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Chelation and Fluorescence Properties of Tetraphenylporphyrin and 5,10,15,20-Tetra(4-hydroxyphenyl)porphyrin in Acetonitrile

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Abstract—The kinetics of complex formation between zinc and 5,10,15,20-tetraphenylporphyrin and 5,10,15,20-tetra(4-hydroxyphenyl)porphyrin in acetonitrile is studied in the temperature range from 298 to 318 K. The fluorescent properties of these compounds are examined, the emission in the red region of the spectrum is measured, and the fluorescence quantum yields are determined. It is found that although the electronic absorption spectra of the studied compounds are almost identical, hydroxyl substituents are observed to have a considerable effect on the chelating ability of ligands. The rate constant of the formation of ZnT(4-OH-Ph)P is thus approximately three times higher than that of ZnTPhP, with the energy consumption being lower (about 20 kJ mol^{-1}). The calculated fluorescence quantum yields of H$_2$TPhP, H$_2$T(4-OH-Ph)P, ZnTPhP, and ZnT(4-OH-Ph)P in acetonitrile are half those in toluene, while the ratio between the quantum yields of ligands and their metal complexes is a constant equal to approximately 3 and does not depend on which solvent is used.

INTRODUCTION

In this work, we investigate the kinetics of complex formation between zinc acetate and 5,10,15,20-tetraphenylporphyrin (H$_2$TPhP) and 5,10,15,20-tetra(4-hydroxyphenyl)porphyrin (H$_2$T(4-OH-Ph)P) in acetonitrile in the temperature range from 298 to 318 K. The fluorescent properties of these compounds are examined, the emission in the red region of the spectrum is measured, and the corresponding fluorescence quantum yields are determined.

EXPERIMENTAL

Electronic absorption spectra (EAS) of solutions of the studied ligands and their metal complexes were recorded on a Cary 100 spectrophotometer (Varian). A Shimadzu RF-5301 spectrofluorophotometer was used to measure the fluorescence of solutions of H$_2$TPhP and H$_2$T(4-OH-Ph)P zinc complexes in acetonitrile. The experimental techniques and the methods for processing the experimental data were similar to those described in [1–3]. Acetonitrile of high purity containing no more than 0.03% water was used as a dipolar aprotic solvent. The spectra confirmed the molecular form of the initial porphyrins in acetonitrile. H$_2$TPhP and H$_2$T(4-OH-Ph)P were synthesized according to the familiar procedures in [4–7].

Zinc acetate of analytical grade was purified by recrystallization from aqueous acetic acid and dehydrated at 380–390 K [8].

RESULTS AND DISCUSSION

The formation of complexes between H$_2$TPhP, H$_2$T(4-OH-Ph)P, and Zn(OAc)$_2$ in system (1) was examined spectrophotometrically [1, 9] in thermostatted quartz cuvettes with ground glass joints at temperatures of 298 to 318 K, with at least three parallel experiments being performed at each temperature (Figs. 1–3, Table 1). The accuracy of temperature control during an experiment was ±0.1 K. Isosbestic points were clearly observed in all spectra of the reaction systems (Figs. 1 and 3).

