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ТЕРМОХИМИЧЕСКОЕ ИССЛЕДОВАНИЕ РЕАКЦИЙ КИСЛОТНО-ОСНОВНОГО ВЗАИМОДЕЙСТВИЯ В ВОДНОМ РАСТВОРЕ ПИРИДОКСИНА

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Витамин B_6 - один из самых важных витаминов, необходимых для жизнедеятельности живых организмов. Витамин B_6 в организме представлен коферментными формами – пиридоксальфосфатом и пиридоксаминфосфатом, входит в состав более чем 100 ферментов. В качестве объекта исследования мы выбрали пиридоксин. Прямым калориметрическим методом измеряли тепловые эффекты взаимодействия раствора пиридоксина с растворами азотной кислоты и гидроксида калия при 298,15 К и значениях ионной силы 0,25; 0,5 и 0,75, фоновый электролит нитрата калия. Измерения проводились в калориметре с изотермической оболочкой, оснащенной реакционным сосудом объемом 60 см^3 и электрической калибровкой, при Т = 298,15 ± 0,01 К и Р = 100,5± 0,7 кПа, а также автоматической записью кривой темпера-время. Относительная погрешность измерения для теплоты растворения стандартного вещества составляла 0,1-0,3%. Расчет равновесного состава системы с учетом процессов ступенчатой диссоциации и диссоциации воды проводился по программе KEV. Тепловые эффекты диссоциации пиридоксина в стандартном растворе были обнаружены путем экстраполяции теплоты ступенчатой диссоциации при фиксированных значениях ионной силы на нулевое значение ионной силы раствора. Поскольку тепловые эффекты разбавления измерялись в трех диапазонах концентраций KNO_3, то число экспериментов в каждой серии было не менее трех. Для расчета доверительного интервала среднее значение критерия Стьюдента ΔH было взято при доверительном интервале 0,95. Рассчитаны стандартные термодинамические характеристики ($\Delta_rH°$, $\Delta_rG°$, $\Delta_rS°$) реакций кислотно-основного взаимодействия в водных растворах пиридоксина. С увеличением концентрации фоновой концентрации электролита увеличивается эндотермичность процессов ступенчатой ионизации пиридоксина.

Ключевые слова: термодинамика, растворы, химия, калориметр, пиридоксин

THERMOCHEMICAL STUDY OF ACID-BASE REACTIONS IN AQUEOUS SOLUTION OF PYRIDOXINE

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Vitamin B_6 is one of the most important vitamins necessary for the life of living organisms. Vitamin B_6, which in the body is represented by coenzyme forms - pyridoxal phosphate and pyridoxamine phosphate, is a part of more than 100 enzymes. As the object of study, we chose pyridoxine. The thermal effects of interaction of the solution of pyridoxine with solutions of nitric acid and potassium hydroxide at 298.15K and ionic strength values of 0.25; 0.5 and 0.75 against the background of electrolyte-supporting potassium nitrate were measured with direct calorimetric method. The measurements were carried out in a calorimeter with an isothermal shell equipped with a 60 cm^3 reaction vessel and electric calibration at T = 298.15 ± 0.01 K and P = 100.5 ± 0.7 kPa and automatic recording of the temperature-time curve. Relative measurement error for heats of dissolution of a standard substance was -0.1-0.3%. Calculation of the equilibrium composition of the system taking into account processes a step dissociation and water dissociation was carried out according to the KEV program. The thermal effects of dissociation of pyridoxine in a standard solution were found by extrapolating the heats of stepwise dissociation at fixed values of ionic strength to zero ionic strength. Since the thermal effects of dilution were measured in three concentration ranges of KNO_3, the number of experiments in each series was at least three. To calculate the confidence interval of the average value of DH the Student's criterion was taken at a confidence interval of 0.95. Standard thermodynamic characteristics (DrH°, DrG°, DrS°) of reactions of acid-base interaction in aqueous solutions of pyridoxine were calculated. With an increase in the background electrolyte concentration, the endothermicity of stepwise pyridoxine ionization processes increases.

