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ТЕРМОХИМИЯ РАСТВОРЕНИЯ ТЕТРАХЛОРИДА 5,10,15,20-ТЕТРАКИС(1'-КАРБОКСИМЕТИЛПИРИД-4-ИЛ)ПОРФИРИНА И 5,10,15,20-ТЕТРАКИС(1'-КАРБОКСИМЕТИЛПИРИД-4-ИЛА) ТЕТРАБРОМИД ПОРФИРИНА 298.15 К

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Синтезированы 5,10,15,20-тетракис(1'-карбоксиметилпирид-4-ил) порфирин тетрахлорид (1) и 5,10,15,20-тетракис(1'-карбоксиметилпирид-4-ил)порфирин тетрабромид (2). Растворимые в воде производные тетрапиридилпорфина представляют собой соли галогенидов с многозарядными катионами со сложной ароматической структурой. Значения стандартных энтальпий образования соединений рассчитывали с использованием метода аддитивных групп, основанного на групповой систематике с классификацией фрагментов типа Бенсона, которая учитывает влияние первичного окружения для атомов. Тепловые эффекты растворения кристаллических тетрапиридилпорфинов (1) и (2) в воде и в водных растворах КОН при 298,15 К определяли прямым калориметрическим методом. Интегральные энтальпии растворения измерялись на калориметре переменной температуры с изотермической оболочкой. Реакционная часть калориметра и все внутренние части, контактирующие с раствором, изготовлены из титанового сплава ВТ1-0. Объем калориметрической ячейки составлял ~60 см^3. Стабильность системы термостатирования при калориметрических измерениях поддерживалась с точностью 10^{-3} К. Работу установки проверяли по интегральной энтальпии растворения кристаллического хлорида калия в воде. Впервые получены значения стандартных энтальпий образования тетрапиридилпорфинов и продуктов их диссоциации в водном растворе. Они являются ключевыми величинами в термохимии этих соединений, открывают возможность проведения строгих термодинамических расчетов в системах с тетрапиридилпорфином. Различия в термодинамических параметрах для порфиринов (1) и (2) связанны, очевидно, с влиянием разных по своей природе противоионов (хлоридом или бромидом). Это открывает возможность использовать полученные калориметрические данные для идентификации этих ионов, что может быть полезно в некоторых областях промышленности. Сложность и многообразие структур порфиринов определяет специфику их поведения в химических реакциях и физико-химических процессах, имеющих место в растворах.

Ключевые слова: термодинамика, растворы, калориметр, энтальпия, константа, тетрапиридилпорфины

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THERMOCHEMISTRY OF THE DISSOLUTION OF 5,10,15,20-TETRAKIS(1'-CARBOXYMETHYL-PYRID-4-YL)PORPHYRIN TETRACHLORIDE AND 5,10,15,20-TETRAKIS(1'- CARBOXYMETHYL -PYRID-4-YL)PORPHYRIN TETRABROMIDE AT 298.15 K

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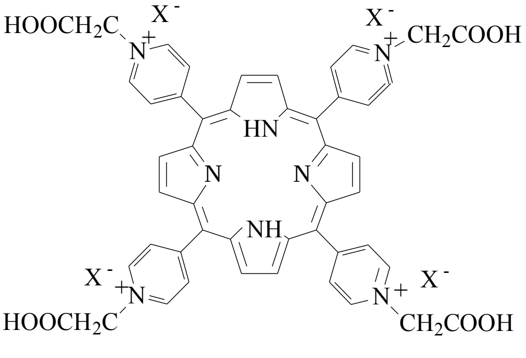
5,10,15,20-tetrakis(1'-carboxymethylpyrid-4-yl)porphyrin tetrachloride (1) and 5,10,15,20-tetrakis(1'-carboxymethylpyrid-4-yl)porphyrin tetrabromide (2) were synthesized. Water-soluble tetrapyridylporphine derivatives are salts of halides with multicharged cations with a complex aromatic structure. Thermal effects of dissolution of crystalline tetrapyridylporphins (1) and (2) in water and in aqueous solutions of KOH at 298.15 K were determined by direct calorimetric method. The integral enthalpies of dissolution were measured on a variable temperature calorimeter with an isothermal shell that we designed. The reaction part of the calorimeter and all internal parts in contact with the solution are made of titanium alloy VT-1. The volume of the calorimetric cell was ~60 cm^3. The stability of the thermostating system during calorimetric measurements was maintained with an accuracy of 10^{-3} K. The standard enthalpies of formation of compounds were calculated using the additive group method. This method takes into account the influence of the primary environment for atoms. The values of the standard enthalpy of tetrapyridylporphine formation and its dissociation products in an aqueous solution were obtained for the first time. They are key quantities in the thermochemistry of this compound, open up the possibility of conducting rigorous thermodynamic calculations in systems with tetrapyridylporphine. The differences in thermochemistry of porphyrins (1) and (2) related to different counter-ion (chloride or bromide) opens a possibility to use solution calorimetry for distinguishing between these ions, which can be useful in some industrial applications.

