

SPECTRAL MANIFESTATIONS OF SPECIFIC SOLVATION OF 5,10,15,20-TETRAKIS-(4-SULFONATOPHENYL)-PORPHYRIN AND ITS DOUBLY PROTONATED FORM IN AQUEOUS SOLUTIONS

P. G. Klimovich, A. B. Krylov, and M. M. Kruk*

UDC 535.34+543.421/.422

The temperature dependence of absorption and fluorescence spectra of 5,10,15,20-tetrakis-(4-sulfonatophenyl)-porphyrin in weakly acidic aqueous solutions was studied in the range 288–333 K. The fraction of molecules in the free-base form in the ground (S_0) and lower excited singlet states (S_1) was found to increase as the temperature increased because the fraction of molecules in the doubly protonated form decreased. The deprotonation was caused by a shift in the acid–base equilibrium in the macrocycle core due to decreases in $pK_a(S_0)$ and $pK_a(S_1)$ with increasing temperature. The difference $pK_a(S_1) - pK_a(S_0) < 0$ for solution temperatures > 293 K with $pK_a(S_1) - pK_a(S_0) > 0$ for $T < 293$ K. The activation energies of deprotonation in the S_0 - and S_1 -states for $T > 293$ K were $E_a = 5.0$ and 3.4 kJ/mol; for $T < 293$ K, they increased to 20.3 and 56.2 kJ/mol. These differences were explained by different specific solvation of the tetrapyrrole macrocycle in the ground S_0 - and lower excited S_1 -states because of a change in the ratio of two forms of water. So-called form A with disordered H-bonds dominated at higher temperatures. The fractions of forms A and B, which possessed a strongly ordered H-bond system, were comparable as the temperature decreased. Stabilization of the porphyrin free base prevailed at high temperatures; of the doubly protonated form, at low temperatures.

Keywords: porphyrin, thermochromism, acid–base equilibrium, activation energy, solvation.

Introduction. Studies of temperature effects on electronic absorption and fluorescence spectra of organic compounds represent an active direction in molecular spectroscopy aimed at fabricating luminescent molecular thermometers, thermally controlled optical switches, and temperature sensors. Phenomena that can be used to divide tetrapyrrole compounds into three groups underly most known thermochromic effects observed in them.

The first group of temperature effects includes thermal population of low-lying electronic (vibronic) states, as a result of which new transitions or considerably altered intensities appear in absorption and/or fluorescence spectra. The energy gap between such states can vary from 1–100 [1–3] to 1000–3000 cm^{-1} [4–7]. A temperature increase with a small energy gap leads to population of higher-lying sublevels of multiplet states [1–3] formed by lifting of degeneracy because the molecular symmetry is lowered via a Jahn–Teller effect [2]. Either high-lying levels in a progression of vibronic states [4] or new electronic states [5] are populated with energy gaps $\geq 10^3$ cm^{-1} . Spectral manifestations of stabilization/destabilization of charge-transfer states formed as a result of peripheral substitution of a tetrapyrrole macrocycle by strongly electron-donating or electron-accepting groups should be assigned to this group [6, 7].

The second group of thermochromic effects is based on conformational lability of tetrapyrroles and supramolecular systems based on them. If several stable conformers can form, their relative concentrations (i.e., the equilibrium between them) can be changed by varying the temperature or transferring the energy necessary to overcome the potential barrier separating the conformers [8–14]. The conformational transformations in such systems can be both the shift of one proton in the macrocycle core, i.e., NH tautomerism [8–12], and the migration of large molecular fragments relative to each other (limited to two macrocycles, converting into a dimer [13, 14]). Thermochromic effects can be observed in the molecular ground and excited states or in only one of them depending on the height of the potential barrier [11, 12].

*To whom correspondence should be addressed.

