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Studies on the Stability Constants of the Complexes of Some Bivalent Metal Ions with Some Ortho Derivatives of β-Naphthol

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Potentiometric studies on metal complexes of Cu^{2+}, Ni^{2+}, Co^{2+} and Mg^{2+} with a series of *ortho* derivatives of β-naphthol have been carried out. The dissociation constants of the reagents and formation constants of their metal chelates have been determined by Bjerrum's method at 30±0.1° and at ionic strength of 0.1 *M* in 75 : 25 (v/v) dioxane-water medium.

IN the present investigation, potentiometric studies on a series of *ortho* derivatives of β-naphthol and their metal complexes with some bivalent metal ions have been carried out. The ligands have been synthesized by varying the substituent at one site. The dissociation constants of the reagents and formation constants of their metal chelates have been determined potentiometrically following the Calvin-Bjerrum *p*H titration technique as adopted by Irving and Rossotti[1].

Experimental

A precision *p*H meter, the Corning Model 12, was used for *p*H measurements. The electrode assembly consisted of glass and calomel electrodes and had an accuracy of measurement of 0.005 *p*H unit on expanded scale.

The ligands, 2-hydroxy-1-naphthalidene-4'-[4''-morpholinyl]aniline (m.p. 202°), 2-hydroxy-1-naphthalidene-3',4'-dimethylaniline (m.p. 125°)[2], 2-hydroxy-1-naphthalidene-4'-N-diethylaminoaniline (m.p. 102°), 2-hydroxy-1-naphthalidene-4'-*n*-butylaniline (m.p. 76°), 2-hydroxy-1-naphthalidene-4'-acetylaniline (m.p. 175°), were synthesized by refluxing alcoholic solutions containing equimolar quantities of 2-hydroxy-1-naphthaldehyde and the respective amines for about 2 hr. The crude products were repeatedly crystallised from appropriate solvents to get analytically pure compounds. Their purity was tested by tlc and elemental analysis.

All the metal perchlorates used were prepared from metal salts and perchloric acid of A. R. grade. These were standardised complexometrically by EDTA titrations[3,4]. Other experimental details are the same as reported earlier[5].

Results and Discussion

The ligands did not undergo hydrolysis under the experimental conditions described as indicated by the rapid attainment of equilibrium during the titrations and by the absence of any significant drift in *p*H even after 2 hr. This was further corroborated by tlc of sample titration mixtures from time to time.

In the ligands, it is the phenolic OH group which takes part in complex formation and the proton is replaced from it by metal ions during chelation. As only one proton per ligand molecule is liberated, 'Y', the number of dissociable protons attached to each ligand molecule is one in all the cases in the present investigation.

From the titration curves, $\bar{n}_A$ values at various 'B' values (*p*H meter readings) were computed and the formation curves (B vs $\bar{n}_A$) of the different ligands were plotted (Fig. 1). The values pK_1^H and pK_2^H, corresponding to phenolic H and to the association of proton to imino nitrogen were determined by half integral method at $\bar{n}_A = 0.5$ and 1.5, respectively. These were further corroborated from the plots of log $[(\bar{n}_A)/(1-\bar{n}_A)]$ vs B and log $[(2-\bar{n}_A)/(\bar{n}_A-1)]$ vs B.

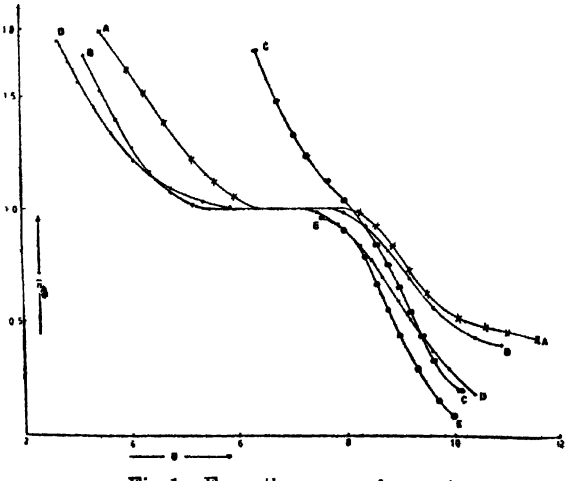


Fig. 1. Formation curves of reagents.

