

Studies on mixed ligand complexes of Cu(II), Ni(II), Zn(II) and Cd(II) with 8-hydroxyquinoline-5-sulphonic acid & anthranilic acid/nicotinic acid

J P S Bisht*, N P S Bisht & S P Singh

Department of Chemistry, J.V. College, Baraut (Meerut)

Received 18 February 1988; revised 17 June 1988;
rerevised and accepted 5 August 1988

pH-metric studies on the interaction of Cu(II), Ni(II), Zn(II) and Cd(II) with 8-hydroxyquinoline-5-sulphonic acid (HQSA) in the presence of anthranilic acid (AnthA) or nicotinic acid (NicoA) indicate the simultaneous formation of 1:1:1 mixed ligand chelates; however, no complex formation occurs in the systems Zn(II)/Cd(II)-HQSA-NicoA.

8-Hydroxyquinoline-5-sulphonic acid (HQSA) is an excellent chelating agent and has been reported¹⁻⁴ to be a biologically and physiologically active compound. Although the binary chelates of HQSA have been studied quite extensively, only a few studies on the mixed ligand chelates are recorded⁵⁻¹². We report here *pH*-metric studies on the mixed ligand chelates of Cu(II), Ni(II), Zn(II) and Cd(II) with HQSA and anthranilic acid (AnthA)/nicotinic acid (NicoA).

Experimental

Preparation of the solutions (5×10^{-3} M) of metal

nitrates and HQSA, and *pH*-metric titration techniques have been described earlier^{8,9}. The solutions of anthranilic acid (BDH) and nicotinic acid (BDH) were prepared by direct weighing and their strengths were checked *pH*-metrically. The formation constant data are given in Table 1.

Results and discussion

The dissociation constant values of HQSA ($pK_1 = 4.06$ & $pK_2 = 8.49$) were taken from the literature¹³ and those of anthranilic acid (4.88 ± 0.04) and nicotinic acid (4.75 ± 0.03) were calculated by the method of Chaberek and Martell¹⁴.

The *pH*-metric titration curves 4, 5, 7, 8, 10, 11, 13, 14, 16 and 18 (Fig. 1) of the solutions containing equimolar quantities of metal nitrates and HQSA/AnthA/NicoA may be explained on the basis of the formation of 1:1 binary chelates and their conversion into the corresponding hydroxo derivatives. The curve for Cu(II)-NicoA system indicates that the reactions for the formation of 1:1 binary complex and its hydroxo derivative overlap with each other whereas in other systems stepwise formation of 1:1 binary complex and hydroxo derivative takes place. No complex formation tendency is observed in the case of Cd(II)/Zn(II) with nicotinic acid under present conditions. The formation constants of 1:1 Cu(II)/Ni(II)/Zn(II)/Cd(II)-HQSA ($\log K_{MA} = 11.92, 9.02, 7.54$ and 7.70 respectively) were taken from the literature^{15,16}. The equilibrium and forma-

Table 1—Formation and equilibrium constants of 1:1 binary and 1:1:1 ternary complexes ($\mu = 0.1$ M KNO₃, temp. = $30 \pm 1^\circ$ C)

System	$\log K_{ML}$	$\log K_{MAL}$	$\log \beta_{MAL}$	$-\log K'$	$-\log K''$
Cu(II)-AnthA	5.00 ± 0.04	—	—	—	—
Ni(II)-AnthA	2.19 ± 0.03	—	—	—	—
Zn(II)-AnthA	1.99 ± 0.08	—	—	—	—
Cd(II)-AnthA	1.89 ± 0.06	—	—	—	—
Cu(II)-NicoA	2.52 ± 0.02	—	—	—	—
Ni(II)-NicoA	2.03 ± 0.05	—	—	—	—
Cu(II)-HQSA-AnthA	—	3.09 ± 0.08	15.00 ± 0.07	1.79 ± 0.08	2.43 ± 0.07
Ni(II)-HQSA-AnthA	—	3.08 ± 0.06	12.11 ± 0.06	1.80 ± 0.06	5.32 ± 0.06
Zn(II)-HQSA-AnthA	—	2.91 ± 0.09	11.45 ± 0.09	1.97 ± 0.09	5.98 ± 0.09
Cd(II)-HQSA-AnthA	—	2.59 ± 0.11	10.29 ± 0.11	2.29 ± 0.11	7.14 ± 0.11
Cu(II)-HQSA-NicoA	—	2.61 ± 0.05	14.53 ± 0.05	2.14 ± 0.05	2.77 ± 0.05
Ni(II)-HQSA-NicoA	—	2.41 ± 0.08	11.44 ± 0.08	2.34 ± 0.08	5.86 ± 0.08