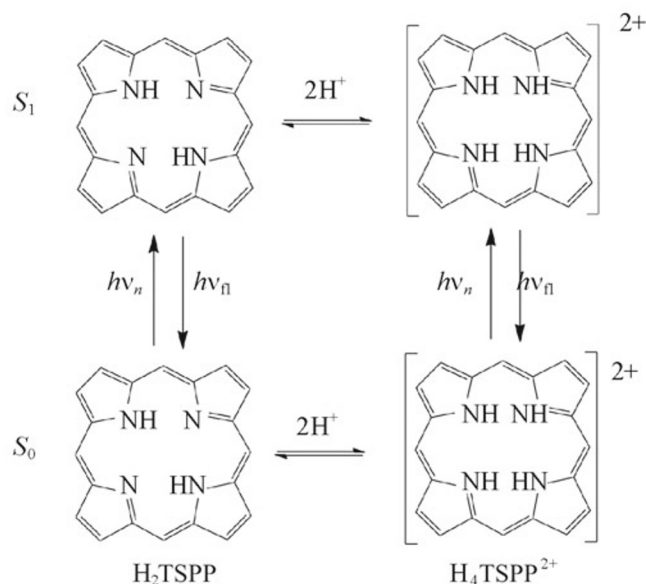


Fig. 1. Diagram of acid–base equilibria of 5,10,15,20-tetrakis-(4-sulfonatophenyl)-porphyrin in the ground S_0 - and lower excited singlet S_1 -states; substituents in the macrocycle *meso*-positions are not shown.

The third group of thermochromic effects refers to intermolecular interactions that can affect the molecular electronic structure. As a rule, these effects are reversible and include dimerization, acid–base equilibria in the core and on the periphery of the tetrapyrrole macrocycle, and specific solvation of the macrocycle core (primarily formation of intermolecular H-bonds) and ionizable groups of peripheral substituents [10, 15–17]. For example, electronic absorption spectra of 5,10,15,20-tetraphenylporphyrin were observed to change in aqueous solutions containing Triton X-100 that were acidified by inorganic acids [15]. Thermochromism was proposed to explain the temperature dependence of the distribution coefficient of porphyrin between an aqueous phase in which the porphyrin existed as the doubly protonated form and the volume within micelles formed by detergent molecules in which the free base was stabilized. Thermochromic effects were detected for a series of 5,10,15,20-tetra-aryl-porphyrins substituted in the phenyl *para*-positions by strongly electron-donating groups ($-\text{NH}_2$, $-\text{OH}$) on going from room temperature to 77 K [16]. They were explained by two phenomena, i.e., an increase in the probability of forming intermolecular H-bonds between the polar phenyl substituents and solvent molecules as the temperature dropped [5,10,15,20-tetra-(*p*- NH_2 -phenyl)-porphyrin] and a shift of the acid–base equilibrium between the free base and the doubly protonated form toward formation of protonated products as the temperature dropped [5,10,15,20-tetra-(*p*- OH -phenyl)-porphyrin]. Thermochromism of a family of 5,10,15-triarylcorrole free bases in EtOH solutions was responsible for specific solvation effects of the macrocycle core that arose because of the temperature dependence of the dielectric permittivity of EtOH [17]. Thermochromic effects were shown to be determined by the basicity of the pyrrole N atoms, which depended on the architecture of the macrocycle peripheral substitution.

Thermochromic effects of the last type have stimulated the most interest because, on one hand, substantial spectral changes can occur through relatively small thermal effects and, on the other, features of the molecular structure and physicochemical properties of molecular solvation spheres in solutions can be studied using thermochromic compounds as molecular probes. Absorption and fluorescence spectroscopy are used in the present work to study temperature dependences of acid–base equilibria in the tetrapyrrole core of the water-soluble macrocycle 5,10,15,20-tetrakis-(4-sulfonatophenyl)-porphyrin in the ground (S_0) and lower excited singlet states (S_1) (Fig. 1). The behavior of $\text{p}K_a(S_0)$ and $\text{p}K_a(S_1)$ upon changing the solution temperature in the range 288–333 K is studied. The role of specific solvation of the macrocycle tetrapyrrole core and polarity changes of the aqueous solution in acid–base equilibria in the ground S_0 - and lower excited singlet S_1 -states is analyzed.

Experimental. The tetrasodium salt of 5,10,15,20-tetrakis-(4-sulfonatophenyl)-porphyrin (free base H_2TSPP , doubly protonated $\text{H}_4\text{TSPP}^{2+}$; Aldrich, USA) was used without further purification. Doubly distilled H_2O was obtained via

distillation using standard methods. Experiments were conducted in quartz cuvettes (1 × 1 cm; Hellma, Germany) that were placed into a thermostatted cuvette compartment of a fluorescence spectrometer. Observed spectral changes were checked for total reversibility during measurements of temperature dependences of absorption and fluorescence spectra, i.e., spectra returned to the initial shape upon cooling heated solutions to the initial temperature. The porphyrin concentration in the solutions was $<3 \cdot 10^{-6}$ M and was determined by spectrophotometry using known extinction coefficients [18]. The porphyrin molecule at these concentrations in aqueous solution existed as the monomer so that aggregation effects were avoided [18]. Electronic absorption and fluorescence spectra were recorded on an SM 2203 fluorescence spectrometer (Solar, Belarus). The fluorescence quantum yield Φ_{fl} of solutions containing H₂TSPP and H₄TSPP²⁺ in an unknown ratio was determined by a relative method using $\Phi_{fl}^0 = 0.058$ for H₂TSPP and $\Phi_{fl}^0 = 0.13$ for H₄TSPP²⁺ as standards [18]. Dielectric permittivities of water at various temperatures were taken from the literature [19, 20].

