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Note

pH-METRIC INVESTIGATIONS ON METAL–BENZOYLGLYCINE SYSTEMS

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Amino acids with biological and physiological background have attracted the attention of scientists. Their affinity for metals has also been appreciably documented [1–9]. The present note concerns pH-metric investigations on Cu(II)-, Cd(II)-, Pb(II)-, Fe(III)- and Pr(III)–benzoylglycine systems, leading to the determination of their stoichiometry, stability constants and thermodynamic functions.

EXPERIMENTAL

All chemicals were of B.D.H. quality. Solutions of benzoylglycine and metal nitrate/chloride in CO_2-free conductivity water were prepared. pH-metric titrations were carried out in aqueous media at 15 ± 0.5°C and 30 ± 0.5°C with carbonate-free 0.1 M NaOH. A constant ionic strength of 0.1 M was maintained by adding an appropriate quantity of potassium nitrate/chloride(M) solution. Stability constants of the metal and proton complexes were determined using the Bjerrum–Calvin technique and Henderson–Hesselback equation. The pH of the solution was measured with a Metrohm Harisan E-520 pH-meter with a sensitivity of ±0.05, duly calibrated with suitable buffers. The shapes of the curves (volume of NaOH vs. pH) were as expected.

RESULTS AND DISCUSSION

Benzoylglycine, unlike glycine or other amino acids, dissociates as

$$C_6H_5CONHCH_2COOH \rightleftharpoons C_6H_5CONHCH_2COO^- + H^+$$

The carboxylic group of the acid does not form the conjugate base intramolecularly, indicating practically the absence of any dipolar form. The presence of a single inflection on titrating the acid with a strong base in aqueous media contributes to the foregoing view.

Examination of the pH-metric curves displayed a separation of the metal–ligand curve from that of the acid. This contributes to the fact that the proton liberation is due to the complexation. The value of $\bar{n}$ increased gradually in all cases. This amounts to the involvement of the anionic form of the acid in complexation. Secondly, the $\bar{n}$ value approached ~2 for Cu(II)-, Pb(II)- and Cd(II)–benzoylglycine systems and ~3 for Pr(III)- and Fe(III)–benzoylglycine systems, indicating the presence of complexes of 1:2 and 1:3 stoichiometry, respectively.

Analysis of the formation curves ($\bar{n}$ vs. pL) indicates that there is not much difference in the values of successive stability constants. The calculation of stepwise formation constants could therefore not be done by the Bjerrum integral method ($\log k_1/k_2 \geqslant 2.5$) [10]. Further, it was seen that the formation curves lost their wave-like character, justifying the similarity in the successive formation constants. Even the systems of higher complexity [Fe(III)-, Pr(III)–benzoylglycine systems; $N = 3$] could not fulfil the conditions, i.e. $k_1 \sim k_2 \gg k_3$ and $k_1 \gg k_2 \sim k_3$ [11]. To minimize the errors, the trial constants obtained by

$$\log k_n = \mathrm{pL}_{n-1/2}$$

were refined by successive approximation using the equation [11]

$$\log K_{\bar{n}} = \mathrm{pL}_{\bar{n}} + \log\left\{ \sum_{t=0}^{t=n-1} (\bar{n} - t)\beta_t[\mathrm{L}]^t \Big/ \sum_{t=n}^{t=N} \frac{(t-\bar{n})\beta_t[\mathrm{L}]^{t-1}}{K_n} \right\}.$$

The pointwise calculation procedure was also employed for evaluating the stability constants using the equation

$$\log k_n = \mathrm{pL} + \frac{\bar{n} - (n-1)}{n - \bar{n}}$$

Values of ΔG^0, ΔH^0 and ΔS^0 are based on standard equations. It was seen that ΔG^0 values for Cu(II)-, Pb(II)-, Pr(III)- and Fe(III)–benzoylglycine systems decreased with the rise of temperature, indicating that the reaction of benzoylglycine and metal under study is a spontaneous process. For the Cd(II)–benzoylglycine system, an increase in ΔG^0 with the rise of temperature was observed. The enthalpy (ΔH^0) is positive for Pb(II)-, Cu(II)-, Pr(III)- and Fe(III)–benzoylglycine systems, justifying the endothermic nature of these reactions; ΔH^0 for the Cd(II)–benzoylglycine system is negative, which is favourable for the complex formation. ΔS^0 is positive for Pb(II)-, Pr(III)- and Fe(III)–benzoylglycine systems only and favours the formation of the complexes.

Table 1 contains the mean values of stability constants of metal and proton complexes at different temperatures and their thermodynamic functions.

TABLE I

Thermodynamic functions and stability constants of metal–benzoylglycine systems

Metal ion	Stability constants of proton/metal complexes	Temp. (°C)		$-\Delta G^0$ (kcal mole^{-1})		ΔH^0 (kcal mole^{-1}) at 30°C	ΔS^0 (kcal mole^{-1}) at 30°C
		15	30	15°C	30°C		
Cu^{2+}	$\log {}^{P}k^{H}$						
	$\log k_1$	2.42	2.44				
	$\log k_2$	2 52	2.58				
	$\log \beta_2$	4.94	5.02	6.51	6.96	2.13	−15.95
Cd^{2+}	$\log k_1$	2.87	2.49				
	$\log k_2$	2.77	2.55				
	$\log \beta_2$	5.64	5.04	7.44	6.58	−23.94	−57.31
Pb^{2+}	$\log k_1$	2.27	2.43				
	$\log k_2$	2.88	2.63				
	$\log \beta_2$	5.15	5.06	6.79	7.27	+2.39	+31.90
Pr^{3+}	$\log k_1$	2.06	2.43				
	$\log k_2$	2.54	2.27				
	$\log k_3$	2.71	2.97				
	$\log \beta_3$	7.31	7.67	9.64	10.64	9.63	+66.31
Fe^{3+}	$\log k_1$	3.07	2.25				
	$\log k_2$	2.66	3.10				
	$\log k_3$	2.56	3.02				
	$\log \beta_3$	8.29	8.37	10.94	11.62	2.13	+45.37

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