DISSOCIATION CONSTANT OF BENZOHYDROXAMIC ACID AND STABILITIES OF ITS COBALT(II) COMPLEXES IN DIFFERENT MEDIA

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Dedicated to Prof Dr A. Okáč, on the occasion of his 70th birthday.

The dissociation constant of benzohydroxamic acid has been determined by pH titration technique at ionic strength 0·25M in different media and at different temperatures. The pK_a values at $20 \pm 0.05°C$ in aqueous and 20% methanolic and ethanolic media have been found to be 8·84, 8·96 and 9·03 $\pm$ 0·05 respectively, and at 30 and 40°C (determined in aqueous medium only) as 8·82 and 8·55 $\pm$ 0·05. The potentiometric investigations on the reaction between cobalt(II) and benzohydroxamic acid reveal the successive formation of two complexes CoA^+ (1 : 1) and CoA_2 (1 : 2). The stability constants in aqueous, 20% aq.-methanol and 20% aq.-ethanol ($\mu = 0.25M$, $20 \pm 0.05°C$) have been found to be 4·80, 5·44, 4·94 (log K_1) 3·80, 4·45, 3·98 (log K_2), and 8·60, 9·89, 8·92 (log β), respectively.

The complexation of benzohydroxamic acid (referred to here in as HA) has been the subject of considerable interest during the past[1–10]. Its complexes with various metal ions have been attempted but most of the workers have confined themselves to the development of this compound as an analytical reagent for the estimation of metal ions spectrophotometrically[4–8] and gravimetrically[9–10].

A survey of literature reveals that the dissociation constant of benzohydroxamic acid in aqueous–alcoholic media and stabilities of its cobalt complexes in aqueous as well as in aqueous-alcoholic media have not been reported so far. The present investigation has, therefore, been carried out. The pK_a values and stability constants in aqueous and aqueous–methanolic and ethanolic media have been reported.

EXPERIMENTAL

Materials and methods. Benzohydroxamic acid was used after proper purification and its freshly prepared solutions were always used with a view to avoid the possible contamination

of results by degradation into benzoic acid. Other chemicals used were p.a. Lachema, Brno and their solutions were prepared in air-free distilled water. pH measurements were made on an electronic pH meter (Acidimeter EK, Czechoslovakia) using a wide range glass electrode calibrated frequently by using buffer solutions of different pH values and coupled with the saturated calomel electrode. The calibration of the glass electrode was checked before and after each series of measurements.

Determination of the dissociation constant. Benzohydroxamic acid solutions (0·005M) in water, 20% methanol and 20% ethanol at ionic strength 0·25M, adjusted by $NaNO_3$, were titrated with carbonate free NaOH solution (0·05M) under an inert atmosphere at 20°C. After accounting for the dilution effect the values of dissociation constant were calculated according to the method described by Albert and Sarjeant[11]. The dissociation constant values have also been determined at 30 and 40°C in aqueous medium:

Media:	aq.	aq. MeOH	aq. EtOH	aq. (30°)	aq. (40°)
$K (\pm 0\cdot 05)$:	8·84	8·96	9·03	8·82	8·55

Stoichiometry and stabilities of the complexes. In order to explore the possibility of successive complexation between cobalt and benzohydroxamic acid the magnitude of the proton displacement was determined by titrating solutions containing ligand and Co^{2+} in different ratios *viz.* 1 : 1, 2 : 1 and 3 : 1 against standard alkali. The stability constants were accomplished as described earlier[12-14] by adopting the Calvin and Melchior's[15] extension of Bjerrum's[16] method, which were further confirmed by the convergence formulae given by Schroder[17].
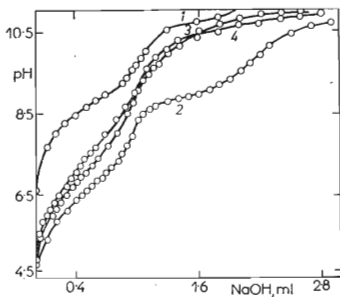

Fig. 1

Potentiometric Titrations of Benzohydroxamic Acid, in Presence and Absence of Cobalt, with 0·05M-NaOH

1 0·005M-HA; 2 0·005M-HA + 0·005M-Co^{2+}; 3 0·005M-HA + 0·0025M-Co^{2+}; 4 0·005M-HA + 0·00166M-Co^{2+}.
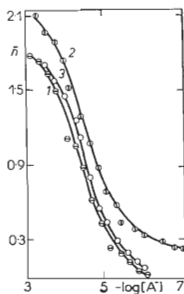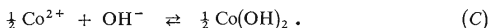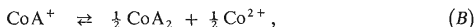
Fig. 2