Results and Discussion. Working solutions should contain molecules of the studied compound in two forms at equilibrium to observe thermochromic phenomena due to temperature effects on the acid–base equilibrium [17]. This means that the basicity of the macrocycle and the solution pH should fulfill the condition $|pK_a(S_0) - \text{pH}| < 1$ for porphyrins. The average $pK_a(S_0)$ for equilibrium between the free base and the doubly protonated form (H₂TSPP + 2H⁺ ↔ H₄TSPP²⁺) at 295 ± 2 K is 4.78 according to the literature [18, 21]. A working solution was prepared by adding a dilute solution of monofluoroacetic acid (5 μL) to distilled H₂O (3 mL). The fraction of H₂TSPP molecules in the ground electronic state S_0 was 0.38 in the prepared solution (pH 4.68) at 293 K. The fraction of H₂TSPP molecules was calculated based on the known extinction coefficients at the Soret band maximum for the free base (414 nm) and the doubly protonated form (434 nm). The fraction of monoprotonated molecules was neglected because it is trivial for porphyrins substituted in the *meso*-position by aryl fragments that do not contain sterically bulky groups in the aryl *ortho*-position [22, 23]. The fraction of free base H₂TSPP is observed to increase/decrease as the temperature increases/decreases because the fraction of doubly protonated H₄TSPP²⁺ decreases/increases (Fig. 2, Table 1).

Solution fluorescence spectra (Fig. 3) were measured at $\lambda_{ex} = 424$ and 570 nm, corresponding to isosbestic points in spectra of free base H₂TSPP and doubly protonated H₄TSPP²⁺. The obtained series of spectra exhibited a single transformation with changing temperature. Therefore, the series of spectra with the best signal-to-noise ratios ($\lambda_{ex} = 424$ nm) were selected for the analysis. The fractions of free base [H₂TSPP] and doubly protonated [H₄TSPP²⁺] = 1 – [H₂TSPP] in the lower excited singlet S_1 -state were calculated from the balance equation using the measured fluorescence quantum yields Φ_{fl} at various temperatures:

$$\Phi_{fl} = [\text{H}_2\text{TSPP}] \Phi_{fl}^0(\text{H}_2\text{TSPP}) + (1 - [\text{H}_2\text{TSPP}]) \Phi_{fl}^0(\text{H}_4\text{TSPP}^{2+}), \quad (1)$$

where $\Phi_{fl}^0(\text{H}_2\text{TSPP})$ and $\Phi_{fl}^0(\text{H}_4\text{TSPP}^{2+})$ are the fluorescence quantum yields of the corresponding forms.

A comparison of the fractions of [H₂TSPP] and [H₄TSPP²⁺] in the S_0 - and S_1 -states given in Table 1 showed that the temperature dependences were in general analogous, i.e., a temperature increase was associated with deprotonation of the porphyrin and an increase in the fraction of the free base in solution. However, it is noteworthy that [H₂TSPP] and [H₄TSPP²⁺] in the S_1 -state changed more over the whole temperature range. In fact, the fraction of [H₂TSPP] in the S_1 -state increased by ~0.75 on going from 288 to 333 K while the increase was only 0.53 for those in the ground S_0 -state. It is noteworthy that the fractions of [H₂TSPP] in the S_0 - and S_1 -states at 293 K coincided by chance because the values were obtained independently of each other based on analyses of the absorption (S_0) and fluorescence spectra (S_1).

