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Study of complex formation of Cs^+, ZrO^{2+}, Sm^{3+}, Eu^{3+} ions with histidine in aqueous solutions

Complexation process of Cs^+, ZrO^{2+}, $Sm^{3+,}$ Eu^{3+} ions with histidine in aqueous solutions were studied using pH-titration method in the temperature range 298–318 K and ionic strength from 0.1 to 1. The stability constants of complex formation and thermodynamic parameters of complex formation (ΔH, ΔG, ΔS) were calculated on the basis of the experimental data.

Key words: histidine, metal ions, thermodynamics, enthalpy, free Gibbs energy, entropy.

Water is involved in the construction of biological structures, and plays a structural and functional role. The authors [1] showed that structure of bio-compounds was changes under the influence of water at studying the sorption and desorption of water proteins. It is known [2, 3] that the intermolecular interactions in the system «water-molecule» define the solubility of the compound and its ability to engage in a variety of biological transformation. Amino acid molecules, acting as monomer units of the protein can be used as model in the study of biological processes.

Crystalline of amino acids is formed bio-polar ions or zwitter-ions, i.e., proton protonates an amino carboxyl group in the same molecule [4]. Papers [5, 6] clearly demonstrate that the molecular crystals of molecular packing are subject to the principle of close packing.

Introduction of water molecules in the structure of amino acids, i.e. formation of co-packaging of small molecules of water and large molecules of basic compound is possible, if the solvent molecules can stay so as to realize the conditions for the formation of hydrogen bonds. Studying of metal ions with histidine molecule in hydrated state in aqueous solutions is very actual problem in field of biochemistry.

This paper presents the results of studying of the interaction of metal ions (Cs^+, ZrO^{2+}, Sm^{3+}, Eu^{3+}) with histidine aqueous solutions.

Experimental

The pH-metric measurements were carried out on the pH-meter of mark Metrohm 827 pH lab with combination electrode. Initial solutions (concentration of 10^{-3} mole/L) of metal salts and amino acids are prepared from salts accurately weighed. All standard solutions contained background electrolyte $NaNO_3$. Stirring was carried out using solutions rotor magnetic stirrer. The thermostat UTU-mark 2/77 was used in experiments with a given temperature range. The free ligand concentration $p[A] = -\lg[A]$, the preliminary formation constants of the complexes were calculated by the method of B'errum.

Results and discussion

Reactions of protolytic equalibriums of histidine in aqueous solution can be written as:

$$HN{-}C{-}CHNCH_2CH(NH_2^+)CHCOOH \leftrightarrow H^+ + HN{-}C{-}CHNCH_2CH(NH_2^+)CHCOO^-$$
$$pK = 1.82$$

and

$$HN{-}C{-}CHNCH_2CH(NH_2^+)CHCOO^- \leftrightarrow H^+ + HN{-}C{-}CHNCH_2CH(NH^+)CHCOO^-$$
$$pK = 9.00$$

It is established that, in the interval of pH > 7.5 result in cleavage of a proton from protonated nitrogen atom in the solution should appear anionic form amino acids (Fig. 1).

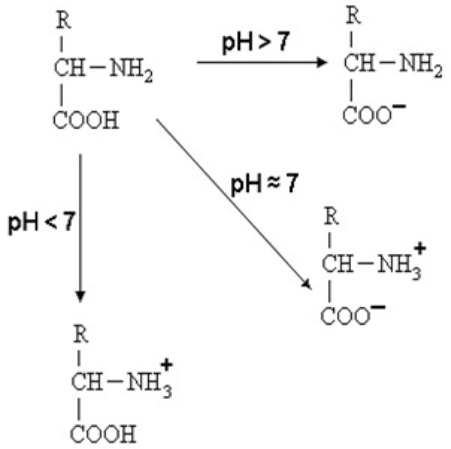

Figure 1. Dissociation of ionogenic groups of amino acids depending on the acidity of the medium

Anionic form of histidine must be appeared in a result of (Cs^+, ZrO^{2+}, Sm^{3+}, Eu^{3+}) profor from profonated nitrogen atom in solution. This potentially results in an increase of the diffusion coefficient of metal ions.

Amino acids largely loses their ability to form hydrogen bonds with the solvent, and the ion motion in a viscous medium is inhibited to a lesser extent.

The effect of the displacement of the protons from protonated ligands by the metal ions (Cs^+, ZrO^{2+}, Sm^{3+}, Eu^{3+}) is clearly observed in the case of complexation of amino acids.

The stability constants of complexes formed in result of interaction of metal ions with histidine in aqueous solution of at 298,15 K (background electrolyte is $NaNO_3$) are presented in Table 1.

