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Formation constants of some bivalent 3*d* metal ion complexes with isatin-3-phenyl imine in aqueous dioxane

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Abstract. Potentiometric investigations have been carried out on binary chelates of Co(II), Ni(II), Cu(II) and Zn(II) with isatin-3-phenyl imine (I-3-Ph-I). The acid dissociation constant of the ligand and the formation constants of its metal complexes have been determined at 30°C, in 10% volume of dioxane-water at ionic strengths of 0·2 M, 0·15 M, 0·1 M and 0·05 M KNO_3.

Keywords. Isatin-3-phenyl imine; equilibrium studies; formation constants.

1. Introduction

Potentiometry has been used extensively for determination of stepwise stability constants of transition metal ions with different ligands by several authors. Literature survey indicated that no work has been carried out involving the complexation of bivalent metal ions Co(II), Ni(II), Cu(II), and Zn(II) with isatin-3-phenyl imine using potentiometry. In this work we report the proton–ligand and metal–ligand stability constants of isatin-3-phenyl imine in 10% volume of dioxane–water.

2. Experimental

The ligand isatin-3-phenyl-imine (mp = 210 – 212°C) was prepared by known procedure (Rajepadhya *et al* 1985) and its purity checked by TLC. The structure was confirmed by IR and NMR spectra. The data are given in table 1.

From the NMR data of the ligand it is evident that the ligand exists both in keto and enol forms.

All the chemicals used were AR grade. Solutions of Co(II), Ni(II), Cu(II) and Zn(II), were estimated by EDTA (Schwarzenbach 1957).

3. Apparatus

A Digisun digital *p*H-meter–model DI-707 with glass and calomel electrode with an accuracy of ± 0·01 was used for *p*H measurements. The electrode is calibrated in 10% dioxane–water as per the procedure reported (Van Uitert 1953).

Solutions (total volume 50 ml containing: (i) acid ($4{\cdot}0 \times 10^{-3}$ M), (ii) ligand, (2×10^{-3} M) and (iii) metal nitrate (4×10^{-4} M) + ligand were titrated *p*H-metrically against standard 0·1 M KOH at 30°C (figure 1). An appropriate amount of 1 M KNO_3

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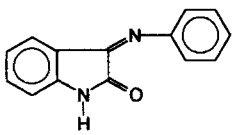
Table 1. Analytical data. Infrared frequencies, NMR and mass spectra of free ligand isatin-3-phenyl imine $C_{14}H_{10}N_2O$



IR(cm^{-1})	NMR	Mass spectra	Calculated mass
3500 (ν N–H) indole ring 1740 (ν C=O) indole ring 1651 (ν C=N) 1613 (ν C=C) aromatic	Signals at $\delta = 6{\cdot}5$–$7{\cdot}7$ ppm Corresponding to the aromatic protons of both isatin and phenyl rings $\delta = 8{\cdot}8$–$9{\cdot}4$ ppm Corresponding to N–H 70% O–H 30%	Molecular ion peak at 222 m/z	222

was added to maintain constant ionic strength of 0·2 M, 0·15 M, 0·1 M or 0·05 M, as required.

4. Results and discussions

Proton–ligand and metal–ligand stability constants were calculated by the method of Irving and Rossotti (1953). The $\bar{n}A$ values were between (pH = 9·8) and (pH = 10·8) indicating that only one proton is dissociating from the ligand. The $\bar{n}A$ values, which is the average number of protons bound to the ligand, were in the range 0·25 (pH = 6) to 2·0 (pH = 9·5) for all the metal ions indicating the formation of 1:1 and 1:2 complexes (figure 2). The stability constants log K_1 and log K_2 were also evaluated by the algebraic method and the least squares methods (Taqui Khan and Martell 1960). The values obtained by these methods agree within $\pm$ 0·05 (table 2).

The stability constants of metal complexes follow the order Co(II) < Ni(II) < Cu(II) > Zn(II), which is in accordance with that in the literature (Irving and Williams (1953).

From table 2, it is clear that log K_1 and log K_2 values decrease with increasing ionic strength. Linear plots were obtained when log K_1 values were plotted against $\mu^{1/2}$. The values of the negative slopes of these plots correspond approximately to the theoretically expected values indicating that the metal ions combine predominantly with the dissociated ligands (Sudhakar Reddy and Ram Reddy 1981). The log K_1 values at zero ionic strength for Co(II), Ni(II), Cu(II) and Zn(II) are 4·84, 5·90, 7·15 and 6·0, respectively.