The increase in the fraction of free-base molecules with increasing temperature indicated that the acid–base equilibrium shifted because $pK_a(S_0)$ and $pK_a(S_1)$ decreased. Theoretical sigmoidal titration curves at each temperature were calculated to determine them using the Henderson–Hasselbach equation [24]:

$$x = x_{\min} + (x_{\max} - x_{\min}) \frac{10^{n(\text{pH} - pK_a)}}{1 + 10^{n(\text{pH} - pK_a)}}, \quad (2)$$

where x , x_{\min} , and x_{\max} are the instantaneous (at the given pH), minimal, and maximal values of the fraction of free-base molecules, respectively, and n , the Hill index describing the deprotonation cooperativity [18]. The sigmoidal titration curve for this temperature was calculated from the magnitude of $pK_a(S_0)$ at 293 K. Assuming that the Hill index was independent of temperature, the sigmoidal curves and the corresponding pK_a values at other temperatures were obtained by a simple shift of the curve along the pH axis so that the calculated fraction of free-base molecules [H₂TSPP] agreed with the sigmoidal

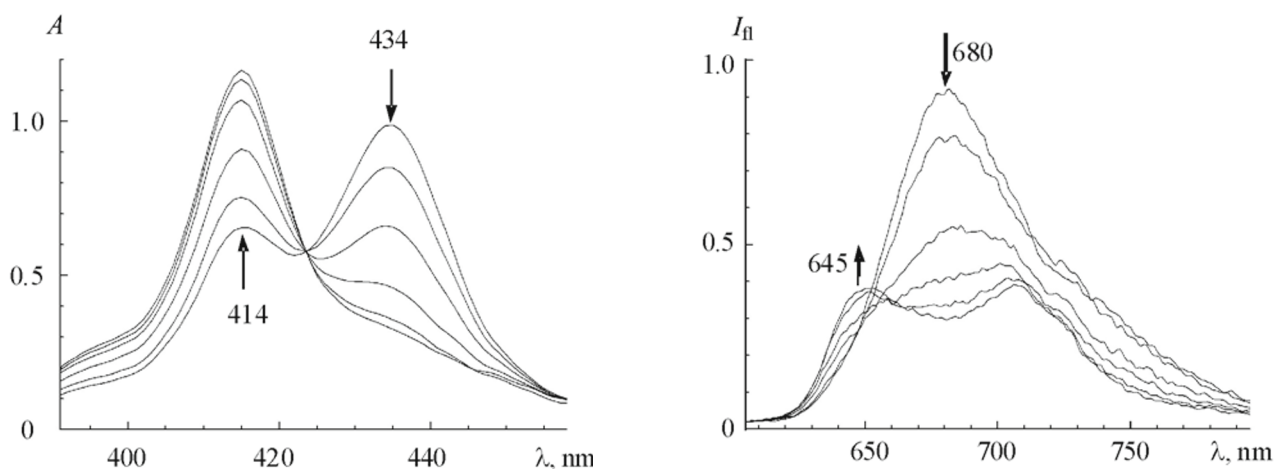


Fig. 2. Electronic absorption spectra of 5,10,15,20-tetrakis-(4-sulfonatophenyl)-porphyrin near the Soret band in aqueous solution at 288–328 K; here and in Figs. 3 and 4, arrows indicate the direction of change with increasing temperature.

Fig. 3. Fluorescence spectra of 5,10,15,20-tetrakis-(4-sulfonatophenyl)-porphyrin in aqueous solution at 288–328 K, $\lambda_{\text{ex}} = 424$ nm.

TABLE 1. Fraction of 5,10,15,20-Tetrakis-(4-sulfonatophenyl)-porphyrin Free Base, Fluorescence Quantum Yield, and $\text{p}K_a$ Values in the Ground (S_0) and Lower Excited Singlet States (S_1) in Aqueous Solution at Various Temperatures

T , K	[H ₂ TSPP]		Φ_{fl}	$\text{p}K_a(S_0)$	$\text{p}K_a(S_1)$	ϵ
	S_0	S_1				
288	0.28	0.25	0.112	4.88	4.92	81.7
293	0.38	0.38	0.102	4.78*	4.78	80.0
303	0.59	0.69	0.080	4.64	4.59	76.2
313	0.70	0.81	0.070	4.49	4.31	72.8
323	0.78	0.91	0.064	4.40	4.17	69.8
333	0.81	0.95	0.062	4.36	4.06	66.5

Note. The fraction of molecules in the doubly protonated form [H₄TSPP²⁺] is not given because it is directly related to the fraction of free-base molecules as $1 - [\text{H}_2\text{TSPP}]$;

* Average of literature data at 295 ± 2 K is used as a standard.

curve (Fig. 4a). The $\text{p}K_a(S_1)$ values were determined analogously (Fig. 4b). Table 1 gives the resulting $\text{p}K_a(S_0)$ and $\text{p}K_a(S_1)$ values.

