phthalocyanine macrocycle. But this negative factor for π–π complex formation is compensated by rearrangement of electron density and increasing polarizable cability of the small aromatic molecules. An analogous conclusion about an effect of polarizable properties on π–π complex formation has been made elsewhere [18]. Probably, the higher energetic and thermal stability of Zn(*tert*-Bu)$_4$Pc π–π complexes with chlorobenzene and nitribenzene in comparison with alkyl derivatives of benzene is connected with electron-donating ability of CI and NO_2 substitutes. This results in a decrease of π-electronic density in the aromatic molecule and, hence, in π–π repulsion between the aromatic molecules in π–π complex.

Let us compare the data for the systems containing *tert*-butyl benzene and toluene. *Tert*-butyl and methyl substitutes promote +I effect. But *tert*-butyl substitute has a higher polarizable effect on aromatic molecule than CH_3 substitute. Moreover, large C_4H_9 substitute may cause a steric distortion of aromatic molecule. This leads to a decrease of π-electronic shielding and π–π repulsion at the complex formation with Zn(*tert*-Bu)$_4$Pc. It is likely that steric hindrance of the *tert*-butyl substitute causes energetic nonequivalence of *tert*-butyl benzene in Zn(*tert*-Bu)$_4$Pc·2(*tert*-butyl benzene) π–π complex.

The obtained data for the complexes of Zn(*tert*-Bu)$_4$Pc with xylenes, toluene, dichlorobenzene and chlorobenzene (Table 1) allow to conclude that an introduction of the second substitute (electron-donating or electron-accepting) into small aromatic molecule promotes the formation of more thermodynamically and energetically stable π–π complexes. This fact emphasizes the influence of electron and orientation polarization as well as dispersion interactions on stabilization of Zn(*tert*-Bu)$_4$Pc π–π complexes with the aromatic solvents.

The energetic stability of the complexes of Zn(*tert*-Bu)$_4$Pc with *o*-xylene is to be 1.5 times larger than that of the complexes with *p*-xylene. It may be connected with steric distortion of *p*-xylene molecule due to near located methyl substitutes resulting in a decrease of intermolecular π–π repulsion in Zn(*tert*-Bu)$_4$Pc·2(*o*-xylene) complex. It is interesting to note that the energetic stability of π–π complex of zinc(II)tetraphenylporphine with *o*-xylene is also significantly higher than that with *p*-xylene [19]. These data demonstrate a possibility of application of conformationally rigid macrocycles such as porphyrins and phthalocyanines to separation of isomeric aromatic molecules.

No correlation was found between the energetic stabilities of the complexes of Zn(*tert*-Bu)$_4$Pc with toluene, *p*- and *o*-xylenes and the π-donor properties of small aromatic molecules. According to literature data [20, 21], these properties increase in the following order: toluene<*p*-xylene<*o*-xylene. Hence, Zn(*tert*-Bu)$_4$Pc π–π complexes with the aromatic molecules can not be considered as donor-acceptor complexes. The lower energetic and thermal stability of the complexes of Zn(*tert*-Bu)$_4$Pc with π-accepting nitrobenzene (Table 1) conforms this supposition. Another character of interactions with aromatic mole-

Table 1 Physical-chemical characteristics of complexes of Zn(*tert*-Bu)$_4$Pc with aromatic molecules

Ligand	Zn(*tert*-Bu)$_4$Pc:ligand	t_{decom}/ °C	$\Delta_{evp}H$/ kJ mol^{-1}	V_w/ m^3 mol^{-1}	Bp/ °C	$\Delta_{evp.sol}H$/ kJ mol^{-1}
Benzene [17]	1:1	71	41.42	48.36		
Toluene	1:2	118	67.4	59.51	110.63	33.18
Tert-butyl benzene	1:2	138	70.3	90.18	169.1	47.71
	1:1	172	105.2			
o-Xylene	1:2	139	140.4	70.66	144.5	36.24
p-Xylene	1:2	127	95.3	70.66	138.37	35.67
Chlorobenzene	1:2	129	112.7	57.84	131.72	35.19
o-Dichlorobenzene	1:2	150	64.2	67.32	180	39.66
	1:1	174	130.0			
Nitrobenzene	1:2	188	120.2	62.64	210.8	55.01

t_{decom} is the temperature of decomposition of compex; $\Delta_{evp}H$ is the enthalpy change accompaning evaporation of solvent from crystallosolvate (the estimated standard deviation on this quantity is ±1.6–3.1 kJ mol^{-1}); V_w is the van der Waals volume; bp is the boiling point of solvent; $\Delta_{evp.sol}H$ is the enthalpy change for evaporation of pure solvent [16] cules has been found for metalloporphyrins which are structural analogs of metallophthalocyanines. The energetic stability of the molecular complexes of metalloporphyrins with π-acceptors is more than ten times larger than that of their complexes with π-donors [22, 23]. Moreover, numerous studies on π–π complexes of the porphyrins and the metalloporphyrins with aromatic molecules show that these complexes are formed due to donor-acceptor interactions [22–26]. The metallophthalocyanines have higher stability in relation to acid or peroxide action as well as the higher ability to complex formation with aromatic molecules in comparison with the metalloporphyrins. These properties make them useful in application as analytical reagents or adsorbent for chromatography.

Conclusions

As can be seen from the present results (Table 1), temperatures of decomposition of Zn(*tert*-Bu)$_4$Pc π–π complexes with toluene, *tert*-butyl benzene and *o*-dichlorobenzene are greater than boiling temperatures of pure solvents. Hence, it can be expected that an application of the above mentioned solvents as solvating media upon synthesis of the metallophthalocyanines leads to an increase of a yield of the product.

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