

NOTE

Thermodynamic Stability of Zn(II) Complexes with Some Amino Acids and Pyridoxine (Vit. B₅)

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Stability constant (log B) and thermodynamic parameters such as enthalpy change (ΔH), free energy change (ΔG) and entropy change (ΔS) of Zn(II) complexes, with L-lysine, L-ornithine, L-threonine, L-serine, L-phenylglycine, L-phenylalanine, L-glutamic acid and L-aspartic acid as primary ligand and pyridoxine (Vit B₅) as secondary ligand, were calculated by applied polarographic method, at pH = 8.50 \pm 0.01 and ionic strength μ = 1.0 NaClO at 25°C.

Amino acids are well known chelating agents and play an important role in biology, pharmacy and industry¹⁻³, as aspartic acid and glutamic acid play important role in transamination, cell-metabolism and neurotransmission⁴⁻⁷. Thermodynamic parameters of Zn(II) complexes with L-amino acids and vitamin B complex on DME (dropping mercury electrode) have been calculated using thermodynamic equations.

The ligands, L-amino acids, were Lobachem products. All the solutions were prepared in double distilled water. The purity of L-amino acid was checked by chromatographic method⁸. The concentrations of metal ions, and NaClO₄ in the test solutions were 0.5 m and 1.0 m respectively.

Polarograms were obtained at 25°C, with the help of Toshniwal manual polarograph (model PE-50). The dropping mercury electrode had capillary characteristic $VS\ SCE\ m^{2/3}t^{1/6} = 2.40\ mg^{2/3}\ s^{-1/2}$ at effective mercury height 60.02 cm calculated. Pure hydrogen gas was passed through each test solution before recording the current-voltage curve. Elico digital pH meter (model LI-180) was used to measure the pH of each test solution at 8.50 \pm 0.01 adjusted with the solutions of NaOH and HNO₃ as required.

Zn gave a well defined two electron quasi-reversible reduction wave at pH = 8.50 \pm 0.01 and μ = 1.0 M NaClO₄. The irreversibility increased with increase of concentration of ligand in each case.

The values of $(E_{1/2})^5$ rev. were calculated by modified Gelling's method. The free ligand concentration of amino acids was determined by pK₂ and pH of each of the test solutions.

TABLE-I
THERMODYNAMIC PARAMETERS

	Stability Constants				ΔH kcal/mole				ΔG kcal/mole				ΔS cal/deg/mole			
	$\log \beta_{11}$	$\log \beta_{12}$	$\log \beta_{21}$		$\log \beta_{11}$	$\log \beta_{12}$	$\log \beta_{21}$		$\log \beta_{11}$	$\log \beta_{12}$	$\log \beta_{21}$		$\log \beta_{11}$	$\log \beta_{12}$	$\log \beta_{21}$	
Zn-L-amino acidate-pyridoxinate				(at 25/35°C)				(at 25°C)				(at 25/35°C)				(at 25/35°C)
Zn-L-lysinate-Pyridoxinate	4.220	6.900	9.540		-9.240	-12.600	-16.800		-5.755	-9.410	-13.010		-11.690	-10.700	-12.720	
	4.000	6.600	9.140		—	—	—		-5.635	-9.300	-12.880		-11.700	-10.710	-12.730	
Zn-L-ornithinate-pyridoxinate	4.380	7.080	9.760		-10.080	-13.860	-17.640		-5.972	-9.654	-13.310		-13.785	-14.110	-14.530	
	4.140	6.750	9.340		—	—	—		-5.830	-9.510	-13.160		-13.798	-14.120	-14.540	
Zn-L-threoninate-Pyridoxinate	4.480	7.710	9.930		-11.340	-15.540	-19.320		-6.110	-10.153	-13.541		-17.550	-16.870	-19.390	
	4.210	7.340	9.470		—	—	—		-5.930	-10.340	-13.345		-17.560	-16.880	-19.400	
Zn-L-serinate-pyridoxinate	4.640	7.860	10.150		-12.180	-16.800	-20.580		-6.330	-10.718	-13.841		-19.630	-20.410	-22.610	
	4.350	7.460	9.660		—	—	—		-6.130	-10.510	-13.612		-19.640	-20.420	-22.620	
Zn-L-phenylglycinate-pyridoxinate	4.790	8.050	10.330		-13.020	-17.640	-23.100		-6.531	-10.977	-14.086		-21.775	-22.360	-30.250	
	4.480	7.630	9.780		—	—	—		-6.314	-10.750	-13.784		-21.785	-22.370	-30.260	
Zn-L-phenylalaninate-pyridoxinate	5.010	8.140	10.560		-15.120	-20.580	-24.780		-6.831	-11.100	-14.400		-27.810	-31.810	-34.830	
	4.650	7.650	9.970		—	—	—		-6.550	-10.780	-14.050		-27.820	-31.820	-34.840	
Zn-L-glutamate-pyridoxinate	5.950	9.130	10.650		-17.640	-22.680	-26.040		-8.113	-12.450	-14.522		-31.970	-34.330	-38.650	
	5.530	8.590	10.030		—	—	—		-7.790	-12.104	-14.132		-31.980	-34.340	-38.660	
Zn-L-aspartate-pyridoxinate	6.120	9.240	10.871		-18.480	-24.360	-27.300		-8.345	-12.600	-14.822		-34.010	-39.460	-41.870	
	5.680	8.660	10.220		—	—	—		-8.000	-12.205	-14.400		-34.020	-39.470	-41.880	

The $E_{1/2}$ values become more negative with the addition of pyridoxine to (Zn-L-amino acidate) system at $\mu = 1.0$ M NaClO_4 and at $\text{pH} = 8.50 \pm 0.01$.

Showing the formation of ternary complexes, Schaap and McMaster's method confirmed the formation of 1 : 1 : 1, 1 : 1 : 2 and 1 : 2 : 1, complexes of Zn(II) with L-amino acids and pyridoxine. Thermodynamic parameters such as enthalpy change, free energy change and entropy change of the complexes have been calculated by the following equations¹⁰:

$$\Delta H = 2.303 RT_1 T_2 \log K_2/K_1$$

$$\Delta G = (T_2 - T_1)(2.303RT \log K)$$

$$\Delta S = \Delta H - T\Delta S$$

It is clear from the values of ΔS , ΔG and ΔH in Table-1 that complexes of transition metals are not stable at higher temperatures^{11, 12}. The value of ΔS is more negative at higher temperatures and ΔG is less negative at higher temperatures confirming that the complexes are not stable at higher temperatures. The negative values at ΔH show that the reactions are exothermic in nature.

The order of solution stability obtained was

L-lysine < L-ornithine < L-threonine < L-serine < L-phenylglycine
< L-phenylalanine < L-glutamic acid < L-aspartic acid.

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