The change of $\text{p}K_a(S_1)$ values was almost twice that of $\text{p}K_a(S_0)$ in the same temperature range. This indicated that the solvation of the S_0 - and S_1 -states differed perceptively. The conformation of the doubly protonated form H₄TSPP²⁺ was considerably relaxed in the S_1 -state based on the significantly increased Stokes shift $\Delta\lambda_{\text{st}}$ of it (702 cm^{-1}) as compared to the free base H₂TSPP (220 cm^{-1}). Thus, although the amplitude of the deviation of macrocyclic atoms from the average macrocycle plane in the S_1 -state increased, the pyrrole N atoms of the saddle-shaped distorted macrocycle of doubly protonated H₄TSPP²⁺ became even more available for interactions with water molecules [25]. The greater availability of the pyrrole protons to water molecules facilitated greater changes of the acid–base equilibrium than in the ground state (Table 1). The number of solvent molecules in the first coordination sphere determined the solvation stoichiometry and was related to the solvent dielectric permittivity [26]. Previously, the temperature dependences of the deprotonation of 5,10,15-triarylcorrole free bases in EtOH solutions were found to be due to specific solvation of the macrocycle tetrapyrrole

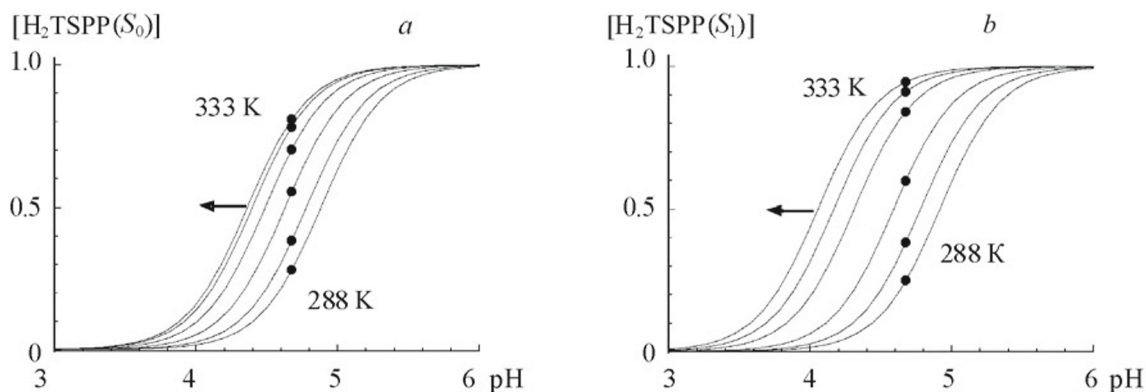


Fig. 4. Theoretical titration curves calculated using Eq. (2) at various temperatures for the ground S_0 - (a) and lower excited singlet S_1 -states (b); points, measured fraction of free-base molecules $[H_2TSPP]$ in solution.

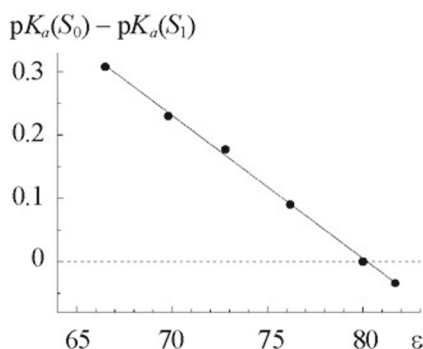


Fig. 5. Dependence of $[pK_a(S_0) - pK_a(S_1)]$ on dielectric permittivity of aqueous solution.

core [17]. It was shown that the dependence of the solvent dielectric permittivity on temperature was responsible for the solution temperature effect. The temperature dependence of the dielectric permittivity is greater for water than for EtOH. The quantity ϵ decreases linearly from 81.7 to 66.5 as the temperature increases from 288 to 333 K [19, 20]. Therefore, the change of solvation free energy ΔG_S , which is clearly dependent on the solvent dielectric permittivity, should be significant according to the Born model [27].

Figure 5 shows the dependence of the difference $pK_a(S_0) - pK_a(S_1)$ on the dielectric permittivity ϵ of the aqueous solution. Obviously, enhanced solvation of the tetrapyrrole macrocycle core upon increasing the water dielectric permittivity prevented proton dissociation for both the ground S_0 - and lower excited singlet S_1 -states and stabilized the protonated form H_4TSPP^{2+} . The decreased dielectric permittivity of water with increased temperature led to loosening of the solvation sphere, promoted proton dissociation, and stabilized the free base H_2TSPP . By analogy of the above phenomena to the thermochromism of 5,10,15-triarylcorrole free bases in EtOH solutions [17], it is notable that different acid–base equilibria are operative in these instances. Equilibrium between the free base and its monodeprotonated form was examined for the thermochromism of the corrole solutions with one proton dissociated from the free base and the temperature rose. In the present work, equilibrium between the free base and its doubly protonated form occurs. Two protons dissociate from the doubly protonated form and the free base is formed as the temperature increases. The common feature for both instances is that a rise in temperature stabilizes the form in equilibrium in which the macrocycle tetrapyrrole core contains fewer protons.