$$\left(\mathrm{H_2TPhP}\right), \left(\mathrm{H_2T\left(4\text{-}OH\text{-}Ph\right)P}\right) - \mathrm{Zn\left(OAc\right)_2} - \mathrm{CH_3CN}. \tag{1}$$
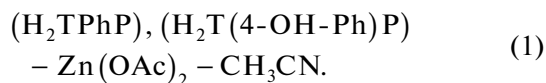
The formation of metal−porphyrin complexes (1) is characterized by a first order kinetics with respect to ligand [1]. Complex formation between doubly charged metal cations and porphyrins in nonaqueous solutions is described by the equation
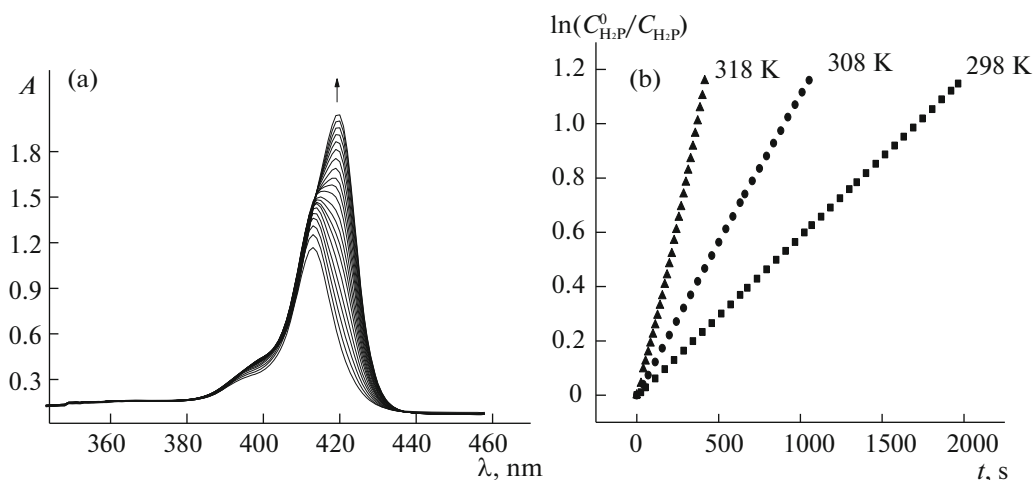
$$\mathrm{H_2P} + [\mathrm{MX_2\left(Solv\right)_{n-2}}] \rightarrow \mathrm{MP} + 2\mathrm{HX} + \left(n-2\right)\mathrm{Solv}, \tag{2}$$
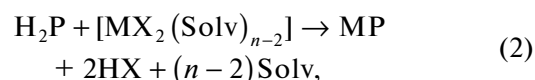
Fig. 1. (a) Changes in EAS during the coordination reaction between H_2TPhP and zinc acetate in system (1) at $C_{porph} = 9.45 \times 10^{-5}$, $C_{Zn(OAc)_2} = 8.84 \times 10^{-3}$ mol L^{-1} and a temperature of 298 K and (b) the dependence of $\ln(C^0_{H_2P}/C_{H_2P})$ on t of the reaction of complex formation between zinc and H_2TPhP (1) at $C_{porph} = 1.85 \times 10^{-5}$, $C_{Zn(OAc)_2} = 1.84 \times 10^{-3}$ mol L^{-1} and temperatures of 298, 308, and 318 K.

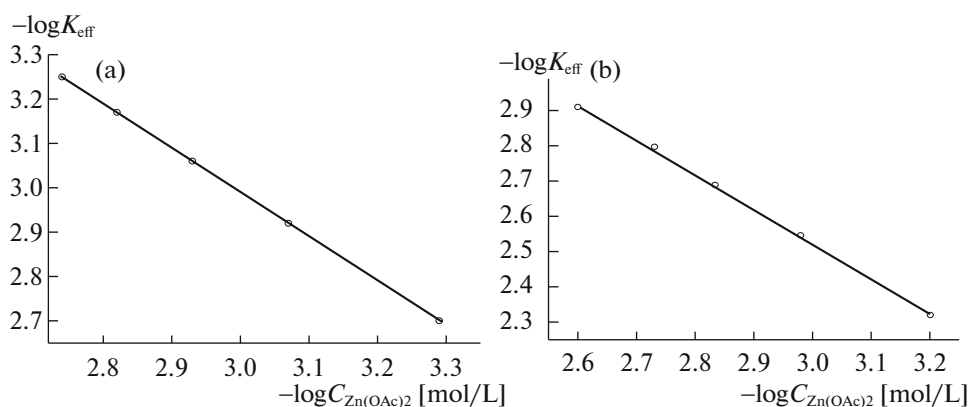**Fig. 2.** (a) Dependence of $-\log k_{eff}$ on $-\log C_{Zn(OAc)_2}$ of the reaction of ZnTPhP formation in system (1) at 298 K (the slope and coefficient of determination are 1.01 and 0.999, respectively) and (b) the dependence of $-\log k_{eff}$ on $-\log C_{Zn(OAc)_2}$ of the reaction of ZnT(4-OH-Ph)P formation in system (1) at 298 K (the slope and coefficient of determination are 1.02 and 0.998, respectively).

where X is the acid ligand, Solv is the solvent molecule, n is the coordination number of the metal cation, H_2P is the porphyrin ligand (H_2TPhP or $H_2T(4-OH-Ph)P$), and M is the metal cation (Zn^{2+}).