Key words: thermodynamics, solutions, calorimeter, enthalpy, constant, tetrapyridylporphines

The complexity and diversity of porphyrin structures determines the specifics of their behavior in chemical reactions and physicochemical processes taking place in solutions. The application of the thermochemical method to the study of the solvation properties of porphyrin molecules is of great practical and theoretical interest, since it allows us to directly characterize the energy of interparticle interactions in solution. Most physicochemical studies of porphyrins and their complexes have been performed in non-aqueous media. The same applies to thermochemical measurements. It is characteristic that foreign researchers, despite the presence of commercially available precision calorimetric measurement techniques, practically did not deal with the issues of solvation of porphyrins in solutions [1-4].

In this work, the 5,10,15,20-tetrakis(1'-carboxymethylpyrid-4-yl)porphyrin tetrachloride (**1**) and 5,10,15,20-tetrakis(1'-carboxymethylpyrid-4-yl)porphyrin tetrabromide (**2**) were chosen as the objects of research (Fig. 1).



$X^- = Cl, Br$

Fig. 1. 5,10,15,20-tetrakis(1'-carboxymethylpyrid-4-yl)porphyrin tetrachloride (**1**) and 5,10,15,20-tetrakis(1'-carboxymethylpyrid-4-yl)porphyrin tetrabromide (**2**)

Рис. 1. Тетрахлорид 5,10,15,20-тетракис(1'-карбоксиметилпирид-4-ил)порфирина (**1**) и тетрабромид 5,10,15,20-тетракис(1'-карбоксиметилпирид-4-ил)порфирин (**2**)

Previously, the authors [5] noted that tetrapyridylporphine derivatives substituted in pyridyl fragments by hydrophilic functional groups are the most convenient model compounds of porphyrins, which are of significant interest for the study of the state, solvation and reactivity of porphyrins in aqueous media. In particular, the enthalpies of dissolution of meso-tetrakis(1'-methylpyrid-4- and 3-yl)porphyrin tetratosylates in water, alcohol and phosphate buffer were measured earlier by the authors [5]. The effect of peripheral substitution and the anion of the porphyrin molecule on the enthalpy of solvation has been studied by calorimetry and uv-vis spectroscopy. It is established that the nature of the anion and the isomer of the pyridylporphyrin substituent significantly affects the thermochemical characteristics of the transition of compounds into solution. In particular, it was found that porphyrin tosylates are solvated several times better than their iodide analogues [6].

In this regard, in order to study the energy of interparticle interactions in solutions that are most accurately determined by the calorimetric method, the processes of dissolution of compound **1** and **2**, differing in the nature of the anion, in water and aqueous solutions of KOH at a temperature of 298.15 K. For the first time, the calculation of the standard enthalpy of formation ($\Delta_f H^0$) of these porphyrins was carried out.

EXPERIMENTAL PART

Water-soluble porphyrins alkylated by carboxymethyl groups were synthesized by quaternizing of corresponding *5,10,15,20*-tetra(pyrid-4-yl)porphine.