The different slopes of the functions $pK_a(S_0)$ and $pK_a(S_1)$ on the solution dielectric permittivity led to their intersection at $\epsilon = 80$ (at 293 K). This meant that the basicity of the lower excited S_1 -state was less than that of the ground S_0 -state [$pK_a(S_1) - pK_a(S_0) < 0$] at $T > 293$ K. Conversely, the basicity of the S_1 -state was greater than that of the S_0 -state

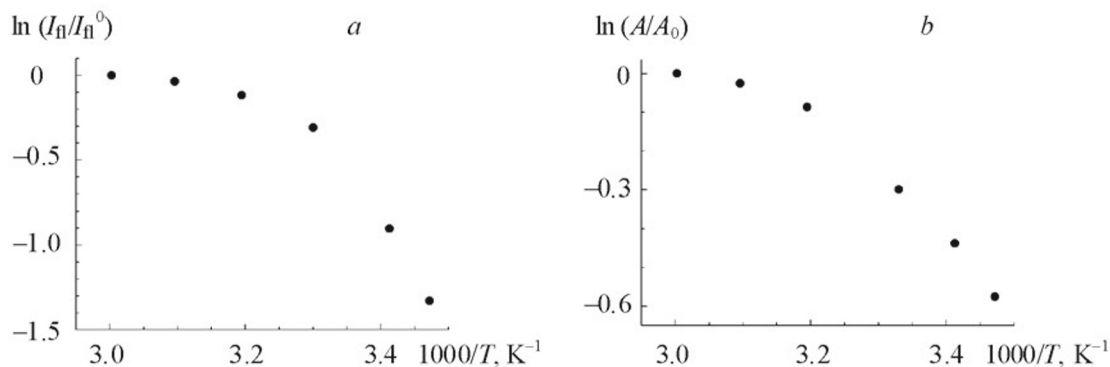


Fig. 6. Van't Hoff dependence for relative concentration of free-base molecules H₂TSPP at 288–333 K; in the ground S_0 -state (fraction of H₂TSPP molecules was calculated from the ratio of absorption at 414 and 434 nm) (a); in the lower excited singlet S_1 -state [fraction of H₂TSPP molecules was calculated using Eq. (1)] (b).

TABLE 2. Activation Energy E_a of Deprotonated Porphyrin Macrocycle in the Ground (S_0) and Lower Excited Singlet States (S_1) in Aqueous Solution at Various Temperatures

T , K	E_a , cm ⁻¹ (kJ/mol)	
	S_0	S_1
313–333	420 ± 100 (5.0)	280 ± 100 (3.4)
<293	1700 ± 200 (20.3)	4700 ± 200 (56.2)

[$\text{p}K_a(S_1) - \text{p}K_a(S_0) > 0$] at $T < 293$ K. The spectral and luminescent characteristics did not exhibit noticeable changes of the Stokes shift $\Delta\lambda_{\text{St}}$ on temperature (Figs. 2 and 3). Therefore, there was no basis to suggest that these changes of $\text{p}K_a(S_0)$ and $\text{p}K_a(S_1)$ were due to changes in the magnitude (or nature) of conformational relaxation in the excited S_1 -state. They were most likely due to the temperature dependence of intermolecular interactions of the porphyrin macrocycle and water molecules in the porphyrin solvation sphere. The thermodynamic characteristics of deprotonation in the S_0 - and S_1 -states were determined using the van't Hoff equation to check this hypothesis. An analysis of the resulting functions (Fig. 6) showed that they were not linear but convex with respect to the abscissa in the studied temperature range. This shape of van't Hoff functions is often encountered for enzymatic reactions and is due to the existence of two competing enzyme forms (active sites), each of which dominates in its own temperature range. The convexity of the function indicates that the process activation energy E_a decreases with increasing temperature [28]. Obviously, the factors influencing the equilibrium between the free base H₂TSPP and the doubly protonated form H₄TSPP²⁺ differ at high (313–333 K) and low (<293 K) temperatures. In fact, the van't Hoff functions can be satisfactorily described by linear functions in these temperature ranges. The corresponding activation energies E_a of the deprotonation reactions were determined (Table 2).

