Asian Journal of Chemistry Vol. 18, No. 4 (2006), 3185–3187

NOTE

Studies of the Effect of Ionic Strengths on Stability Constants of Co(II) Prolyl-Alanine Complexes

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The interaction of Co(II) with prolyl-alanine has been studied at various ionic strengths pH-metrically. The values of pK (proton-ligand stability constant) and log K (metal-ligand stability constant) are utilized to estimate the thermodynamic stability constants at various ionic strengths to know the exact nature and mechanism of complexzation equilibria.

Key Words: Stability constant, Complexes, Peptide derivatives.

Many authors[1–5] have studied the stability constants of some bi- and trivalent metal chelates with various organic ligands at different ionic strengths.

The present work deals with the determination of proton-ligand stability constant and metal-ligand stability constant of Co(II) with prolyl-alanine at different ionic strengths at 27 ± 0.1°C temperature. Elico pH-meter L1-10 was used (accuracy ±0.05 unit) for measuring the pH of the solution prepared in double distilled water. Nitric acid, soldium hydroxide and potassium nitrate used were of AR grade.

The titrations were conducted in an inert atmosphere of nitrogen. The ionic strength of the solution was maintained constant by adding an appropriate amount of 1 M KNO_3 solution. The values were recorded by pH-meter and converted into $[H^+]$ values by applying the corrections proposed by Van Uitert and Hass[6].

Propyl-alanine may be considered as dibasic acid having two replaceable H^+ ions from carboxylic —OH group and amine group.

$$HL_2 \rightleftharpoons HL^+ + L^-$$

$$HL^+ \rightleftharpoons H^+L^-$$

The titration data were used to construct the curves between volume of NaOH *vs.* pH called as acid ligand and metal titration curves.

TABLE-1
PROTON-LIGAND STABILITY CONSTANTS AT VARIOUS IONIC STRENGTHS

Ionic strength μ	$\sqrt{\mu}$	$\frac{\sqrt{\mu}}{1+\sqrt{\mu}}$	$\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.3\sqrt{\mu}$	PK_1	PK_2
0.04	0.2000	0.1660	0.1060	6.80	10.67
0.06	0.2440	0.1960	0.1228	6.80	10.40
0.08	0.2820	0.2190	0.1344	6.38	10.28
0.10	0.3162	0.2406	0.1542	6.10	9.00

TABLE-2

METAL-LIGAND STABILITY CONSTANTS AT VARIOUS IONIC STRENGTHS

Ionic strength μ	$\sqrt{\mu}$	$\frac{\sqrt{\mu}}{1+\sqrt{\mu}}$	$\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.3\sqrt{\mu}$	$\log K_1$	$\log K_2$
0.04	0.2000	0.1660	0.1060	12.60	11.60
0.06	0.2440	0.1960	0.1228	12.30	11.35
0.08	0.2820	0.2190	0.1344	12.05	11.20
0.10	0.3162	0.2406	0.1542	11.76	10.95

TABLE-3

ΔZ^2 VALUES FOR DISSOCIATION AND ASSOCIATION EQUILIBRIA

Constant	Reaction equilibria	Expected	Observed
pK_1^0	$H_2L \rightleftharpoons H^+ + HL^-$	2.00	2.500
pK_2^0	$HL^- \rightleftharpoons H^+ + L^-$	4.00	2.625
$\log K_1^0$	$Co^{2+} + H_2L \rightleftharpoons [Co]H^+L$	–2.00	–3.125
$\log K_2^0$	$Co^{2+} + HL^- \rightleftharpoons [Co]L + H^+$	–4.00	–2.500

The pK values of ligand and log K values of Co(II) complexes at various ionic strengths were calculated by Irving and Rossotti's method[7] and are presented in Tables 1 and 2, respectively. It could be seen from Tables 1 and 2 that the stability constant values of Co(II) complexes are found to decrease with increasing ionic strengths.

$$\log K = \log K^0 + A\Delta Z^2 - \sqrt{\mu}$$

and

$$pK = pK^0 - A\Delta Z^2 - \sqrt{\mu}$$

where A is the Debye-Huckel constant, ΔZ^2 is the difference of squares of charges of product and reactant ions and K^0 the formation constant at zero ionic strength value of pK_1^0, pK_2^0 and $\log K_1^0$, $\log K_2^0$ plotted against $\sqrt{\mu}$, $\sqrt{\mu}/(1+\sqrt{\mu})$ and $\sqrt{\mu}/(1+\sqrt{\mu}) - 0.3\sqrt{\mu}$ and give straight lines. The magnitudes of ΔZ^2 (slope) were the values calculated from the graph. The data obtained for pK^0 and $\log K^0$ that could be utilized to know the expected and observed values of ΔZ^2 for the corresponding dissociation and association equlibria are given in Table-3.

It is observed from Table-3 that the slopes of pK^0 and $\log K^0$ did not give the conclusive evidence regarding the magnitude of the charges of reacting species. The discrepancy may be due to limited applicability of Bronsted equation.

It shows that modified Debye-Huckel equation also did not show much improvement in the slope values. The discrepancy between the observed and expected slope value was thought to be due to concentration and not the reactivity terms used in the equation of stability constant[8].

Thermodynamic stability constants ($pK^0/\log K^0$) observed from the various plots at zero ionic strengths are presented in Table-4 which shows good agreement among thermodynamic constants obtained from various plots.

TABLE-4
THEMODYNAMIC DISSOCIATION CONSTANT AT ZERO IONIC STRENGTH
($pK^0/\log K^0$)

Plots	$pK^0/\log K^0$	Plots	$pK^0/\log K^0$
$\sqrt{\mu}$ vs. pK_1	6.90	$\sqrt{\mu}$ vs. $\log K_1$	12.82
$\frac{\sqrt{\mu}}{1+\sqrt{\mu}}$ vs. pK_1	7.25	$\frac{\sqrt{\mu}}{1+\sqrt{\mu}}$ vs. $\log K_1$	13.08
$\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.3\sqrt{\mu}$ vs. pK_1	7.15	$\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.3\sqrt{\mu}$ vs. $\log K_1$	12.85
$\sqrt{\mu}$ vs. pK_2	10.84	$\sqrt{\mu}$ vs. $\log K_2$	11.90
$\frac{\sqrt{\mu}}{1+\sqrt{\mu}}$ vs. pK_2	10.94	$\frac{\sqrt{\mu}}{1+\sqrt{\mu}}$ vs. $\log K_2$	12.25
$\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.3\sqrt{\mu}$	10.82	$\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.3\sqrt{\mu}$ vs. $\log K_2$	12.05

ACKNOWLEDGEMENTS

The authors are very much thankful to the Head of Chemistry Department and Director of Government Vidarbha Institute of Science and Humanities, Amravati for providing necessary facilities.

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(*Received*: 19 July 2005; *Accepted*: 2 May 2006) AJC-4876