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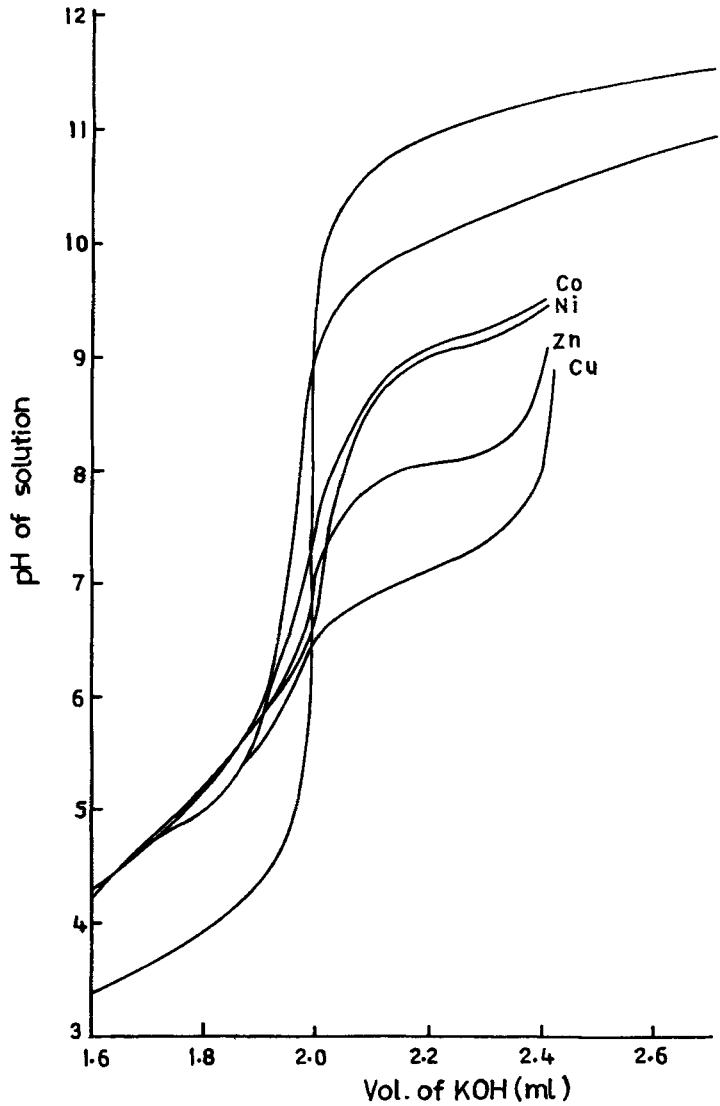

Figure 1. Potentiometric titration curves of isatin-3-phenyl imine in presence and absence of metal ions in aqueous dioxane medium at 303°K and 0·1 M KNO_3 ionic strength.

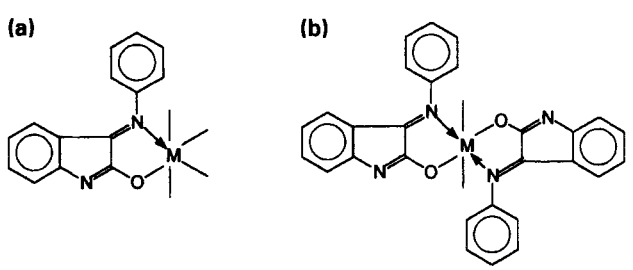

Figure 2. Structures of the 1:1 (**a**) and 1:2 (**b**) metal–ligand complexes.

Table 2. Stepwise and overall stability constants of Co(II), Ni(II), Cu(II) and Zn(II) chelates of isatin-3-phenylimine in 10% by volume of dioxane in-dioxane–water at different ionic strengths at 30°C.

Metal ion/ ligand	Stability constants	Ionic strengths			
		0·05 M	0·10 M	0·15 M	0·20 M
Isatin-3-phenyl-	pK_a	10·75	10·70	10·64	10·57
Co(II)	$\log K_1$	4·82	4·80	4:79	4·77
	$\log K_2$	4·41	4·36	4·26	4·23
	$\log \beta_2$	9·23	9·16	9·05	9·00
Ni(II)	$\log K_1$	5·05	5·02	4·98	4·92
	$\log K_2$	4·71	4·69	4·66	4·59
	$\log \beta_2$	9·76	9·71	9·64	9·51
Cu(II)	$\log K_1$	6·91	6·71	6·60	6·47
	$\log K_2$	6·55	6·31	6·09	5·93
	$\log \beta_2$	13·46	13·00	12·69	12·40
Zn(II)	$\log K_1$	5·86	5·76	5·57	5·62
	$\log K_2$	5·60	5·45	5·35	5·22
	$\log \beta_2$	11·46	11·26	10·92	10·84

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