$\log K_{ML}: M^{2+} + L^- = ML^-$; $\log K_{MAL}: MA + L^- = MAL^-$;

$\log \beta_{MAL}: M^{2+} + A^{2-} + L^- = MAL^-$;

$-\log K': MA + HL = MAL^- + H^+$;

$-\log K'': M^{2+} + H_2A + HL = MAL^- + 3H^+$

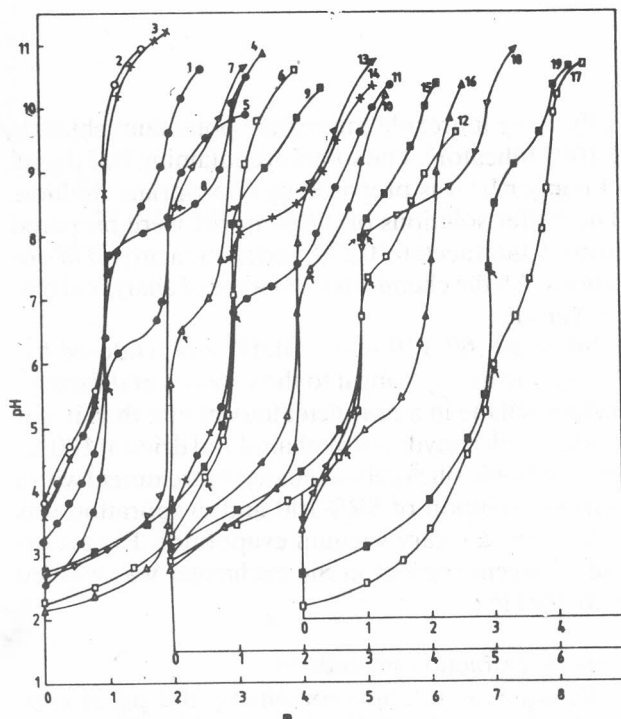


Fig. 1—Potentiometric titration curves of mixed ligand chelates: Cu(II)/Ni(II)/Zn(II)/Cd(II)-HQSA-AnthA/NicoA: curve 1, HQSA; 2, AnthA; 3, NicoA; 4, Cu(II)-HQSA; 5, Cu(II)-AnthA; 6, Cu(II)-HQSA-AnthA; 7, Ni(II)-HQSA; 8, Ni(II)-AnthA; 9, Ni(II)-HQSA-AnthA; 10, Zn(II)-HQSA; 11, Zn(II)-AnthA; 12, Zn(II)-HQSA-AnthA; 13, Cd(II)-HQSA; 14, Cd(II)-HQSA; 15, Cd(II)-HQSA-AnthA; 16, Cu(II)-NicoA; 17, Cu(II)-HQSA-NicoA; 18, Ni(II)-NicoA; 19, Ni(II)-HQSA-NicoA. Arrow indicates appearance of a solid phase.

tion constants of 1:1 M(II)-AnthA/NicoA complexes were calculated by algebraic method as described earlier¹⁷. Constant values were found up to $m=1$, except in the Cu(II)-NicoA system, where the values were constant up to $m=0.5$ (Table 1).