Our kinetic experiments were performed with a tenfold excess of $Zn(OAc)_2$ with respect to porphyrin. The effective rate constants (k_{eff}) of complex formation reaction (2) were calculated using the equation

$$k_{eff} = (1/t)\ln[(A_o - A_\infty)/(A - A_\infty)], \qquad (3)$$

where A_0, A, and A_∞ are the absorbances of solution at the initial time, to time t and at the end of the reaction, respectively.

The ($n + 1$)th order rate constants were found via Eq. (4):

$$k_{n+1} = k_{eff}/c^n_{M(OAc)_2}, \qquad (4)$$

where n is the order of reaction (2) with respect to salt ($n = 1$ in the case of $Zn(OAc)_2$ in acetonitrile [10]); the k_{n+1} values are given in Table 2 as kv^{298} at a standard temperature.

Activation energy E_a was calculated in the studied range of temperatures using the Arrhenius equation:

$$k = Ae^{-E_a/RT} \quad \text{or}$$
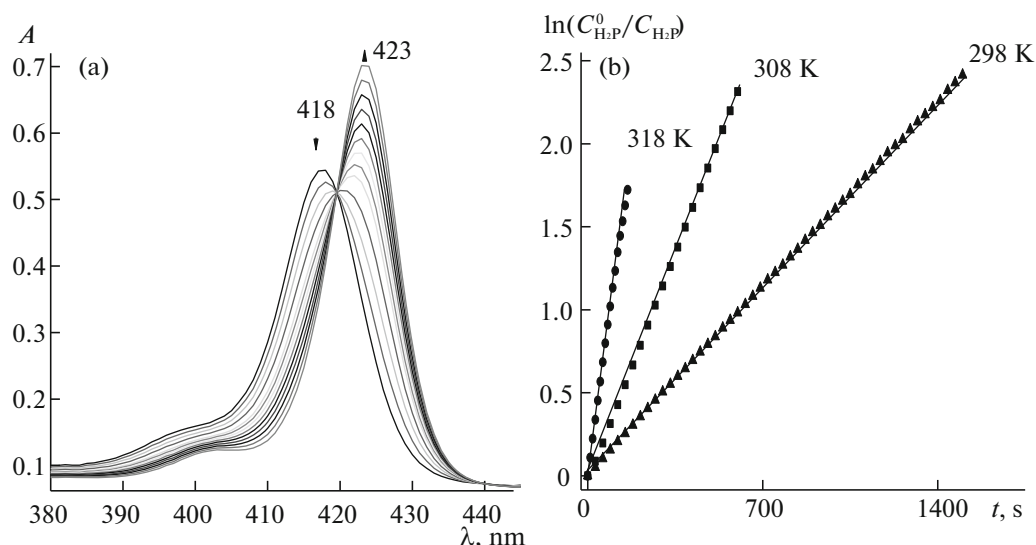$$E_a = 19.1[(T_1T_2)/(T_2 - T_1)]\log(k_2/k_1), \qquad (5)$$

Fig. 3. (a) Changes in EAS during the coordination reaction between $H_2T(4\text{-OH-Ph})P$ and zinc acetate in system (1) at $C_{porph} = 1.01 \times 10^{-5}$, $C_{Zn(OAc)_2} = 1.84 \times 10^{-3}$ mol L^{-1} and a temperature of 298 K and (b) the dependence of $\ln(C_{H_2P}^0/C_{H_2P})$ on t of the reaction of complex formation between zinc and $H_2T(4\text{-OH-Ph})P$ (1) at $C_{porph} = 1.01 \times 10^{-5}$, $C_{Zn(OAc)_2} = 1.84 \times 10^{-3}$ mol L^{-1} and temperatures of 298, 308, and 318 K.

