

Mixed ligand complexes of copper(II), nickel(II), cobalt(II) & zinc(II) with iminodiacetic acid as a primary ligand & imidazole as a secondary ligand

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The stability constants of the title mixed ligand complexes determined potentiometrically in aqueous medium, follow the order: $\text{Cu} > \text{Zn} > \text{Ni} > \text{Co}$. K_{MLA} values are greater than $K_4(\text{Im})$ for simple imidazole complexes. At higher concentrations of imidazole (MLA_2 systems), Cu(II) and Ni(II) form both MLA and MLA_2 types of complexes, but with Co(II) and Zn(II) only MLA is formed.

Mixed ligand complexes containing iminodiacetic acid (IMDA) or imidazole have been investigated by many workers¹⁻³. Sigel³ has observed that the participation of an imidazole group favours the formation of more strong mixed ligand complexes than that of an amino group, if an O donor ligand is also involved. In our earlier publication⁴ we studied the mixed ligand complexes of Cu(II) , Ni(II) , Co(II) and Zn(II) with aspartic acid or glutamic acid as the primary ligands, and imidazole as the secondary ligand. In the present note, the stability constants of the title mixed ligand systems have been determined potentiometrically in aqueous medium.

Experimental

Imidazole (Sigma) and iminodiacetic acid (Sigma) were used as such. Other reagents, apparatus and procedure were the same as described earlier^{4,5}. All the titration mixtures also contained a fixed amount (one equivalent) of free perchloric acid. The ionic strength was kept constant at 0.1 M with sodium perchlorate.

Similar titration curves have been obtained for all the mixed ligand systems: M(II) -iminodiacetic acid-imidazole. The titration curve for the binary 1:1 Cu(II) -iminodiacetic acid system (ML) (Fig. 1) shows an inflexion at $a = 2$ (pH 4-8.5), beyond which it is however drifted below. This indicates the formation of neutral ML and the hydroxo chelate ML(OH) respectively. The mixed ligand MLA titration curve shows two inflexions at $a = 2$ and 3 at pH

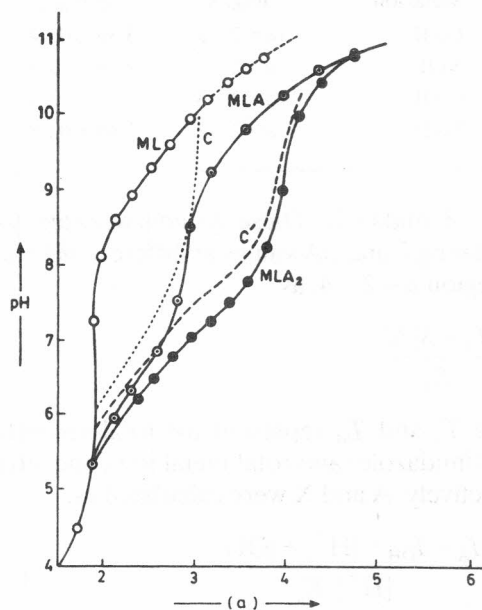


Fig. 1—Titration curves for Cu(II) -IMDA-imidazole systems. ML: 1:1 molar ratio of Cu(II) to IMDA, MLA: 1:1:1 molar ratio of Cu(II) to IMDA and imidazole, MLA_2 : 1:1:2 molar ratio of Cu(II) to IMDA and imidazole, C: composite curve for MLA_2 system, C': for MLA_2 system, ---- indicates turbidity.

5 and 8.5 respectively. It is also coincident with the ML titration curve up to $a = 2$, but beyond that the MLA curve runs below the ML curve. In the 1:1 Cu(II) -imidazole system, the titration curve shows an inflexion at $a = 1$, followed by a buffer region ($a = 1 - 2$) and the final inflexion appears at $a = 3$. In the ternary system the solution remains clear throughout the titration, whereas in ML system a turbidity appears at $a = 3$ ($\text{pH} \sim 10$); in the Cu(II) -imidazole system, the precipitation starts at $\text{pH} \sim 7$ ($a = 2$). Moreover, the experimental MLA curve is well displaced from the theoretical composite curve and the colour of the solution is intense blue, much more than in ML system, whereas in the simple MA system the colour of the solution is bluish green. These observations indicate the formation of the mixed complex in the region $a = 2 - 3$.