5,10,15,20-Tetra(pyrid-4-yl)porphyrin. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 9.06 d (8H, 2'-H, 3,5'-H, $J = 5.7$,), 8.89 s (8H, β-H), 8.21 d (8H, 2,6'-H, $J = 5.7$), –2.80 s (2H, NH).

Compounds (**1**) and (**2**) were synthesized according to the method [7].

5,10,15,20-Tetrakis(1'-carboxymethyl-pyrid-4-yl)porphyrin tetrachloride (**1**). UV-vis (H_2O) λ_{max} (lgε) нм: 641 (3.65), 585 (4.81), 554 (3.80), 518 (4.21), 422 (5.59). FT-IR (KBr, см$^{-1}$): 807 (δ(C-H)); 1550 (δ(N-H)); 1436 (ν(C-C)); 1186 (ν(C-N)); 1466 (ν(C=C), 1592 (ν(C=N)); 3129 (ν(C-H)); 3468 (ν(N-H)); 3419 (ν(O-H)); 1023 (ν(C-O)); 1640 (ν(-CH_2-COO^-)).

5,10,15,20-Tetrakis(1'-carboxymethyl-pyrid-4-yl)porphyrin tetrabromide (**2**). UV-vis (H_2O) λ_{max} (lgε) нм: 641 (3.81), 585 (4.32), 554 (4.31), 518 (4.72), 422 (5.44). FT-IR (KBr, см−1): FT-IR (KBr, см$^{-1}$): 807 (δ(C-H)); 1551 (δ(N-H)); 1440 (ν(C-C)); 1191 (ν(C-N)); 1466 (ν(C=C), 1591 (ν(C=N)); 3125 (ν(C-H)); 3473 (ν(N-H)); 3421 (ν(O-H)); 1023 (ν(C-O)); 1642 (ν(-CH_2-COO^-)).

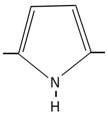
UV-vis spectra of solutions porphyrins were recorded with SF-56 spectrophotometer (LOMO, Russia). FT-IR spectra of water-soluble porphyrins **1-2** and pyridinium salts were recorded on a VERTEX 80v spectrometer with a KBr pellet in the wave number range from 4000-400 cm^{-1}. ^{1}H NMR experiments were performed in DMSO-d_6 on a Bruker 500 NMR spectrometer.

The integral enthalpies of dissolution were measured on a variable temperature calorimeter with an isothermal shell that we designed [8]. The reaction part of the calorimeter and all internal parts in contact with the solution are made of titanium alloy VT-1. The volume of the calorimetric cell was ~60 cm^3. The stability of the thermostating system during calorimetric measurements was maintained with an accuracy of 10^{-3} K. The thermometric and energy sensitivities of the calorimeter were $2 \cdot 10^{-4}$ K·mm^{-1} and $1 \cdot 10^{-3}$ J·mm^{-1} of the scale of the recording instrument. The thermal effect was compensated by electric current. To assess the accuracy and reliability of the calorimetric setup, we measured the thermal effects of KCl dissolution in water at 298.15 K. From ten independent measurements of the enthalpies of KCl dissolution in H_2O and data on dilution enthalpies, we obtained the standard value $\Delta_{sol}H^0 = 17.23 \pm 0.06$ kJ·mol^{-1}, which is in good agreement with the recommended value in the literature (17.22 ± 0.04 kJ·mol^{-1}) [9].

Table 1

Numerical values of energy contributions to the values of the enthalpy of formation according to the Benson classification

***Таблица 1.* Численные значения энергетических вкладов в значения энтальпии образования по классификации Бенсона**

№	Group	Number ofgroups (n)	$-\Delta_f H^0_{(cr)i}$, kJ·mol^{-1}
1	(C)-COOH	4	453.30±2.30 [13]
2		2	-330.00±41.13 [12]*
3	$(C)_3$-CH	12	-19.90±29.30 [13]
4	$(C)_3$-N	6	-102.00±64.30 [13]
5	$(C)_4$-C	8	-9.40 [11]
6	$(C)_3$(N)-C	4	15.48 [10]
7	$(C)_2$(N)-CH	8	21.60±20.40 [13]
8	(C)(N)-CH_2	4	42.60±20.60 [13]
9	Cl^-	4	15.90 [10]
10	Br^-	4	20.92 [10]