Key words: thermodynamics, solutions, chemistry, calorimeter, pyridoxine

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Vitamin B_6 is one of the most important vitamins necessary for the life of living organisms [1-12]. The history of studies of the chemical characteristics of the group of compounds related to vitamin B_6 is more than 30 years old, but only recently has a number of aspects of their electrochemistry been revised and new information has appeared that allows us to understand the nature of their catalytic activity. Vitamin B_6, which in the body is represented by coenzyme forms - pyridoxal phosphate and pyridoxamine phosphate, is part of more than 100 enzymes. As the object of study, we chose pyridoxine ($C_8H_{11}NO_3$):

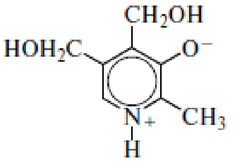

Fig. 1. Structural formula of pyridoxine molecule (HL± pH=6.9)
Рис. 1. Структурная формула молекулы пиридоксина (HL± pH=6,9)

The dissociation of pyridoxine in an aqueous solution can be represented by the scheme:

$$H_2L^+ \leftrightarrow H^+ + HL^\pm \qquad (1)$$

$$HL^\pm \leftrightarrow H^+ + L^- \qquad (2)$$

Reliable data on the pyridoxine ionization constants are available in the literature [13-17]. These works were performed at various values of ionic strength, against the background of supporting electrolytes differing in nature. In order to be able to compare the values of the stepwise dissociation constants of pyridoxine obtained by different authors, we recalculated the values of pK_1 and pK_2 to zero ionic strength. The thermodynamic constants of stepwise dissociation of pyridoxine were also determined graphically by the equation [18]:

$$pK^c = pK^o \quad - \Delta Z^2 A \frac{\sqrt{I}}{1+1.6\sqrt{I}} + \delta \cdot I \qquad (3)$$

After graphic processing of the literature data [13-17], the most probable values of the thermodynamic constants of pyridoxine dissociation can be taken at 298.15 K: pK_1^0 = 4.85 ± 0.02, pK_2^0 = 8.96 ± 0.03. In Fig. 2 shows the equilibrium diagram in an aqueous pyridoxine solution constructed on the basis of calculations of the equilibrium composition of pyridoxine solutions at various pH values using the “KEV” program [19].

Data on the heats of the reactions of the acid-base interaction with the participation of pyridoxine are not available in the literature.

The aim of this work is to study the effect of the background electrolyte concentration on the thermal effects of pyridoxine dissociation by direct calorimetry, to calculate the standard thermodynamic characteristics of acid-base reactions in pyridoxine solutions and to discuss the results.

EXPERIMENTAL PART

The choice of concentration conditions for calorimetric experiments was carried out on the basis of the equilibrium diagram in an aqueous pyridoxine solution (Fig. 2).

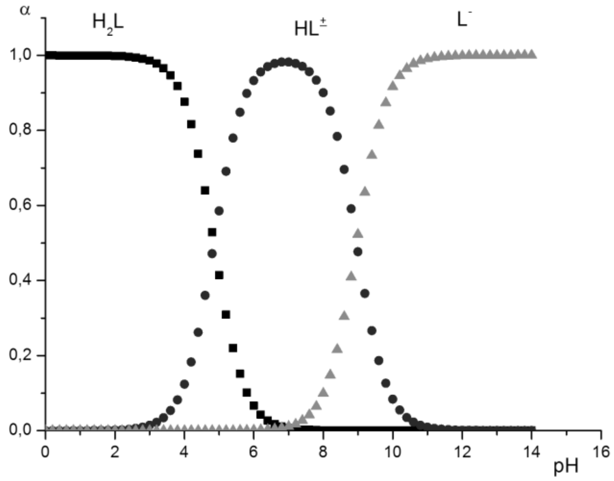

Fig. 2. The equilibrium diagram in an aqueous solution of pyridoxine at 298.15K and ionic strength of I = 0.0
Рис. 2. Диаграмма равновесий в водном растворе пиридоксина при 298,15К и ионной силе I = 0,0

Fractional distribution of particles H_2L^+, $HL^{\pm}$ and L^- at various pH values of the medium (Fig. 2) indicates the possibility of independent determination of the heats of dissociation of pyridoxine. The heats of mixing pyridoxine solutions with HNO_3 and KOH solutions were measured in various pH ranges using isoperibol calorimeter with automatic recording of the temperature – time curve [20, 21]. This type of calorimeter has successfully proven itself in many calorimetric studies of biologically active compounds both in aqueous and non-aqueous media [22-24]. The operation of the calorimetric installation was checked according to the generally accepted calorimetric standard - the heat of dissolution of crystalline potassium chloride in water. The KCl preparation was purified by double recrystallization of the “Kh.Ch.” grade reagent from bidistillate. Before taking the samples, potassium chloride was dried in an oven at 393.15 K to constant weight. Coordination of the experimentally obtained enthalpies of the dissolution of KCl(k) in water $\Delta_{sol}H(\infty H_2O) = 17.25 \pm 0.06$ kJ/mol with the most reliable literature data indicates the absence of a noticeable systematic error in the operation of the calorimetric setup [25]. Weighed portions of solutions were weighed on a VLR-200 balance with accuracy of $2 \cdot 10^{-4}$ g.