and the entropy of the formation of the transition state ($\Delta S^{\neq}$) was determined using the equation

$$\Delta S^{\neq} = 19.1 \times \log k_{298} + E_a/T - 253. \quad (6)$$

Samples of 40−50 experimental points from the linear regions of the corresponding dependences of absorbance $\ln(C_{H_2P}^0/C_{H_2P})$ on t (s) were used to determine k_{eff} values for each of the three parallel experiments at temperatures ranging between 298 and 318 K. The average values were then used to calculate the kv^{298} values at a confidence level of 0.90 and an accuracy of ±0.03. The E_a and $\Delta S^{\neq}$ values were determined for each of the parallel experiments using Eqs. (5) and (6), with the average values being recorded as final results and the errors being calculated as deviations from the arithmetic means.

The kinetic parameters of the coordination reaction between H_2TPhP, $H_2T(4\text{-OH-Ph})P$ porphyrins and zinc acetate in system (1) are summarized in Table 2. The processes of the partial destruction and deformation of the coordination sphere of the salt solvate complex, e.g., the detachment of two Solv molecules from metal cation and the stretching of other bonds (M−Solv and M−X), are main contributors to the activation energy [1]. The lengths of N−H bonds of porphyrin change in the transition state; this also undoubtedly affects the process energy [1, 11]. The electronic effects of peripheral substituents are weaker but contribute to the destabilization of N−H bonds, thereby also affecting the complex formation rate.

Electron-acceptor substituents reduce the electron density on tertiary nitrogen atoms and contribute to the stretching of N−H bonds and the detachment of protons. Electron-donor groups have the opposite

Table 1. Spectral characteristics of the molecular forms of H_2TPhP and $H_2T(4\text{-OH-Ph})P$ porphyrins and their zinc complexes prepared in system (1)

Porphyrin	Impurities	$\lambda_4(\log \varepsilon)$	$\lambda_3(\log \varepsilon)$	$\lambda_2(\log \varepsilon)$	$\lambda_1(\log \varepsilon)$
H_2TPhP	413(4.09)	511(3.02)	545(2.87)	589(2.82)	646(2.83)
$ZnTPhP$	420(4.34)		555(3.42)	594(3.08)	
$H_2T(4\text{-OH-Ph})P$	417(4.73)	516 (3.72)	553 (3.60)	593 (3.37)	649(4.41)
$ZnT(4\text{-OH-Ph})P$	423(4.84)		556(3.75)	598(3.66)	

H_2TPhP is 5,10,15,20-tetraphenylporphyrin; $H_2T(4\text{-OH-Ph})P$ is 5,10,15,20-tetra(4-hydroxyphenyl)porphyrin; $ZnTPhP$ is the zinc complex of H_2TPhP; $ZnT(4\text{-OH-Ph})P$ is the zinc complex of $H_2T(4\text{-OH-Ph})P$; and ε, mol L^{-1} cm^{-1}, is the molar extinction coefficient. The error of determination in three parallel experiments ranged from 1 to 3%.

Table 2. Kinetic parameters of the coordination reaction between H$_2$PhP and H$_2$T(4-OH-Ph)P porphyrins and zinc acetate in system (1)

Porphyrin	$C_{\text{Zn(OAc)}_2}$, mol L^{-1}	kv^{298}, L mol^{-1} s^{-1}	E_a, kJ mol^{-1}	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}
H$_2$TPhP	1.84×10^{-3}	0.302 ± 0.029	70 ± 2	46 ± 2
H$_2$T(4-OH-Ph)P	1.84×10^{-3}	0.875 ± 0.018	60 ± 3	53 ± 2