*The contribution value and the error are calculated based on the error of the experimental values of the enthalpy of formation of 2,4-dimethyl-3-ethyl-5-carbethoxypyrrole [$(Me)_2$EtCEOP] and 5.5-dicarbethoxy-4,4-dimethyl-3,3-diethyldipyrrolylmethane-2,2- [$(CEO)_2(Me)_2(Et)_2$DPM]

*Величина вклада и погрешность рассчитаны исходя из погрешности экспериментальных значений энтальпии образования 2,4-диметил-3-этил-5-карбэтоксипиррола [$(Me)_2$EtCEOP] и 5,5-дикарбэтокси-4,4.-диметил-3,3-диэтилдипирролилметан-2,2-[$(CEO)_2(Me)_2(Et)_2$DPM]

RESULTS AND DISCUSSION

The values of the standard enthalpies of formation of porphyrins (**1**) and (**2**) are calculated using the additive group method. This method is based on the fact that in the disproportionation reaction (ABA + + CBC → 2ABC, where A, B, C are atoms or groups), the change in the thermodynamic functions of the system is associated only with a change in symmetry. This circumstance makes it possible to calculate the thermodynamic functions of organic substances by summing the thermodynamic values of the fragments or groups that make up the molecule.A group is a central atom together with ligands, for example, a carbon atom in an alkane bonded to three hydrogen atoms and one carbon atom ($C\text{–}(H)_3(C)$). The carbon atoms of aromatic compounds, alkenes and alkynes are marked with subscripts: C_b, C_d, C_t. For the nitrogen atom in various compounds, the following designations are accepted: N - nitrogen with simple bonds; N_I is nitrogen with a double bond in imines; $N_I\text{–}(C_b)$ is nitrogen in pyridine; N_a is nitrogen with a double bond in azo compounds [10-12].

The initial data for the calculation of $\Delta_f H^0_{(cr)}$ = = -695.92 ± 86.78kJ·mol^{-1} (**1**) and $\Delta_f H^\circ_{(cr)}$ =-716.00 ± ± 86.78kJ·mol^{-1} (**2**) of the test compounds is given in Table 1.

The process of dissolution of compounds (**1**) and (**2**) in water can be represented by the scheme:

$$H_4P(cr) + nH_2O = H_4P\ (sol., nH_2O). \qquad (1)$$

Table 2

Enthalpy of dissolution of compounds (1) and (2) in water at 298.15 K

***Таблица 2.* Энтальпия растворения соединений (1) и (2) в воде при 298,15 К**

m, comp. (**1**), g	$m \cdot 10^3$, mol H_2P /1000 g H_2O	n, mol H_2O/mol H_4P	$\Delta_{sol}H$, kJ·mol^{-1}	$\Delta_f H^0$(H_2P, sol., nH_2O, 298.15К)
0.0101	0.2351	230616	56.23±(0.25)*	-639.63
0.0113	0.2631	206126	56.35	-639.51
0.0126	0.2933	184859	56.48	-639.38
0.0205	0.4773	113620	56.69	-639.17
0.0313	0.7287	74416	56.82	-639.04
0.0404	0.9406	57654	57.23	-638.63
0.0481	1.1190	48424	57.59	-638.27
m, comp. (**2**), g	$m \cdot 10^3$, mol H_4P /1000 g H_2O	n, mol H_2O/mol H_4P	$\Delta_{sol}H$, kJ·mol^{-1}	$\Delta_f H^0$(H_4P, sol., nH_2O, 298.15К)
0.0092	0.1817	298321	76.50±(0.25)*	-639.5
0.0103	0.2035	266462	76.56	-639.44
0.0132	0.2608	207921	76.82	-639.18
0.0215	0.4248	127653	76.89	-639.11
0.0314	0.6204	87406	76.99	-639.01
0.0422	0.8338	65036	77.09	-638.91
0.0501	0.9900	54781	77.12	-638.88