Pyridoxine (manufactured by Sigma-Aldrich USA, $C_8H_{11}NO_3$) used without preliminary purification. The purity of the reagents declared by the manufacturer was more than 98 wt. %. Solutions of the drug were prepared by dissolving weighed portions in freshly prepared bidistillate immediately before the experiment. The carbon-free KOH solution and the HNO_3 solution were prepared from the chemical grade reagent according to the usual procedure [26].

When determining the thermal effect of process (1), 0.02 M pyridoxine solution (pH = 5.5) was used as a calorimetric liquid, and an exact weighed portion of the HNO_3 solution (with a concentration of 0.8814 mol/kg solution) was respectively placed in the ampoule. After mixing the solutions, the pH was close to 4.3. The experimental data on the heats of mixing and dilution are given in Table 1.

When determining the thermal effects of process (2), the heats of interaction of an aqueous pyridoxine solution (solution concentration 0.8827 mol/kg solution) with 0.1M KOH solution, as well as the heat of dilution of the pyridoxine solution in background electrolyte solutions (KNO_3) were measured. The obtained values of the heats of mixing and dilution of pyridoxine are presented in Table 2.

Table 1

Thermal effects (J/mol) of the interaction of a 0.02M solution of pyridoxine with HNO_3 solution, T = 298.15K

Таблица 1. **Тепловые эффекты (Дж/моль) взаимодействия 0,02М раствора пиридоксина с раствором HNO_3, T = 298,15К**

I	m, g.	$\Delta_{mix}H$, J/mol	m, g.	$\Delta_{dil}H$, J/mol	α	$\Delta_{dis}H(H_2L^+)$, J/mol
0.25	0.5021	-16066	0.5001	-1052	0.8238	-18175 ± 300
	0.5021	-16052	0.5005	-1089	0.8237	
	0.5021	-16069	0.5006	-1076	0.8238	
0.5	0.5028	-16754	0.5006	-890	0.8279	-19110 ± 300
	0.5027	-16722	0.5002	-896	0.8278	
	0.5028	-16785	0.5001	-894	0.8279	
0.75	0.5026	-16307	0.5002	-394	0.7963	
	0.5025	-16300	0.5003	-383	0.7962	-20105 ± 300
	0.5026	-16310	0.5006	-362	0.7963	

Table 2

Thermal effects (J/mol) of solution interaction of pyridoxine with 0.02M solutions of KOH at T=298.15 K

***Таблица 2.* Тепловые эффекты (Дж/моль) взаимодействия раствора пиридоксина с 0,02M растворами KOH при T = 298,15K**

I	m, g	$-\Delta_{mix}H^1$, J/mol	$-\Delta_{dil}H^1$, J/mol	$-\Delta_{neut}H$, J/mol	$-\Delta_{dis}H(HL^{\pm})$, J/mol
0.25	0.5002 0.4993 0.5003	31102 31210 31298	2258 2232 2296	28845 28836 28841	28160 ± 340
		$\Delta_{mix}H$ = 31203 ± 260	$\Delta_{dil}H$ = 2262 ± 150	$\Delta_{neut}H$ = 28840 ± 260	
0.5	0.5002 0.4999 0.4998	31148 31256 31146	3804 3771 3815	27342 27351 27360	29562 ± 300
		$\Delta_{mix}H$ = 31183 ± 210	$\Delta_{dil}H$ = 3797 ± 150	$\Delta_{neut}H$ = 27351 ± 220	
0.75	0.5003 0.5000 0.4995	29744 29719 29745	4256 4225 4143	25531 25536 25543	31195 ± 310
		$\Delta_{mix}H$ = 29736 ± 200	$\Delta_{dil}H$ = 4208 ± 120	$\Delta_{neut}H$ = 25536 ± 220	

Each series of experiments included from 3 to 5 measurements. To calculate the confidence interval, the average student's criterion was taken at a confidence level of 0.95. The error was calculated by the formula: $S = t_{p,f} \times [\Sigma\Delta^2/n(n-1)]^{1/2}$, where $t_{p,f}$ is the Student criterion with a confidence level of 0.95 and the number of degrees of freedom f = 5.