Table 2 shows that the height of the activation barrier is considerably greater than kT at lower temperatures so that the equilibrium is shifted toward stabilization of the doubly protonated form. Also, the activation barrier is significantly increased in the lower excited S_1 -state, which shifts the equilibrium even more toward formation of H₄TSPP²⁺. These changes of E_a are explained by the greater increase of $\text{p}K_a(S_1)$ as compared to $\text{p}K_a(S_0)$ at lower temperatures. The activation energy E_a decreases by 4 and 17 times in the ground (S_0) and lower excited singlet states (S_1) as the temperature increases. As a result, the height of the activation barrier in the S_1 -state becomes comparable to kT . The acid–base equilibrium at such activation energies shifts toward stabilization of the free base H₂TSPP, which is reflected in the decreases of $\text{p}K_a(S_0)$ and $\text{p}K_a(S_1)$ with $\text{p}K_a(S_1) < \text{p}K_a(S_0)$.

The macroscopic (bulk) characteristics of water in the studied temperature range change smoothly and cannot explain the sharp differences in the acid–base equilibrium of the porphyrin in aqueous solution with relatively small temperature changes. The reason for this involves specific intermolecular interactions in the solvation sphere of the dissolved molecule.

A branched network of H-bonds is known to form in water. Its structure in the studied temperature range is described by the coexistence of two forms of water, A and B [29]. Form A is characterized by disordered H-bonds and dominates at high temperatures. The fraction of water molecules in form A at 333 K is $f_A = 0.72$. The fraction f_A of water molecules in form A decreases upon lowering the temperature because the fraction of water molecules in form B, f_B , increases. Form B is characterized by a tetrahedrally structured network of H-bonds. The ratio of the fractions of the two forms is ~ 1 in the range 273–293 K ($f_A/f_B = 0.53/0.47$ at 293 K; $0.47/0.53$, at 273 K [29]). The enthalpy of activation of the structural transition between the two forms of water is 12.5 kJ/mol (1060 cm^{-1}) [29] and corresponds to the enthalpy of H-bond cleavage in water [30]. The temperature dependence of the changes in acid–base properties of the S_0 - and S_1 -states of H_2TSPP reflect the formation of structurally different (and, as a result, different properties manifested in the different activation energies E_a for deprotonation of the macrocycle core) solvation spheres of the porphyrin. A loose solvation sphere with relatively small solvation energy forms at higher temperatures where form A dominates in solution. It can provide effective solvation of dissociated protons and again solvate the porphyrin macrocycle after dissociation of the protons. As a result, the free base H_2TSPP is stabilized. The fraction of form B in solution increases if the temperature is lowered so that a significant part of the porphyrin molecules is solvated by water in form B. Significant energy losses are required for rearrangement of the rigid structured network of H-bonds in order to solvate dissociated protons. This makes deprotonation of the macrocycle thermodynamically unfavorable and stabilizes the doubly protonated form $\text{H}_4\text{TSPP}^{2+}$.

Conclusions. Thermochromism of 5,10,15,20-tetrakis-(4-sulfonatophenyl)-porphyrin in aqueous solution is due to a shift of the acid–base equilibrium between the free base and the doubly protonated form. It was found that the fraction of free-base molecules increased with increasing solution temperature because of universal interactions caused by the decreased polarity of the porphyrin microenvironment at elevated temperatures and specific solvation caused by the existence of two forms of water that solvated differently the dissolved molecules. The activation energy E_a for deprotonation of the porphyrin macrocycle at reduced temperatures, where a significant part of the porphyrin molecules was solvated by water in form B, was significantly greater than that at elevated temperatures, where the porphyrin molecules were solvated primarily by water in form A. The nature of the change of $\text{p}K_a(S_1)$ of the lower excited singlet S_1 -state relative to $\text{p}K_a(S_0)$ of the ground S_0 -state was determined by different ratios of activation energies E_a . The activation energy in the S_1 -state was greater at $< 293 \text{ K}$; in the ground S_0 -state, at higher temperatures.