*error in thermal effects of compounds (1) and (2) dissolution in water

*ошибка в тепловых эффектах растворения соединений (1) и (2) в воде

The standard enthalpy of formation of a solution of compounds (**1**) and (**2**) at different dilutions was calculated by the equation:

$$\Delta_f H^0(H_4P, \text{sol., n}H_2O, 298.15\ K) = \Delta_f H^0(H_4P, \text{cr., } 298.15\ K) + \Delta_{sol} H(H_4P, \text{cr., } 298.15\ K), \quad (2)$$

where $\Delta_f H^0(H_4P$, cr., 298.15 K) is the standard enthalpy of formation of crystalline porphyrin; $\Delta_{sol} H(H_4P$,cr., 298.15 K) is the heat of dissolution of porphyrin. The experimental data are presented in Table 2.

The standard enthalpy of formation of porphyrin in a hypothetically undissociated state upon final dilution in an aqueous solution was found using the equation:

$$\Delta_f H^0(H_4P, \text{sol., n}H_2O, \text{hyp. nedis., } 298.15\ K) = \Delta_f H^0(H_4P, \text{sol., n}H_2O, 298.15\ K) - \alpha_1 * \Delta_{dis} H^0{}_1 - \alpha_2 * \Delta_{dis} H^0{}_2 - \alpha_3 * \Delta_{dis} H^0{}_3 - \alpha_4 * \Delta_{dis} H^0{}_4, \quad (3)$$

where α_i are fractions of particles H_3P^-, H_2P^{2-}, HP^{3-}, P^{4-} respectively; $\Delta_{dis} H^0{}_i$ were calculated by using the HEAT computer program.

We used universal software (HEAT [13, 14]), which allows you to work with any user defined systems. If the changes in the enthalpy of any reactions are unknown (which is usually encountered in practice), then it is necessary to solve a system of linear equations, the form of which depends on the type of experimental setup. Thus, for an ampoule calorimeter with an isothermal shell, the expression

$$\Delta H_{exps} = \frac{1}{C_{Bjs}} \sum_{i=1}^{N} \Delta a_{is}\, \Delta H_i, \quad (4)$$

where ΔH_{exps} is the experimentally determined thermal effect in series s, C_{Bjs} is the total concentration of the reagent *B*j in experimental series s, relative to which ΔHexps, Δais are calculated change in the equilibrium concentration of the product i^{th} reaction in the experimental series *s*, *N* is the total number of reactions, ΔH_i – enthalpy change i^{th} reaction. The obtained values are presented in Table 3.

Table 3

Enthalpies of stepwise dissociation of compounds (1) and (2) at a temperature 298.15 К (kJ·mol⁻¹)

***Таблица 3.* Энтальпии ступенчатой диссоциации соединений (1) и (2) при температуре 298,15 К (кДж·моль⁻¹)**

Process	p*K*i [7]	$\Delta_r H_{dis}$, kJ·mol⁻¹ (compounds **1**)	p*K*i	$\Delta_r H_{dis}$, kJ·mol⁻¹ (compounds **2**)
$H_4P \to H_3P^- + H^+$	3.25±0.26	25.9±2.5	3.11±0.50	27.1±2.8
$H_3P^- \to H_2P^{2-} + H^+$	5.34±0.33	43.3±2.7	6.01±0.56	53.3±2.7
$H_2P^{2-} \to HP^{3-} + H^+$	8.26±0.36	76.4±2.9	7.89±0.52	79.8±2.6
$HP^{3-} \to P^{4-} + H^+$	9.02±0.53	93.4±2.6	9.34±0.56	111.8±2.9