RESULTS AND DISCUSSION

Thermal effect of particle dissociation H_2L^+ ($\Delta_{dis}H_{H2L}{}^+$) was calculated by the equation:

$$\Delta_{dis}H_{H2L}{}^+ = -(\Delta_{mix}H - \Delta_{dil}H)/\alpha_1 \qquad (4)$$

where $\Delta_{mix}H$ – is heat of interaction 0.1M solution HNO_3 with a solution of pyridoxine, $\Delta_{dil}H$ – is heat of dilution of a solution of a mineral acid in a solution of a background electrolyte, α_1 – is completeness of the protonation of the particle $HL^{\pm}$ ($\alpha = 0.83$). The calculation results are presented in Table 1.

The process of neutralizing an aqueous solution of pyridoxine can be represented by the equation:

$$HL^{\pm} + OH^{-} \leftrightarrow L^{-} + H_2O \qquad (5)$$

Thermal effect of dissociation ($\Delta_{dis}H_{HL}{}^{\pm}$) calculated by the equation:

$$\Delta_{neut}H = (\Delta_{mix}H^1 - \Delta_{dil}H^1)/\alpha_2 \qquad (6)$$

$$\Delta_{dis}H_{HL}{}^{\pm} = \Delta_{neut}H - \Delta H_w \qquad (7)$$

where $\Delta_{mix}H^1$ – is thermal effect of mixing a pyridoxine solution with a solution KOH; $\Delta_{dil}H^1$ – is the thermal effect of diluting a pyridoxine solution in a background electrolyte solution; α_2 – is process completeness (5) 0.99; ΔH_w – is the heat of neutralization of a strong acid with a strong base against the background of a supporting electrolyte (potassium nitrate).

The found thermal effects of pyridoxine dissociation are given in Table 2. The error is defined as the standard deviation of the average value from three to four parallel experiments.

The thermal effects of dissociation of pyridoxine in a standard solution were found by extrapolating the heats of stepwise dissociation at fixed values of ionic strength to zero ionic strength according to the equation proposed in [18]:

$$\Delta rH_i - \Delta z^2\Psi(I) = \Delta\, rH_i^0 + bI \qquad (8)$$

where, ΔrH_i, ΔrH_i^0 – is change in enthalpy at a finite value of ionic strength and at I = 0, respectively, $\Psi(I)$ – is theoretically calculated ionic strength function, Δz^2 – is the difference between the squared charges of the reaction products and the starting components, *b*- is empirical coefficient.

Points in coordinates *(ΔH-$\Delta Z^2\Psi(I)$ as a function of I)*, satisfactorily fit on a straight line. The corresponding graph is shown in Fig. 3. With an increase in the background electrolyte concentration, the endothermicity of stepwise pyridoxine ionization processes increases.

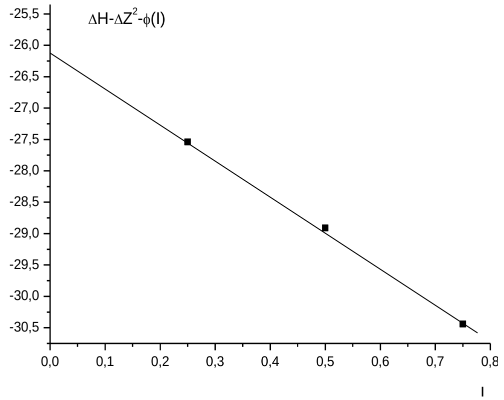

Fig. 3. Determination of standard thermal effects of HL± particle dissociation at 298.15 K

Рис. 3. Определение стандартных тепловых эффектов диссоциации частицы HL± при 298,15 K

When processing by MNC, pyridoxine dissociation enthalpies at zero ionic strength were obtained: $\Delta_{dis}H(H_2L^+)$ = -17.25 ± 0.30 kJ/mol and $\Delta_{dis}H(HL^{\pm})$ = -26.17 ± 0.30 kJ/mol.

The standard thermodynamic characteristics of the processes of stepwise dissociation of pyridoxine, obtained by us for the first time, are presented in Table 3.

Table 3

Standard thermodynamic characteristics of the processes of stepwise dissociation of pyridoxine

***Таблица 3*. Стандартные термодинамические характеристики процессов ступенчатой диссоциации пиридоксина**

T	pK^0	ΔG^0 kJ/mol	ΔrH^0, kJ/mol	$-\Delta S^0$, J/molK
$H_2L^+ = HL^\pm + H^+$				
298.15	4.85 ± 0.05	27.68 ± 0.6	-17.25 ± 0.30	150.7 ± 0.9
$HL^\pm = L^- + H^+$				
298.15	8.96 ± 0.05	51.14 ± 0.6	-26.17 ± 0.30	259.3 ± 0.9

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