REFERENCES

1. N. N. Kruk and A. S. Starukhin, *J. Appl. Spectrosc.*, **74**, 508–513 (2007).
2. M. M. Kruk, A. S. Starukhin, and R. Czerwieńiec, *J. Porphyrins Phthalocyanines*, **12**, 1201–1210 (2008).
3. N. N. Kruk and A. S. Starukhin, *Opt. Spektrosk.*, **111**, 756–763 (2011).
4. D. J. Quimby and F. R. Longo, *J. Am. Chem. Soc.*, **97**, 5111–5117 (1975).
5. J. M. Lupton, *Appl. Phys. Lett.*, **81**, 2478–2480 (2002).
6. F. J. Vergeldt, R. B. M. Koehorst, A. Van Hoek, and T. Schaafsma, *J. Phys. Chem.*, **99**, 4397–4405 (1995).
7. N. N. Kruk, *J. Appl. Spectrosc.*, **73**, 686–693 (2006).
8. R. J. Abraham, G. E. Hawkes, and K. M. Smith, *Tetrahedron Lett.*, **15**, 1483–1486 (1974).
9. A. Sarai, *J. Chem. Phys.*, **76**, 5554–5562 (1982).
10. E. I. Zenkevich, A. M. Shulga, I. V. Filatov, A. V. Chernook, and G. P. Gurinovich, *Chem. Phys. Lett.*, **120**, 63–68 (1985).
11. M. M. Kruk, T. H. Ngo, P. Verstappen, A. S. Starukhin, J. Hofkens, W. Dehaen, and W. Maes, *J. Phys. Chem. A*, **116**, 10695–10703 (2012).
12. Y. H. Ajeeb, T. B. Karlovich, L. L. Gladkov, W. Maes, and M. M. Kruk, *J. Appl. Spectrosc.*, **86**, 389–395 (2019).
13. F. V. A. Camargo, H. L. Anderson, S. R. Meech, and I. A. Heisler, *J. Phys. Chem. B*, **119**, 14660–14667 (2015).
14. A. Visniakauskas, D. Din, M. Qourashi, I. Boczarov, M. Balaz, H. L. Anderson, and M. K. Kuimova, *Chem. Eur. J.*, **23**, 11001–11010 (2017).
15. K. Tsukahara, M. Tsunumori, and Y. Yamamoto, *Inorg. Chim. Acta*, **118**, L21–L22 (1986).
16. Y. Mori, M. Sasaki, C. Daian, S. Yamada, and K. Maeda, *Bull. Chem. Soc. Jpn.*, **65**, 3358–3361 (1992).
17. Y. H. Ajeeb, A. A. Minchenya, P. G. Klimovich, W. Maes, and M. M. Kruk, *J. Appl. Spectrosc.*, **86**, 788–794 (2019).
18. T. Gensch, C. Viappiani, and S. Braslavsky, *J. Am. Chem. Soc.*, **121**, 10573–10582 (1999).
19. G. Akerlof, *J. Am. Chem. Soc.*, **54**, 4125–4139 (1932).
20. A. Cattenecio, Y. Dariuch, and C. Magallanes, *Chem. Phys. Lett.*, **367**, 669–671 (2003).

21. G. M. Williams and P. Hambright, *Inorg. Chem.*, **19**, 562–578 (1980).
22. M. Presselt, W. Dehaen, W. Maes, A. Klamt, T. J. Martinez, W. J. D. Beenken, and M. M. Kruk, *Phys. Chem. Chem. Phys.*, **17**, 14096–14106 (2015).
23. I. V. Vershilovskaya, S. Stefani, P. Verstappen, T. H. Ngo, I. G. Scheblykin, W. Dehaen, W. Maes, and M. M. Kruk, *Macroheterocycles*, **10**, 257–267 (2017).
24. I. Ya. Bershtein and Yu. L. Kaminskii, *Spectrophotometric Analysis in Organic Chemistry* [in Russian], Khimiya, Moscow (1986).
25. M. O. Senge, S. A. MacGovan, and J. O'Brien, *Chem. Commun. (Cambridge, U. K.)*, **51**, 17031–17063 (2015).
26. C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, VCH, Weinheim, Fed. Rep. Germany (1988).
27. K. S. Krasnov (ed.), *Physical Chemistry*, in 2 books, *Electrochemistry. Chemical Kinetics and Catalysis, Textbook for Higher Education Institutions* [in Russian], Vysshaya Shkola, Moscow (2001).
28. M. V. Vol'kenshtein, *Biophysics* [in Russian], Nauka, Moscow (1988).
29. H. Hamaguchi, *Bull. Chem. Soc. Jpn.*, **21**, 991–997 (2018).
30. D. M. Carey and G. M. Korenowski, *J. Chem. Phys.*, **108**, 2669–2676 (1998).