The equilibrium composition of the solutions was calculated using the KEV program [15]. The paper describes an algorithm for determining unknown equilibrium constants from UV-Vis or potentiometric experimental data using a minimizing function (maximum likelihood method). Recommendations are given for estimating the equilibrium constants from experimental data. We found thatthe fractions of particles H_3P^-, H_2P^{2-}, HP^{3-}, P^{4-} were no morethan $2.8 \cdot 10^{-3}$; $1.3 \cdot 10^{-4}$; $3.5 \cdot 10^{-6}$and $4.8 \cdot 10^{-7}$, respectively. The total contribution from the summands ($\alpha_1 * \Delta_{dis} H^0{}_1 + \alpha_2 * \Delta_{dis} H^0{}_2 + \alpha_3 * \Delta_{dis} H^0{}_3 + \alpha_4 * \Delta_{dis} H^0{}_4$) in the right part of Eq. (3) thus did not exceed 0.06 kJ·mol⁻¹ and changed slightly in the studied range of concentrations, due to which these contributions can be ignored. From the Table 2 it can be seen that the heat of formation of compounds (**1**) and (**2**) in an aqueous solution in the studied concentration range practically does not depend on the dilution value, which is not surprising for such large dilutions.

In order to calculate the standard enthalpy of formation of compounds (**1**) and (**2**) in a hypothetical undissociated state at infinite dilution, we built Fig.2. These values were found by extrapolating the values obtained by equation (4) to the zero value of the molality *m* of the solution (Fig. 2).

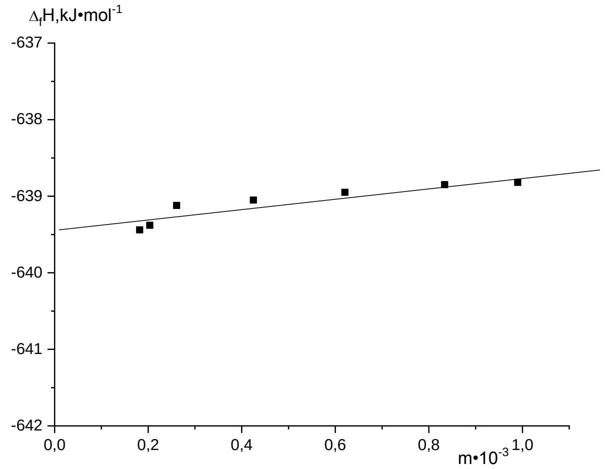


Fig. 2. Graphical definition of the standard enthalpy of formation H_4P particles in aqueous solution

Рис. 2. Графическое определение стандартной энтальпии образования частиц H_4P в водном растворе

According to least squares, we found:

compound (**1**)

$$\Delta_f H^\circ(H_4P, \text{sol.}H_2O, \text{std. s., hyp. non-dis., } 298.15\ K) = -639.9 \pm 1.9\ \text{kJ·mol}^{-1},$$

compound (**2**)

$$\Delta_f H°(H_4P, \text{sol. } H_2O, \text{std. s., hyp. non-dis, } 298.15\ К) = \\ = -639.4 \pm 1.9\ \text{kJ·mol}^{-1}.$$

We also used the second method. An independent series of experiments was carried out to determine the enthalpies of dissolution of the studied compounds (**1**), (**2**) in alkaline solutions at an equivalent ratio of at least 1:4. This was done to independently determine the standard enthalpy of formation of P^{4-} particles and other products of the dissociation of compounds (**1**), (**2**) in an aqueous solution.

The process of dissolving in a KOH solution can be represented by the following scheme:

$$\begin{gathered} H_4P(\text{cr.}) + 4OH^-(\text{sol.}, nH_2O) \rightarrow \\ \rightarrow P^{4-}(\text{sol.}, nH_2O) + 4H_2O. \qquad (5) \end{gathered}$$

The experimental data of thermal effects of the dissolution of crystalline compounds (**1**) and (**2**) in aqueous solutions КОН at 298.15 K are presented in Fig. 3 and Table 4.

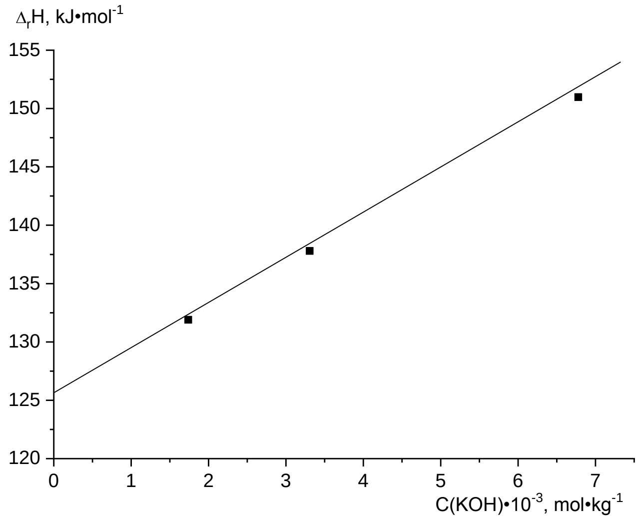


Fig. 3. Graphical determination of the enthalpy of dissolution of H_4P in KOH solution at infinite dilution