From the titration curves, $\bar{n}$ and pL values for metal-ligand systems were also calculated. From the curves $\bar{n}$ vs pL, [Figs. 2(A)-2(E)], log K_1 and log K_2

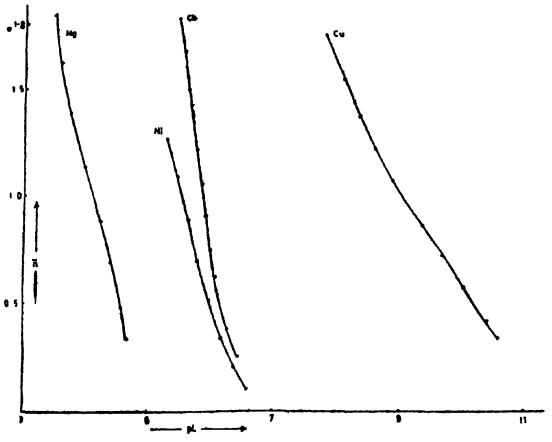


Fig. 2(A). Metal-ligand systems of 2-hydroxy-1-naphthalidene-4′-[4″-morpholinyl]-aniline.

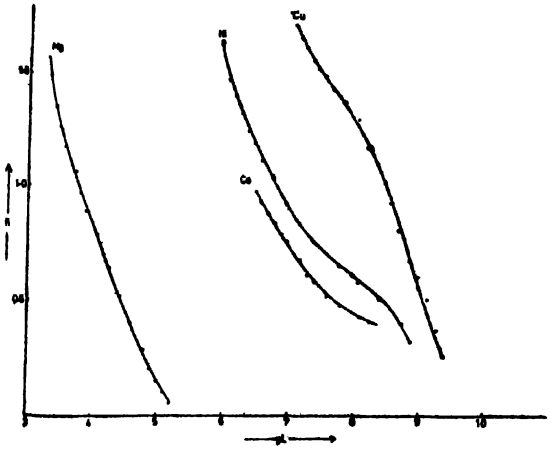


Fig. 2(B). Metal-ligand systems of 2-hydroxy-1-naphthalidene-3′-4′-dimethylaniline.

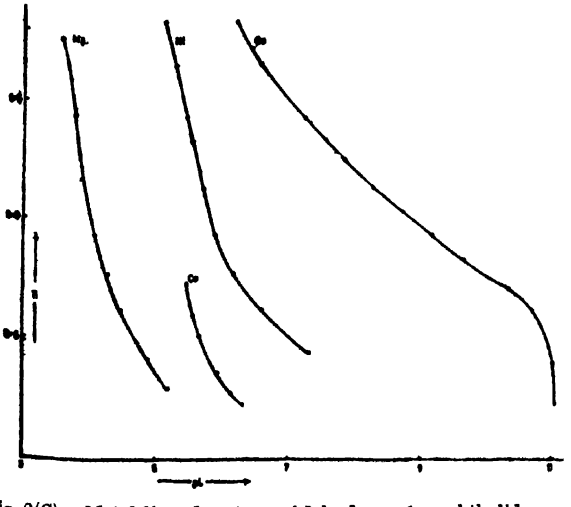


Fig. 2(C). Metal-ligand systems of 2-hydroxy-1-naphthalidene-4′-N-diethylaminoaniline.

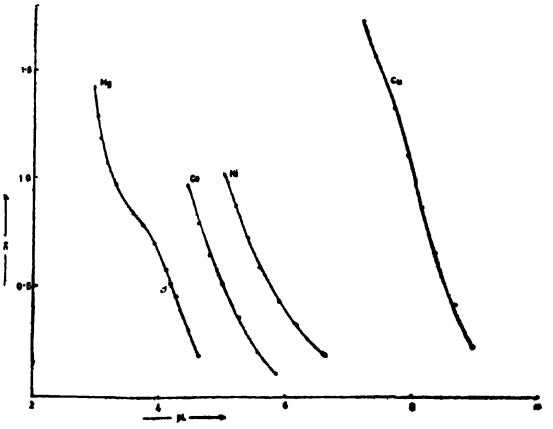


Fig. 2(D). Metal-ligand systems of 2-hydroxy-1-naphthalidene-4′-n-butylaniline.

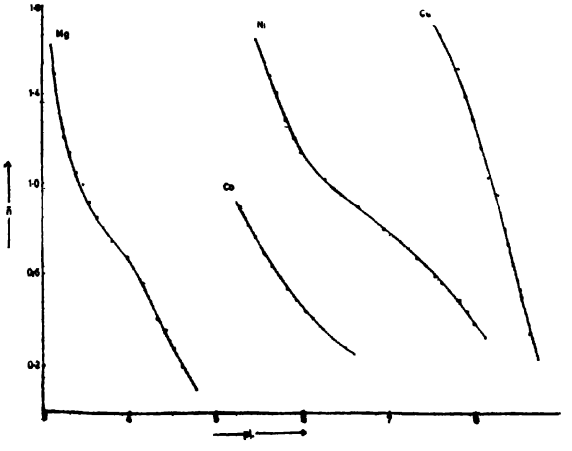


Fig. 2(E). Metal-ligaud systems of 2-hydroxy-1-naphthalidene-4′-acetylaniline.

