

Stability Constants of Some Bivalent Metal Ion Chelates of Schiff Bases Derived from 2-Hydroxy-5-bromobenzaldehyde

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Potentiometric studies have been carried out on metal chelates of Mg^{2+} , Cd^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} with N-(2-hydroxy-5-bromobenzylidene)-aniline, N-(2-hydroxy-5-bromobenzylidene)-4-methylaniline, and N-(2-hydroxy-5-bromobenzylidene)-4-chloroaniline. The dissociation constants of the reagents and formation constants of their metal chelates have been determined by Calvin-Bjerrum pH titration technique as adopted by Irving and Rossotti, at $28 \pm 0.1^\circ C$ and at an ionic strength of 0.1 M in 75:25 (v/v) dioxan-water medium.

The chelating properties of schiff bases of *o*-hydroxyaldehydes and ketones are well established. These ligands show useful analytical applications as well as biological activities. In view of this, in the present study, schiff bases of 2-hydroxy-5-bromobenzaldehyde have been synthesised and the stability constants of their metal chelates have been determined potentiometrically, by Calvin-Bjerrum technique, as adopted by Irving and Rossotti¹.

The reagents (A) N-(hydroxy-5-bromobenzylidene)aniline, (B) N-(2-hydroxy-5-bromobenzylidene)-4-methylaniline and (C) N-(2-hydroxy-5-bromobenzylidene)-4-chloroaniline were prepared by condensing equimolar ethanolic solutions of 2-hydroxy-5-bromobenzaldehyde and the respective amines. The products obtained were repeatedly crystallised to obtain analytically pure samples. Their purities were tested by TLC and elemental analyses.

The experimental details and computational methods were the same as described in our earlier publication².

Calculations

From the titration data, \bar{n}_A values were determined and were plotted against *B* (pH meter readings) to obtain values of pK_1 and pK_2 . These values were further corroborated by straight line plots of $\log \bar{n}_A/1 - \bar{n}_A$ versus *B* and $\log 2 - \bar{n}_A/\bar{n}_A - 1$ versus *B* respectively.

From the metal ion titration curves, \bar{n} and *pL* values were calculated. The \bar{n} values were plotted

Table 1—Stability Constants of the Ligands and Their Metal Complexes

[Temp. = $28 \pm 0.1^\circ C$; $\mu = 0.1 M$]

<i>N</i> -(2-Hydroxy-5-bromobenzylidene)aniline							
	H ⁺	Cu ²⁺	Co ²⁺	Ni ²⁺	Zn ²⁺	Cd ²⁺	Mg ²⁺
Log K_1	9.27	7.95	5.73	5.72	5.56	4.51	3.72
Log K_2	2.72	6.82	—	—	—	—	—
<i>N</i> -(2-Hydroxy-5-bromobenzylidene)-4-methylaniline							
	H ⁺	Cu ²⁺	Zn ²⁺	Ni ²⁺	Co ²⁺	Cd ²⁺	Mg ²⁺
Log K_1	10.05	9.60	6.32	6.24	6.02	4.97	4.32
Log K_2	3.30	8.49	—	—	—	—	—
<i>N</i> -(2-Hydroxy-5-bromobenzylidene)-4-chloroaniline							
	H ⁺	Cu ²⁺	Ni ²⁺	Co ²⁺	Zn ²⁺	Cd ²⁺	Mg ²⁺
Log K_1	8.78	7.56	5.32	5.15	5.07	4.00	3.64
Log K_2	1.86	6.25	—	—	—	—	—

against the corresponding *pL* values to get the formation curves of the metal complex-ion equilibria. From these plots, values of $\log K_1$ and $\log K_2$ were evaluated. These were further corroborated by straight line plots of $\log \bar{n}/1 - \bar{n}$ versus *pL* and $\log 2 - \bar{n}/\bar{n} - 1$ versus *pL* respectively.

The pK_{OH}^H value of (B), i.e., N-(2-hydroxy-5-bromobenzylidene)-4-methylaniline, (10.05) is found to be higher than that of (A), i.e., N-(2-hydroxy-5-bromobenzylidene)aniline (9.27). The methyl group at *para* position increases the electron density on the azomethine N through hyperconjugation as well as through +*I* effect resulting in stronger chelation. This accounts for the higher pK_{OH}^H value of the compound (B) as compared to that of compound (A).

In the case of compound (C), i.e., N-(2-hydroxy-5-bromobenzylidene)-4-chloroaniline, the pK_{OH}^H value is found to be 8.78 which is lower than that of (A) (9.27). This is due to the -*I* effect exerted by the chloro substituent at the *para* position in (C).