Рис. 3. Графическое определение энтальпии растворения H_4P в растворе КОН при бесконечном разбавлении

In order to obtain the thermal effects of dissolution of compounds (**1**) and (**2**) at zero ionic strength, we used the equation presented in [16]. It is designed to calculate the standard thermodynamic characteristics of reactions in solution - equilibrium constants, thermal effects, and so on at zero ionic strength according to experimental data relating to solutions with finite ionic strength.

Graphical extrapolation of the heats of dissolution of the compounds under study in potassium hydroxide solutions to zero ionic strength is shown in Fig. 2.

Using the values of the standard enthalpies of formation of hydroxide ion and water (H_2O) in an aqueous solution, we calculated the standard enthalpy of formation of the deprotonated P^{4-} ion:

$$\begin{gathered} \Delta_f H°(P^{4-}, \text{sol.}, H_2O, \text{std. s.}, 298.15\ К) = \\ = \Delta_f H°(H_4P, \text{cr.}, 298.15\ К) + \\ + 4\Delta_f H°(OH^-, \text{sol.}, H_2O, \text{std. s.}, 298.15\ К) + \\ + \Delta_r H°_{(6)} - 4\ \Delta_f H°(H_2O, \text{liq.}, 298.15\ К). \qquad (6) \end{gathered}$$

The standard enthalpies of formation of HP^{3-}, H_2P^{2-}, H_3P^-, H_4Pparticles in an aqueous solution were calculated using the equations:

$$\begin{gathered} \Delta_f H°(HP^{3-}, \text{sol.}, H_2O, \text{std.}, \text{hyp.}, \text{non} - \\ -\text{dis.}, 298.15\ К) = \Delta_f H°(P^{4-}, \text{sol.}, \\ H_2O, \text{std.}, 298.15\ К) - \\ -\Delta_{dis} H°(HP^{3-}, 298.15\ К). \qquad (7) \end{gathered}$$

$$\begin{gathered} \Delta_f H°(H_2P^{2-}, \text{sol.}, H_2O, \text{std.}, \text{hyp.}, \text{non} - \\ -\text{dis.}, 298.15\ К) = \Delta_f H°(HP^{3-}, \text{sol}, \\ H_2O, \text{std. hyp.}, \text{non} - \text{dis.}, 298.15\ К) - \\ -\Delta_{dis} H°(H_2P^{2-}, 298.15\ К). \qquad (8) \end{gathered}$$

$$\begin{gathered} \Delta_f H°(H_3P^-, \text{sol.}, H_2O, \text{std.}, \text{hyp.}, \text{non} \\ -\text{dis.}, 298.15\ К) = \Delta_f H°(H_2P^{2-}, \text{sol}, \\ H_2O, \text{std. hyp.}, \text{non} - \text{dis.}, 298.15\ К) - \\ -\Delta_{dis} H°(H_3P^-, 298.15\ К). \qquad (9) \end{gathered}$$

$$\begin{gathered} \Delta_f H°(H_4 P, \text{sol.}, H_2O, \text{std.}, \text{hyp.}, \text{non} - \\ -\text{dis.}, 298.15\ К) = \Delta_f H°(H_3P^-, \text{sol}, \\ H_2O, \text{std. hyp.}, \text{non} - \text{dis.}, 298.15\ К) - \\ -\Delta_{dis} H°(H_4 P, 298.15\ К). \qquad (10) \end{gathered}$$