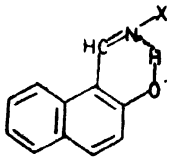
values were determined by half integral and graphical method. In some cases, where the difference between log K_1 and log K_2 was found to be less than 1.78 log units, the same were calculated by least square method. The most representative values are recorded in the table below :

TABLE 1

		A	B	C	D	E
H^+	pK_1	10.34	9.86	9.28	9.23	8.90
	pK_2	4.35	3.55	6.75	3.26	—
Cu^{2+}	log K_1	10.16	9.07	10.96	8.45	8.45
	log K_2	8.20	7.50	7.03	7.74	7.85
Ni^{2+}	log K_1	6.00	8.50	6.71	5.80	7.80
	log K_2	—	6.13	5.21	—	—
Co^{2+}	log K_1	6.16	7.80	5.66	5.03	5.93
	log K_2	5.66	—	—	—	—
Mg^{2+}	log K_1	4.06	4.41	4.47	4.13	4.06
	log K_2	3.38	3.26	3.76	2.72	2.99

The order of stability of metal complexes of compounds B, C, D and E was found to be Cu > Ni > Co > Mg, which is in accordance with that of Malley and Mellor[6]. In compound A, however, the order was Cu > Ni ≃ Co > Mg as reported by Murakami *et al*[7].

The structure of the metal complexes is similar to the proton-ligand complexes viz., a close ring structure due to hydrogen bonding between imino nitrogen and phenolic H or metal ion as shown in below :



On the basis of this structural similarity, the log K values of various metal-ligand complexes are expected to vary linearly with the *p*K values of the respective reagents. Such plots are shown in Fig. 3.

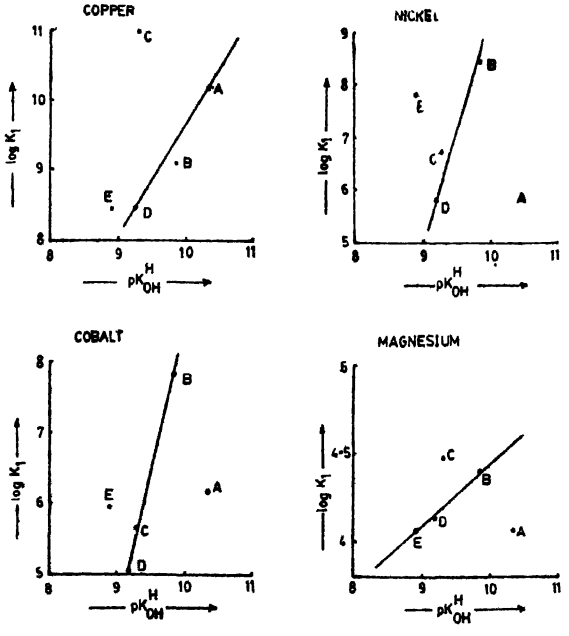


Fig. 3. A. 2-hydroxy-1-naphthalidene-4′-[4″-morpholinyl]aniline.
B. 2-hydroxy-1-naphthalidene-3′,4′-dimethylaniline.
C. 2-hydroxy-1-naphthalidene-4′-N-diethylaminoaniline.
D. 2-hydroxy-1-naphthalidene-4′-*n*-butylaniline.
E. 2-hydroxy-1-naphthalidene-4′-acetylaniline.

Apparently the linearity as suggested by Bjerrum's equation[8],

$$\log K = a\,pK + b$$

is found to be applicable in a rather crude manner. The conditions under which this could be expected have been discussed by Irving and Rossotti[9]. Williams *et al*[10] suggested that linear relationship is not of universal validity, since it requires that the dependence of partial molal free energy of the metal complexes, $\bar{G}^{o}_{ML}$, upon the ligand must be similar to that of $\bar{G}^{o}_{HL}$. This cannot be generally true, especially when the substituents in the ligands influence their ability to accept electrons from the metal to form π bonds. Another factor responsible for this deviation could be structural changes in the ligand and the mode of formation of the metal-ligand bond which may cause a change in the strength of the bond between metal and ligand.

The ir spectra of the Schiff bases and their metal chelates with Cu and Ni were determined to compare the shifts in the assigned frequency of the free ligands and their metal chelates. The strong band in the region 1610-1630 cm^{-1} is assigned to the C=N stretch in the free Schiff base[11].

Compound	pK_1	C=N stretching frequency cm^{-1}		
		Comp.	Cu^{2+}	Ni^{2+}
A	10.34	1635	1620	1418
B	9.86	1620	1618	1615
C	9.28	1619	1615	1610
D	9.23	1618	1612	1608
E	8.90	1615	1610	1605

From the values above, it can be observed that the change in the *p*K values is directly proportional to the change in C=N stretching frequency. It was also noted that the C=N stretching frequency is shifted to lower values in the spectra of metal complexes. This behaviour has been observed by a number of workers[12,13].

Acknowledgement

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