Stepwise Stability Constants of Silver-2-Hydroxy Methylbenzimidazole in Ethanol

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The stepwise stability constants of silver 2-hydroxy-methylbenzimidazole complex have been determined potentiometrically employing Leden method

The determination of stability constants by emf measurements of metal in equilibrium with complexes of the metal was first attempted by Riley and Gal'afent[1]. In the present investigation, Leden method was employed to determine the stepwise stability constants of silver 2-hydroxymethylbenzimidazole (Ag-HMBMA) complex in 50% ethanol.

Experimental and Rusults

The following two cells were set up,

Cell - A

(—) SCE	KNO_3 salt bridge	2 ml. 0.01 M $AgNO_3$ + 2 ml 1.0 M KNO_3 + 4 ml. EtOH + 12 ml. 50% EtOH	(+) Ag

Cell—B

(—) SCE	KNO_3 salt bridge	2 ml 0.01 M $AgNO_3$ + 2 ml. 1.0 M KNO_3 + 4 ml. EtOH + x ml. 0.1M HMBMA in 50% EtOH + a ml. 50% EtOH	(+) Ag

(x + y = 12 ml.)

The emf of Cell-B is given by

$$E_2 = E^1 + \frac{RT}{nF} \ln [M] \qquad (1)$$

where [M] is the free metal ion concentration; E^1 includes the potential of the calomel electrode, the liquid junction potential and the correction term for activity coefficient in the mixed solvent.

In the case of Cell–A,

$$E_1 = E^1 + \frac{RT}{nF} \ln [C] \qquad (2)$$

Where [C] is the metal ion concentration. When ligand (L) is added, some of the metal ions are removed to from a complex and new potential, E_2 will be set up. Hence,

$$\triangle E = E_1 - E_2 = \frac{RT}{nF} \ln \{[C] / [M]\} \qquad (3)$$

$$= \frac{0.06105}{n} \log \{[C] / [M]\} \text{ at } 35°$$

The quantity [C] / [M] is known as the degree of formation ($\emptyset$), so that,

$$\log \emptyset = \triangle E\, [nF/2.303RT]$$

According to Leden (2)

$$F_1[L] = \frac{[C] / [M] - 1}{[L]} = B_1 + B_2 [L] + B_3 [L]^2 + \ldots (4)$$

$$F_2[L] = \frac{F_1 [L] - B_1}{[L]} = B_2 + B_3 [L] + \ldots\ldots \qquad (5)$$

Similarly,

$$F_n [L] = \frac{F_{n-1} [L] - B_{n-1}}{[L]} = B_n \qquad (6)$$

where $B_n = K_1.K_2.K_3 \ldots K_n$,

and K_n is the stability constant of n^{th} stage.

0.1 M and 0.01 M $AgNO_3$, 1.0 M KNO_3 in water and 0.1 M HMBMA in 50% EtOH were prepared. $AgNO_3$ solution was standardized volumetrically using NaCl solution. The potentiometric measurements were carried out at 35±1° using Leeds and Northrup potentiometer with an accuracy of ±0.1 mV. Silver electrode was prepared[3] and its reversibily was checked from time to time during the measurements. The results are shown in the table 1.

TABLE—1. DATA ON COMPLEX FORMATION.

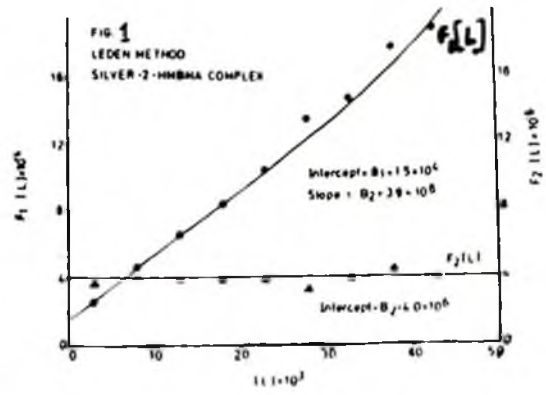
No.	'x'	'y'	F_y (v)	ΔE (E_1–E_2)	[C]/[M] $\times 10^{-3}$	[L] $\times 10^{3}$	F_1[L] $\times 10^{-4}$	F_2[L] $\times 10^{-6}$
1.	0	12	0.3632	—	—	—	—	—
2.	1	11	0.2472	0.1160	0 079	3.0	2.615	3.716
3.	2	10	0.2061	0 1571	0.375	8.0	4.676	3.970
4.	3	9	0.1841	0.1791	0.859	13.0	6.601	3.925
5.	4	8	0.1693	0.1939	1.503	18.0	8.343	3.802
6.	5	7	0.1570	0.2062	2.387	23.0	10.380	3.861
7.	6	6	0.1477	0.2155	3.741	28.0	13.350	3.362
8.	7	5	0.1385	0.2247	4.798	33.0	14.540	3.951
9.	8	4	0 1280	0.2352	7.128	38.0	18.750	4.538
10.	9	3	0.1246	0.2386	8.091	43.0	18.810	3.996

Discussion

Free ligand concentration [L] was determined using the equation,

$$L - T_L - \bar{n} T_M$$

where T_L is the total added ligand and T_M is the total metal ion taken. $\bar{n}$ is taken to be equal to 2 because the complex formation (1 : 2) may be considered complete due to the presence of excess ligand. From eq 4 it is seen that if F_1 [L] is plotted against [L] (Fig 1) the intercept will be B_1 and slope of the graph will give B_2. Similarly if F_2 [L] is plotted against [L], the limiting slope will be B_3 and intercept will be B_2. In the present



case, the slope of the graph of F_2 [L] vs [L] becomes zero indicating absence of higher complexes. The values of B_2 determined from the slope of the graph of F_1 [L] vs [L] and intercept of graph of F_2 [L] vs [L] are found to be in agreement.

The intercept of the graphs (B_1) is 1.5×10^4 and slope of the graph (B_2) is 3.9×10^6. The stepwise stability constants obtained by this method are given below :

Complex	log K_1	log K_2
Ag HMBMA)$_2$ NO_3	4.18	2.41

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