Formation Curves

1 Aqueous; 2 20% aq. ethanol; 3 20% aq. methanol.

RESULTS AND DISCUSSION

Fig. 1 illustrated the changes occurring in H^+ concentration during the titration of HA solution and HA solutions with Co^{2+} added with 0·05M-NaOH. Curve *1* shows an ill defined inflection at one mol of NaOH added per mol of HA suggesting the weak dissociation of benzohydroxamic acid. Titration in presence of an equimolar concentration of Co^{2+} greatly alters the shape of the free ligand titration curve (curve 2) as a result of the liberation of H^+ due to complex formation, which is indicated by the considerable lowering in the buffer region and slightly more pronounced inflection at one mol of NaOH/mol of ligand at lower pH level. The interaction may be represented as follows;

$$HA + Co^{2+} + OH^- \rightleftarrows CoA^+ + H_2O . \qquad (A)$$

The appearance of precipitation after the addition of one mol of NaOH/mol of HA (curve 2) and the second inflection at two moles of NaOH/mol of HA indicate the disproportionation of the 1 : 1 complex into 1 : 2 complex (*B*) and the precipitation of the cobalt as its hydroxide at higher pH,

$$CoA^+ \rightleftarrows \tfrac{1}{2} CoA_2 + \tfrac{1}{2} Co^{2+} , \qquad (B)$$

$$\tfrac{1}{2} Co^{2+} + OH^- \rightleftarrows \tfrac{1}{2} Co(OH)_2 . \qquad (C)$$

When the ligand and metal are in the ratios of 2 : 1 and 3 : 1 the titration curves show only one feeble inflection at one mol of alkali per mol of ligand exhibiting the combined neutralisation of H^+ liberated due to complexation and the dissociation of HA. No distinct inflection for the removal of displaced H^+ has been observed due to weak complexation. However, the values of $\bar{n}$ (the number of ligand molecules bound per metal ion) and rise in buffer region at low concentration of cobalt (HA : Co^{2+} = 3 : 1) reveal that the reaction stops after the formation of 1 : 2 complex.

Stability constants. The succesive reactions of the complex formation between Co(II) and benzohydroxamic acid may be represented by the following equations;

$$Co^{2+} + A^- \rightleftarrows CoA^+ , \qquad (D)$$

$$CoA^+ + A^- \rightleftarrows CoA_2 . \qquad (E)$$
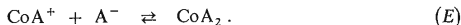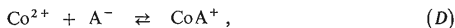
The overall stability constant is given by

$$\beta = [CoA_2]/[Co^{2+}] [A^-]^2 = K_1 K_2 , \qquad (1)$$

where K_1 and K_2 are the formation constants of the above reactions. The evaluation

TABLE I

Stability Constants ($\mu = 0.25$M; $20 \pm 0.05°C$) of Cobalt-Benzohydroxamic Acid Complexes

Media	Bjerrum's method			Conver. formulae		
	$\log K_1$	$\log K_2$	$\log \beta$	$\log K_1$	$\log K_2$	$\log \beta$
Aqueous	4·82	3·78	8·60	4·78	3·82	8·60
20% aq. methanol	5·48	4·43	9·91	5·41	4·46	9·87
20% aq. ethanol	4·97	3·93	8·90	4·91	4·02	8·93

of $\bar{n}$ values was made from potentiometric titrations between HA and NaOH solutions in absence and presence of cobalt in aqueous and 20% methanolic and ethanolic media. At any pH, or the total number of $[A^-]$ complexes have been measured. This number divided by the cobalt concentration is $\bar{n}$. The $\bar{n}$ values in the region of pH (above 8·25) in which the system became heterogeneous (by precipitation of the metal as some complexed or hydrolysed species) have been not calculated. At any pH, $[A^-]$ was calculated as

$$[A^-] = \frac{[HA]_{total} - \{[CoA^+] + 2[CoA_2]\}}{([H^+]/K_a) + 1}, \qquad (2)$$

where K_a is the dissociation constant of the ligand (respective dissociation constants were used for the different media). The $\bar{n}$ values obtained in different media were plotted against $-\log [A^-]$ and the values of $\log K_1$ and $\log K_2$ were read directly from the formation curves (Fig. 2) at $\bar{n} = 0.5$ and 1·5 respectively, which were further confirmed by the convergence formulae of Schroder for successive approximations. Table I compares the values of $\log K_1$, $\log K_2$ and $\log \beta$ obtained for different media.

It is apparent from the Table I that the direct expressions

$$K_1 = 1/\{[L]_{\bar{n}=0.5} - 3/[L]_{\bar{n}=1.5}\}$$

and

$$K_2 = 1/\{[L]_{\bar{n}=1.5} - 3[L]_{\bar{n}=0.5}\}$$

given for the convergence values of successive approximations as a modification of the method of successive approximations is strictly followed by our data and that no divergence of the convergence formulae is noted. This method is, however, recent and directly gives the true values of the successive stability constants.

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