The orders of the stability constants (Table 1) for the ligands are:

(A) *N*-(2-Hydroxy-5-bromobenzylidene)-aniline:
 $Cu^{2+} > Co^{2+} \approx Ni^{2+} > Zn^{2+} > Cd^{2+} > Mg^{2+}$

(B) *N*-(2-Hydroxy-5-bromobenzylidene)-4-methylaniline:
 $Cu^{2+} > Zn^{2+} \approx Ni^{2+} > Co^{2+} > Cd^{2+} > Mg^{2+}$

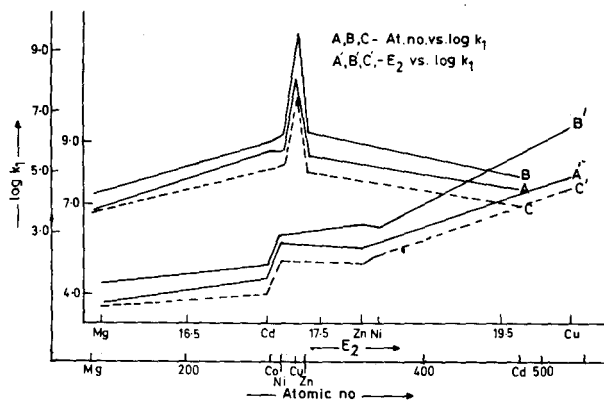


Fig. 1—Plots of $\log K_1$ values against atomic numbers (A, B and C) and $\log K_1$ values against ionization potential (A', B' and C')

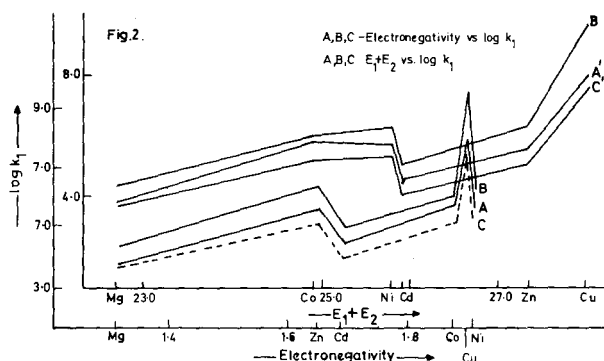
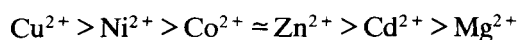


Fig. 2—Plots of $\log K_1$ values against electronegativities (A, B and C) and $\log K_1$ values against $E_1 + E_2$ (A', B' and C')

(C) *N*-(2-Hydroxy-5-bromobenzylidene)-4-chloroaniline.



The $\log K_1$ values of the metal-ligand systems were plotted against the atomic numbers of the metal ions (Fig. 1). The plots showed a monotonic rise with a maximum at Cu, followed by a fall and lower value of Zn. A similar relationship was observed by Irving and Williams³. The above plot shows that stability decreases with increase in basicity of the metal, i.e., weakly basic metal Cu forms stronger chelates and strongly basic metal like Mg forms weaker chelates⁴.

In the plots of $\log K_1$ versus second ionisation potential of the metal (Fig. 1), it is observed that for ligands A and C, stability increases from Mg to Co, falls marginally at Zn and then again increases upto Cu, whereas in the case of ligand B, it increases steadily from Mg to Cu, Zn and Ni having practically same stability. This is in conson-

ance with the fact that Zn is not a member of the first transition series⁶.

The $\log K_1$ values of the metal-ligand systems were plotted against the electronegativities of the metals (Fig. 2). The stabilities of complexes formed by any ligand with a series of metals may be expected to increase with the increase in electronegativity⁵. In the present case, it is observed that stability increases with the electronegativity of the metal except for Cd and Ni. In the case of Ni it falls rather abruptly.

The stability constants for the ligands A, B and C increase approximately linearly with the sum of the first two ionisation potentials of the gaseous metal atoms, with the exception of Cd where the value falls down (Fig. 2). This presumably indicates an underlying similarity between the electron energy levels in the complex ions and in the corresponding metal atoms⁷.

The reagents used in the present investigation are good chelating agents and like EDTA they form strong chelates with Ca^{2+} . It was thought worthwhile to investigate their anticoagulant properties. The anticoagulant activity of these reagents was evaluated by employing 'Dale and Laidlaw' technique⁸. The *in vitro* test was carried out using rabbits whole blood. Normal clotting time was first determined using capillary technique with twenty blood samples drawn from the marginal ear vein of the animal. In order to test for the anticoagulant activity of the compounds, the freshly drawn sample was mixed with about 3-4 mg of the test compound in a glass vial. The capillary was then quickly filled with the blood sample and the clotting time was determined. The normal clotting time was found to be (2.5 ± 0.5) min. The clotting time observed for the compound (A) was 2.5 ± 0.5 min, for compound (B) was 8.25 ± 0.5 min and that for (C) was 15.5 ± 0.2 min.

References

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