Curves 6, 9, 12, 15, 17 and 19 (Fig. 1) represent the pH-metric titrations of solutions containing copper(II), nickel(II), zinc(II) or cadmium(II) nitrate in the presence of equimolar concentrations of HQSA and AnthA/NicoA respectively. These curves exhibit a sharp inflection at $m=3$ except for the Cu(II)-NicoA system, which shows a poor inflection at $m=3$ followed by a sharp inflection at $m=4$. Initially, all these curves run slightly above the corresponding 1:1 M(II)-HQSA titration curves due to zwitter-ion formation tendency of anthranilic and nicotinic acids in solution, indicating that in the beginning 1:1 M(II)-HQSA binary complexes are formed. The lowering of the curves for the ternary systems, Cu(II)/Ni(II)/Zn(II)/Cd(II)-HQSA-AnthA/NicoA in comparison with the curves for binary systems

M(II)-HQSA after $m=1.8, 1.3, 0.8, 0.2, 1.8$ and 1.2 respectively, indicates the simultaneous formation of 1:1:1 mixed ligand complexes, MAL, in these systems. Further, an inflection at $m=4$ in the case of the system Cu(II)-HQSA-NicoA and buffer regions after $m=3$ in other systems, except in Cu(II)-HQSA-AnthA, indicate the conversion of ternary complexes into the corresponding hydroxo derivatives in the high pH-range. The values of the formation constants of the ternary complexes were determined by algebraic method as described earlier⁸ (Table 1).

Anthranilic acid forms stronger ternary complexes than nicotinic acid because the former ligand is coordinated to the metal ion in such a way that the benzene ring is coplanar with the rest of the complex molecule since the amino and COOH groups are in the *ortho*-positions. In the latter case, the pyridine ring of nicotinic acid is probably perpendicular to the plane of the rest of the molecule as the COOH group is in *meta* position with respect to nitrogen atom.

Acknowledgement

The authors are thankful to the authorities of J.V. College, Baraut, for providing necessary facilities and to Dr G.S. Malik, Head, Chemistry Deptt., J.V. College, Baraut, for valuable suggestions and criticism.

References

- 1 Ewe K, *Chem Abstr*, 68 (1968) 94055a.
- 2 Cavier R, Loger N, Royer R, Reme L & Demersiman P, *Ann Sci Pharm Fr*, 32 (1974) 623.
- 3 Manzo L, Passoni R, Segre A D, Berte F & Crema A, *Experimentia*, 32 (1976) 1318.
- 4 Pettison S E & Michael F D, *Biochem*, 15 (1976) 3691.
- 5 Scharff J P & Paris M R, *C R Acad Sci Paris Ser*, C263 (1966) 935.
- 6 Singh B P, Verma H S & Singh S P, *J Indian chem Soc*, 57 (1980) 102.
- 7 Makitie O, Lujnen L H J & Laakoneu A, *Finn Chem Lett*, (1977) 31.
- 8 Verma H S, Singh B P, Singh S P & Bisht N P S, *J Indian chem Soc*, 58 (1981) 611.
- 9 Malik G S, Singh S P & Tandon J P, *J inorg nucl Chem*, 39 (1977) 1279.
- 10 Abbasi S A, *Pol J Chem*, 57 (1983) 355.
- 11 Kambara T, Maeyma M & Hasebe K, *Bunski Kogaku*, 20 (1971) 1949; *Chem Abstr*, 76 (1972) 54055j.
- 12 Galus M & Hujanicki A, *Essays Anal Chem*, (1977) 89.
- 13 Singh S P & Tandon J P, *Mh Chem*, 106 (1975) 271.
- 14 Chaberek (Jr) S & Martell A E, *J Am chem Soc*, 74 (1952) 5052.
- 15 Richard C P, Gustafson R L & Martell A E, *J Am chem Soc*, 81 (1959) 1033.
- 16 Nasanen R & Euisitala, *Acta chem scand*, 8 (1954) 112, 835.
- 17 Singh S P & Tandon J P, *Acta chim Acad sci hung*, 84 (1975) 419.