effect. Bulk *meso*-substituents change the conformation of porphyrin molecules and can distort the planar structure of macrocycles [12, 13]. Analysis of the obtained data shows that although the EASes of the studied compounds were almost identical, the hydroxyl substituents significantly affect the chelating ability of ligands. In other words, the rate constant of formation of ZnT(4-OH-Ph)P is approximately three times higher than that of ZnTPhP, and the energy consumption is lower (about 20 kJ mol^{-1}). Introducing four electron-donor groups into the tetraphenylporphyrin molecule seems to increase the electron density on the tertiary nitrogen atoms and accelerate complex formation (1). This conclusion agrees with earlier data on the total inductive and resonance effects of electron-donor substituents (−OH and −NH$_2$) in position 4 of *meso*-aryl groups of tetraphenylporphyrins, leading to a substantial increase in the basicity of tetrapyrrole ligands, compared to unsubstituted tetraphenylporphyrin [14]. The drop in the $\Delta S^{\neq}$ values in the case of ZnTPhP formation agrees with the obtained values of the constants, since the increase in the concentration of molecules of the formed zinc-ligand complex depends on the number of collisions between molecules (the degree of disorder) in the chemical process.

The fluorescence of acetonitrile solutions of H$_2$T(4-OH-Ph)P, ZnT(4-OH-Ph)P, H$_2$TPhP and ZnTPhP was measured with a Shimadzu RF-5301 spectrofluorophotometer. H$_2$TPhP and its zinc complex, known to be characterized by quantum yields of 0.11 and 0.033 (measured in toluene) [15], were used as references.

Fluorescence was measured as follows.

1. A solution of the test sample (H$_2$T(4-OH-Ph)P, ZnT(4-OH-Ph)P, H$_2$TPhP, or ZnTPhP) in acetonitrile was placed in an optical quartz cuvette with an optical path length of 1 cm, the absorbance at the excitation wavelength being $A < 0.1$ to avoid fluorescence quenching.

2. A correction for dark current (the photomultiplier output current in the absence of incident light) was introduced to avoid error in determining the intensity of the sample solution's fluorescence.

3. The intensity of the pure solvent's (acetonitrile's) fluorescence, measured at the same parameters of the spectrofluorophotometer, was subtracted to allow for the effect the solvent had on the intensity of the test sample's fluorescence.

4. Rayleigh scattering was calculated by varying the excitation wavelengths in the range of ±40 nm until stable coordinates of the fluorescence peaks of samples were achieved (the fluorescence bands should not change according to the excitation wavelength [16]).

5. The resulting fluorescence spectra of the studied samples in acetonitrile were compared with the literature data [15], and the corresponding integral fluorescence intensities were calculated.

6. The fluorescence quantum yields of the studied acetonitrile solutions of porphyrins and metal-porphyrin complexes were calculated using the standard technique [17] by the equation

$$Q_x = \frac{I_x A_r}{I_r A_x} Q_r, \tag{7}$$

where Q_x and Q_r are the quantum yields of the test and reference samples, respectively; A_x and A_r are the absorbances of these samples at the excitation wavelength, respectively; and I_x and I_r are their integral intensities.