The pH titration curves of the mixed ligand systems with other transition metal ions, such as Co(II) , Ni(II) and Zn(II) also reveal that in all these cases as well, the mixed complexes are formed in the region $a = 2 - 3$.

Similarly pH titrations were also carried out at the metal: ligand ratios of 1:1:2 (MLA_2 systems) to see the formation of a MLA_2 chelate at higher concentr-

Table 1—Stability constants of mixed ligand complexes (M-IMDA-Im systems)

[$\mu = 0.1 M \text{ NaClO}_4$; temp. = 35°C]

Metal ion	Region	log K_{MLA}
Cu(II)	($a = 2-3$)	3.38 ± 0.04
Ni(II)	($a = 2-3$)	2.78 ± 0.05
Co(II)	($a = 2-3$)	2.51 ± 0.03
Zn(II)	($a = 2-3$)	2.86 ± 0.05

Table 2—Stability constants for mixed ligand complexes (MLA_2) (M-IMDA-Im₂) systems[$\mu = 0.1 M \text{ NaClO}_4$; temp. = 35°C]

Metal ion	Region	log K_1	log K_2	log β_2 (MLA_2 systems)
Cu(II)	($a = 2-4$)	3.35 ± 0.05	2.95 ± 0.03	6.30 ± 0.08
Ni(II)	($a = 2-4$)	2.74 ± 0.04	1.60 ± 0.03	4.34 ± 0.07

ations of imidazole. These systems were analysed by calculating $\bar{n}$ and pA values at different pH values in the region $a = 2-4$, as

$$\bar{n} = \frac{(T_A - X[A])}{T_M} \quad \dots (1)$$

where T_A and T_M represent the total secondary ligand (imidazole) and total metal ion concentrations respectively. A and X were calculated as:

$$[A] = \frac{T_A - T_{OH} - [H^+] + [OH^-]}{[H^+]/K_a} \quad \dots (2)$$

$$\text{and } X = \frac{[H^+]}{K_a} + 1 \quad \dots (3)$$

K_a represents dissociation constant of the ligand imidazole. The value of T_{OH} was calculated from the amount of alkali added beyond the ML curve in MLA_2 titration.

Results and discussion

The results have shown that for Cu(II) and Ni(II) systems, $\bar{n}$ values tend to approach a maximum value (~ 2), but in the case of Co(II) and Zn(II) systems the maximum value reached is approximately 1(1-1.2). In Cu(II) and Ni(II) systems formation curves were drawn from $\bar{n}$, pA data, from which the two stability constants K_1 and K_2 (for MLA_2 systems) were estimated. These were further refined by successive approximations.

The protonation constant of imidazole was determined by Irving and Rossotti's method as $\log K^H = 7.07$ at 35°C and $0.1 M (\text{NaClO}_4)$ which compares well with those reported in literature^{6,7}.

The stability constants of the ternary systems (Table 1) follow the sequence $\text{Cu} > \text{Zn} > \text{Ni} > \text{Co}$. Thus, it is evident that in the present case the mixed

Ni(II) complex is slightly less stable than the corresponding Zn(II) complex, whereas in general Ni(II) forms stronger complexes with amines than with Zn(II). But such reversal in the stability of Ni(II) and Zn(II) complexes has also been observed earlier^{8,9}. Sigel³ has remarked that the mixed-ligand complexes containing Ni^{2+} are less favoured, in general as long as an aromatic amine such as a pyridyl or imidazole group is involved. Moreover, the mixed IMDA-Im complexes of Cu(II) and Ni(II) are less stable than the corresponding mixed NTA-Im complexes, but in the case of Co(II) and Zn(II), the mixed IMDA-Im complexes are somewhat more stable.

Further, a comparison of the stability constants of the mixed ternary complexes (K_{MLA}) with those of the corresponding binary imidazole complexes^{10,11} (K_1) shows the following trends: In Co(II) and Zn(II) complexes $K_{\text{MLA}} > K_1 (\text{Im})$, but with Cu(II) and Ni(II) $K_{\text{MLA}} < K_1 (\text{Im})$, whereas $K_{\text{MLA}} > K_4 (\text{Im})$ in all the cases. Similarly with Ni(II), K_2 (for MLA_2 system) $> K_5 (\text{Im})$ ¹¹ (Table 2).

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