Table 1

The stability constants of complexes formed in result of interaction of metal ions with histidine in aqueous solution

Process	lgβ				
	$I = 0.1$	$I = 0.25$	$I = 0.5$	$I = 0.75$	$I = 1$
Cs^+ + HNC-CHN $CH_2CH(NH_2^+)CHCOO^-$	4.23	3.94	3.45	2.97	2.48
ZrO^{2+} + HNC-CHN $CH_2CH(NH_2^+)CHCOO^-$	11.64	11.65	11.63	11.65	11.89
Sm^{3+} + HNC-CHN $CH_2CH(NH_2^+)CHCOO^-$	4.39	6. 61	7.98	9.81	11.66
Eu^{3+}+ NC-CHN$CH_2CH(NH_2^+)CHCOO^-$	15.33	15.35	15.36	15.39	15.42

The concentration stability constants of amino acid complexes with metal ions were converted into stability constant at zero ionic strength of the equation with one individual parameter [7] (Table 2):

$$\lg\beta_C - \Delta Z^2 A\frac{\sqrt{I}}{1+\sqrt{I}} = \lg\beta_0 + bI\,,$$

where $lg\beta_C$ and $lg\beta_0$ are logarithms of stability constants at finite and zero ionic strength of the solution; ΔZ^2 is difference of charge in squares of the products and initial substances of reactions; A is limiting factor of Debye-Huckel theory; b is empirical coefficient.

Table 2

The stability constants (lgβ) of complexes of histydine with metal ions at 298.15 K, $I = 0$

Cs^+	ZrO^{2+}	Sm^{3+}	Eu^{3+}
4.42	10.26	3.81	15.32

Tables 3–6 show the results of calculations of thermodynamic parameters of complex formation processes.

Table 3

Thermodynamic parameters of complex formation of histidine with Sm^{3+} ions under the influence of the ionic strength in the aqueous medium

I	298 K	303 K	308 K	313 K	318 K
$\Delta_r H_T^o$, kJ/mole					
0.1	543.53	405.40	267.27	129.14	–8.98
0.25	291.39	301.32	311.24	321.17	331.09
0.5	183.04	189.27	195.50	201.74	207.97
0.75	445.26	113.38	–218.50	–550.38	–882.26
1	690.00	26.99	–636.01	–1299.00	–1962.00
$-\Delta_r G_T^o$, kJ/mole					
0.1	25.1	37.76	45.55	56.02	67.84
0.25	32.93	42.65	48.62	60.64	73.78
0.5	40.76	47.53	51.69	60.04	69.40
0.75	48.59	52.42	54.76	54.22	54.69
1	42.28	57.31	57.83	43.18	29.65
$-\Delta_r S_T^o$. J/mole·K					
0.1	1908.18	1487.15	1049.77	621.36	1970.51
0.25	1088.35	1154.27	1207.62	1281.26	1358.67
0.5	751.00	794.66	829.52	878.47	930.79
0.75	1657.24	556.40	549.44	1664.94	2777.06
1	2457.34	282.91	1940.18	4214.18	6484.44

Table 4

Thermodynamic parameters of complex formation of histidine with Cs^{+} ions under the influence of the ionic strength in the aqueous medium

I	298 K	303 K	308 K	313 K	318 K
$\Delta_r H_T^o$. kJ/mole					
0.1	477.98	223.04	–31.88	–286.81	–541.74
0.25	456.95	222.00	–12.94	–247.89	–482.84
0.5	421.92	220.27	18.62	–183.02	–384.67
0.75	386.89	218.54	50.19	–118.15	–286.5
1	351.85	216.80	81.76	–53.28	–188.33
$-\Delta_r G_T^o$. kJ/mole					
0.1	24.15	22.49	19.72	16.95	14.18
0.25	29.94	28.10	25.03	21.95	18.88
0.5	24.64	21.38	15.95	10.52	5.09
0.75	23.71	24.35	25.40	26.46	27.52
1	22.84	22.32	21.44	20.57	19.69
$-\Delta_r S_T^o$. J/mole·K					
0.1	1685.00	823.96	40.79	905.55	1770.32
0.25	1633.90	839.29	40.56	758.16	1556.90
0.5	1498.50	810.94	116.04	578.85	1273.75
0.75	1377.90	815.07	253.70	307.67	869.04
1	1257.40	802.45	346.34	109.76	565.86

Table 5

Thermodynamic parameters of complex formation of histidine with ZrO^{2+} ions under the influence of the ionic strength in the aqueous medium