The recorded fluorescence spectra of acetonitrile solutions of H$_2$T(4-OH-Ph)P, ZnT(4-OH-Ph)P, H$_2$TPhP, and ZnTPhP, normalized to the maximum
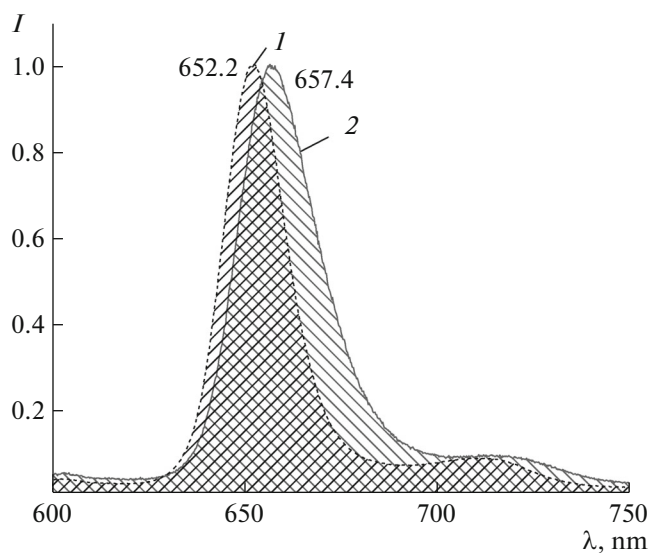
Fig. 4. Fluorescence spectra of (*1*) H$_2$TPhP (1.01×10^{-5} mol L^{-1}) and (*2*) H$_2$T(4-OH-Ph)P (1.50×10^{-5} mol L^{-1}) in acetonitrile at 298 K and $\lambda_{\text{ex}} = 555$ nm.
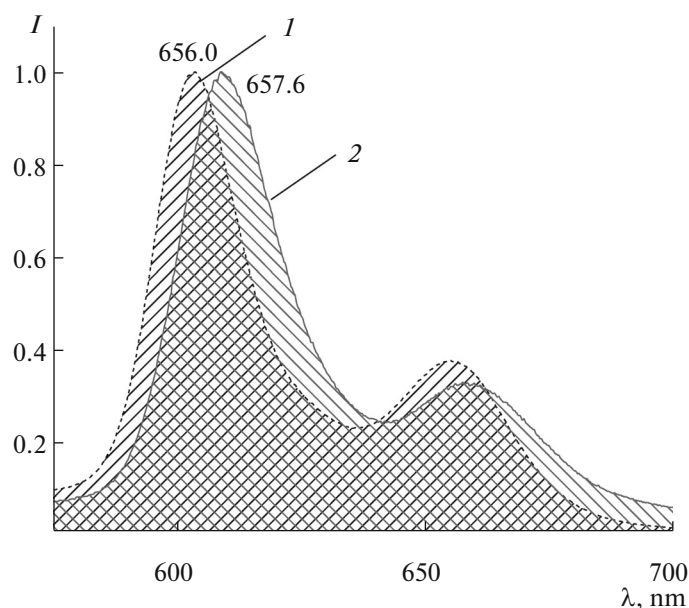
Fig. 5. Fluorescence spectra of (*1*) ZnTPhP (1.76×10^{-6} mol L^{-1}) and (*2*) ZnT(4-OH-Ph)P (1.86×10^{-6} mol L^{-1}) in acetonitrile at 298 K and $\lambda_{ex} = 555$ nm.

of the fluorescence intensity, are shown in Figs. 4 and 5. The fluorescence quantum yields of ZnTPhP and ZnT(4-OH-Ph)P (Fig. 5) in toluene and acetonitrile are close at 0.033 [15], 0.032 and 0.017, 0.016, respectively. The fluorescence quantum yields of H$_2$TPhP and H$_2$T(4-OH-Ph)P (Fig. 4) in acetonitrile are 0.059 and 0.048, respectively. Fluorescence was measured at room temperature (295 K) with an accuracy of approximately 10%. Our data show that the hydroxy groups of ligands have a slight affect on their own fluorescence and that of the zinc complex, while the nature of the solvent makes the main contribution to changes.

It was found that acetonitrile, a dipolar aprotic solvent, ensures considerable quenching of the fluorescence of solutions of ligands and their zinc complexes, while the fluorescence quantum yields of H$_2$TPhP, H$_2$T(4-OH-Ph)P, ZnTPhP, and ZnT(4-OH-Ph)P complexes in toluene, a stable chemically inert low-polar solvent, are higher. A similar effect on the photophysical parameters of the solutions of tetraazaporphyrin in isobutanol, isopropanol and toluene was reported in [18]. The calculated fluorescence quantum yields of H$_2$TPhP, H$_2$T(4-OH-Ph)P, ZnTPhP, and ZnT(4-OH-Ph)P in acetonitrile were half those determined in toluene solutions. At the same time, the ratio between the quantum yields of ligands and their metal complexes was a constant equal to approximately 3 and did not depend on which solvent was used. This interesting experimental result suggests that modifications of the peripheral fragments of ligand not only increase the rate of metal complex formation and reduce the energy consumption for complex for-

mation, but also allow us to stabilize the fluorescent properties of compounds.

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