Formation constant

The formation constants were calculated both graphically and by calculations. The average number of ligand molecules bound per metal ion is given by the expression

$$\bar{\eta} = \frac{C_A - (H^{\oplus}/K + 1)A^{\ominus}}{C_M}$$

Where $A^{\ominus}$ is the free ligand concentration and is given by the expression.

$$A^{\ominus} = \frac{(1-\alpha)C_A - H^{\oplus} + OH^{\ominus}}{H^{\oplus}/K}$$

The formation curve was obtained by plotting $\bar{\eta}$ against $-\log A^{\ominus}$. The $-\log A^{\ominus}$ value at $\bar{\eta} = 0.5$ gives the value of $\log K$. The values are given in the Table II.

Further the values of the stability constants were calculated by the formula

$$K = \frac{C_A - \beta(A^{\ominus})}{A^{\ominus}[C_M + \beta A^{\ominus} - C_A]}$$

where
$$\beta = \frac{(H^{\oplus})}{K} + 1.$$

The free energy of the complex formation at 25 °C has been calculated by the formula

$$-\Delta F = RT \ln k.$$

Results and Discussion

The dissociation of the reagent can be represented as

The probable structure of the metal-complex may be represented as

where $R = CH_3, C_2H_5$; $M = Cu(II), Fe(II)$.

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Formation Constants of some Bivalent Metal Ion Chelates of *N*-(2-hydroxy-1-naphthalidene) Anthranilic Acid (Schiff Base)

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Protonation constants ($\log K_1^H$ and $\log K_2^H$) of the Schiff base derived from 2-hydroxy-1-naphthaldehyde and anthranilic acid and, the formation constants of certain bivalent metal ion chelates have been determined potentiometrically in 50 per cent (vol./vol.) dioxan solutions ($\mu = 0.1 M NaClO_4$). The stabilities of these metal chelates are in the order, $UO_2 > Cu > Ni > Co > Zn > Cd$, in which the sequence of those of first transitional metal ion chelates are in agreement with Irving and Williams order.

No systematic study of the formation constants of bivalent metal ion chelates of *N*-(2-hydroxy-1-naphthalidene) anthranilic acid (abbr. H_2NA) has been carried out. It is, therefore, of interest to investigate

the protonation constants of H_2NA and formation constants of its metal chelates. The measurements were carried out in 50 per cent dioxan at $30 \pm 0.1^\circ C$ as the ligand and its metal chelates are insoluble in water.

Experimental

Apparatus and reagents

Precision pH-meter Type: OP-205 No. 837 made in Hungary, with glass-calomel electrode assembly was used to determine the change in hydrogen ion concentration of the solution due to complexation. An inert atmosphere of nitrogen was maintained by bubbling oxygen free nitrogen gas through the solution. The electrode system was calibrated at two pH values; at pH 4.0 with potassium hydrogen phthalate and at pH 7.0 with potassium hydrogen phosphate and sodium hydroxide buffers. Metal ion solution were prepared from their nitrates (BDH-AnalaR) and standardised by the usual methods¹. Chemically pure sodium perchlorate was used to keep the ionic strength constant. Standard carbonate-free sodium hydroxide was prepared and its solution in 50 per cent dioxan was used as a titrant². Dioxan was refluxed with sodium for 24 hours and distilled before use. The H₂NA was prepared, purified by repeated crystallisation from ethanol; m.p. 239 °C, and its solution was standardised potentiometrically. All the chemicals used were of reagent grade quality.

pH-titration procedure

The determination of formation constants was carried out using CALVIN-BJERRUM pH-titration techni-

que^{3,4} as used by IRVING and ROSSOTTI⁵. The following mixtures (total vol. 20.0 ml) were titrated against 0.1 N NaOH and the titration curves were plotted:

1. 5.0 ml 0.01 M HClO₄ + 2.0 ml 1.0 M NaClO₄ + 10.0 ml dioxan + 3.0 ml water; 2. 5.0 ml 0.01 M HClO₄ + 2.0 ml 1.0 M NaClO₄ + 10.0 ml 0.01 M H₂NA + 3.0 ml water; 3. 5.0 ml 0.01 M HClO₄ + 2.0 ml 1.0 M NaClO₄ + 10.0 ml 0.01 M H₂NA + 2.0 ml 0.01 M metal ion solution + 1.0 ml water.

In the mixture, the metal-ligand ratio of 1 : 5 was maintained to fulfil the maximum coordination number of the metal. From the proton-ligand formation curve (Fig. 1) the log K_1^H and log K_2^H of H₂NA have been found to be 8.00 and 6.50 respectively.

Fig. 1. Formation curve of proton-ligand system of H₂NA.

Metal Chelates	Interpolation at half $\bar{n}$ values method	Interpolation at various $\bar{n}$ values method	Correction term method	Successive Approximation method	Mean
UO ₂ (II) chelate					
log K_1	11.60	11.89	11.38	11.60	11.62
log K_2	7.65	7.21	7.65	7.60	6.53
Cu(II) chelate					
log K_1	10.85	11.27	10.92	10.80	10.96
log K_2	6.30	6.26	6.65	6.30	6.37
Ni(II) chelate					
log K_1	7.95	8.29	7.98	7.90	8.03
log K_2	5.10	5.19	5.35	5.10	5.19
Co(II) chelate					
log K_1	7.45	7.74	7.28	7.40	7.47
log K_2	4.42	4.24	4.67	4.40	4.43
Zn(II) chelate					
log K_1	7.10	7.58	7.21	7.00	7.22
log K_2	3.60	3.38	3.83	3.60	3.60
Cd(II) chelate					
log K_1	6.85	7.02	6.54	6.80	6.80
log K_2	3.35	2.95	3.47	3.30	3.26

Table I. Formation Constants of some bivalent metal ion chelates of H₂NA (Temp. = 30 ± 0.1 °C, μ = 0.1 M NaClO₄).

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Results and Discussion

The method of IRVING and ROSSOTTI⁵ was used for deducing the values of $\bar{n}$ and pL from the above data. The $\bar{n}$ values exceeding one indicate the formation of two different complex species. Approximate values of stability constants were read directly from their formation curves (Fig. 2) using BJERRUM half $\bar{n}$ values method. Different methods⁶ have been used to compute the formation constants and the corrected values are given in Table I.

It is evident from the data presented in Table I, that the sequence of formation constants of the bivalent metal ion chelates is, $UO_2 > Cu > Ni > Co > Zn > Cd$, in which that of the first transitional metal ion chelate is in agreement with IRVING and WILLIAMS rule⁷.

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⁷ H. IRVING and R. J. P. WILLIAMS, J. chem. Soc. [London] 1953, 3192.

Fig. 2. Formation curves of bivalent metal complexes with H_2NA .

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