I	298 K	303 K	308 K	313 K	318 K
$\Delta_r H_T^o$. kJ/mole					
0.1	119.25	123.30	127.37	131.43	135.49
0.25	121.63	125.77	129.91	134.05	138.2
0.5	125.37	129.64	133.91	138.18	142.45
0.75	129.28	133.68	138.09	142.49	146.90
1	133.20	137.73	142.27	146.80	151.34
$-\Delta_r G_T^o$. kJ/mole					
0.1	66.42	66.50	66.40	66.5	66.57
0.25	68.42	68.54	68.50	68.66	68.81
0.5	70.42	70.58	70.60	70.83	71.04
0.75	72.42	72.62	72.70	73.00	73.27
1	74.42	74.66	74.80	75.17	75.51
$-\Delta_r S_T^o$. J/mole·K					
0.1	623.05	636.95	650.28	664.19	678.07
0.25	637.75	652.05	665.87	680.27	694.65
0.5	657.02	671.89	686.34	701.39	716.41
0.75	676.86	692.31	707.42	723.13	738.83
1	696.70	712.73	728.50	744.88	761.24

Table 6

Thermodynamic parameters of complex formation of histidine with Eu^{3+} ions under the influence of the ionic strength in the aqueous medium.

I	298 K	303 K	308 K	313 K	318 K
$-\Delta_r H_T^o$. kJ/mole					
0.1	0.01	0.01	0.01	0.009	0.01
0.25	0.12	0.12	0.13	0.131	0.14
0.05	0.34	0.35	0.36	0.375	0.39
0.75	0.51	0.53	0.55	0.562	0.58
1	0.68	0.70	0.73	0.75	0.77
$-\Delta_r G_T^o$. kJ/mole					
0.1	87.49	87.59	87.7	87.86	88.029
0.25	87.49	87.58	87.69	87.85	88.017
0.5	87.49	87.58	87.68	87.84	88.006
0.75	87.49	87.58	87.68	87.84	87.994
1	87.49	87.58	87.67	87.83	87.983
$-\Delta_r S_T^o$. J/mole·K					
0.1	293.56	289.03	284.70	280.68	276.78
0.25	293.19	288.65	284.29	280.26	276.35
0.5	292.45	287.89	283.51	279.45	275.53
0.75	291.88	287.30	282.90	278.83	274.88
1	291.31	286.71	282.29	278.20	274.24

It is shown that with the increasing of temperature and ionic strength the endothermicity of complex formation in the histidine-metal ion increases. The linear dependence between the enthalpy of the complex formation reaction of histidine and absolute temperature is shown [7].

It is known that the complexation processes in aqueous solutions in the case of compounds with heteroatomic ligands are characterized by the entropy value above –84 J/(mole·K).

In this case, entropy increment with increasing of amount of the background electrolyte, and temperature can be explained by a number of effects related to the restructuring of hydrated of layer ions in the complex formation reaction, and with the advent of in the solution of «free» water molecules, which is the result of processes of structuring of the solvent, i.e., water.

It has been found that the growth of background electrolyte concentration and temperature increases endothermal processes of complexation of metal ions with histidine, therefore, in such systems the stability of complexes in the range 298–318 K will drop with absorption of heat.

The relation between the stability constants of metal-amino acids' complex and the enthalpy of formation of these complexes are considered. The result was obtained by a linear relationship between these parameters with a correlation coefficient $R^2 = 0.9968$.

The established simultaneous nature of the between $\lg\beta$ and $\Delta_r H_T^0$ allows thermodynamic stability of similar composition and structure of the complex.

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Сулы ерітіндідегі металл иондары Cs^+, ZrO^{2+}, Sm^{3+}, Eu^{3+} мен гистидин арасындағы кешен түзілуін зерттеу

Мақалада температура 298–318 К және иондық күш 0,1–1 аралығында гистидин мен металл иондарының (Cs^+, ZrO^{2+}, Sm^{3+}, Eu^{3+}) кешен түзілу қабілеті pH-метрлік титрлеу әдісін қолдану арқылы зерттелді. Алынған нәтижелерге сәйкес кешен түзілу процесінің константа тұрақтылары, сонымен қатар термодинамикалық параметрлері (ΔH, ΔG, ΔS) есептелінді.

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Исследование комплексообразования ионов Cs^+, ZrO^{2+}, Sm^{3+}, Eu^{3+} с гистидином в водных растворах

В статье процессы комплексообразования гистидина с ионами (Cs^+, ZrO^{2+}, Sm^{3+}, Eu^{3+}) были изучены с применением метода pH-метрического титрования в области температур 298–318 К от 0,1 до 1. На основании полученных данных были проведены расчеты констант устойчивости образования комплексов, а также термодинамических параметров процессов комплексообразования (ΔH, ΔG, ΔS).