The thermodynamic characteristics of porphyrin dissolution will allow us to obtain a lot of useful information about the state of tetrapyridylporphine in solutions. Moreover, the study of porphyrin solvation can also shed light on the behavior of other related macrocycles, such as phthalocyanines. These molecules have similar structures and properties to porphyrins, and their solvation behavior can be studied using

Table 4

Solubility enthalpies of 5,10,15,20-tetrakis(1'- carboxymethyl -pyrid-4-yl)porphyrin tetrabromide in KOH solution at various concentrations and T = 298.15 K

Таблица 4. **Энтальпии растворимости тетракис(1'-карбоксиметилпирид-4-ил)порфирина тетрабромида в растворе КОН при различных концентрациях и T = 298,15 K**

m, g	C_{KOH}, mol kg^{-1}	$-\Delta_{sol}H$, kJ mol^{-1}
0.00221	$1.739 \cdot 10^{-4}$	131.9±0.40
0.00222		131.8±0.35
0.00220		131.9±0.41
0.00421	$3.308 \cdot 10^{-4}$	137.7±0.40
0.00422		137.5±0.30
0.00420		137.9±0.42
0.00863	$6.778 \cdot 10^{-4}$	150.9±0.40
0.00862		150.9±0.42
0.00861		151.0±0.39

similar methods. The values of the standard enthalpy of porphyrin formation in an aqueous solution are obtained in this work for the first time. Overall, the study of solvation properties of porphyrin molecules is an important area of research. The use of thermochemical methods can provide valuable insights into the behavior of these molecules in solution and their applications in various fields. The obtained values are presented in Table 5.

Table 5

Standard enthalpies of formation of 5,10,15,20-tetrakis(1'-carboxymethyl-pyrid-4-yl)porphyrin tetrachloride and 5,10,15,20-tetrakis(1'- carboxymethyl -pyrid-4-yl)porphyrin tetrabromide and products of its dissociation in aqueous solution (kJ·mol^{-1})

Таблица 5. **Стандартные энтальпии образования 5,10,15,20-тетракис(1'-карбоксиметилпирид-4-ил)тетрахлорида порфирина и 5,10,15,20-тетракис(1'-карбоксиметилпирид-4-) ил)тетрабромид порфирина и продуктов их диссоциации в водном растворе (кДж•моль$^{-1}$)**

Particle	State	$\Delta_f H^\circ$(298,15 K), kJ·mol^{-1} (compounds (1))	$\Delta_f H^\circ$(298,15 K), kJ·mol^{-1} (compounds (2))
H_4P	cr.	-695.9±1.9	-716.0±1.9
	sol., H_2O, std. s., hyp. non-dis.	-639.9±2.9	-639.4±2.9
H_3P^-	sol., H_2O, std. s., hyp. non-dis	-613.9±2.9	-612.3±2.9
H_2P^{2-}	sol., H_2O, std. s., hyp. non-dis.	-570.7±2.9	-559.0±2.9
HP^{3-}	sol., H_2O, std. s., hyp. non-dis	-494.3±2.9	-479.2±2.9
P^{4-}	sol, H_2O, std. s.	-400.8±2.9	-367.4±2.9

CONCLUSIONS

Water-soluble cationic pyridyl-substituted porphyrins are widely studied as model compounds and new materials for their possible use as sensitizers. Even for fairly simple cases, it is difficult to quantify the thermodynamic aspects of the behavior of sensitizers in solution. We present new experimental information on the dissolution of these structurally complex macrocyclic compounds in aqueous and aqueous-alkaline solutions. The dependence of the influence of their structure on the thermochemical characteristics of their dissolution is shown. We hope that the results of our study and the calculated thermodynamic characteristics of the dissolution of tetrapyridylporphyrin derivatives will be useful in further studies of this series of compounds in aqueous solutions and the solid phase. The thermal effects of dissolution of compounds (1) and (2) in water differ from each other by 20 kJ·mol^{-1}, and when these substances are dissolved in aqueous solutions of alkaline, the sign of the thermal effect changes. Such significant differences in thermal effects can be considered as a potential tool for distinguishing Cl^-, Br^-, OH^- ions in an aqueous solution. The physicochemical study of bioligand solutions is a very urgent task for today [17-27].

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