

Studies on binary and ternary complexes of Co(II) and Ni(II) ions

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Abstract. Potentiometric investigations on the binary and ternary complexes of the type MA, MB and MAB have been carried out, where M(II) = Co(II) and Ni(II); A = iminodiacetic acid (IMDA) and B = oxydiacetic acid (ODAA). The formation constants and free energies of formation for binary and ternary complexes have been reported.

Keywords. Iminodiacetic acid; oxydiacetic acid; formation constant; free energy of formation.

1. Introduction

Binary complexes of iminodiacetic acid (IMDA) and oxydiacetic acid (ODAA) with various metals have been extensively investigated by Chaberek and Martell (1952), Misumi and Aihara (1966), Liberty and Napoli (1971), Napoli (1972), Klein and Kersels (1964), Ramamoorthy and Santapa (1969), Miyazaki and Toei (1975). Mixed ligand complexes of various metals ions with IMDA are widely studied (Kuglar and Carey 1970; Ramamoorthy and Santapa 1971; Joshi and Bhattacharya 1980; Katkar and Munshi 1985). However, literature survey further reveals that mixed ligand complexes of Co(II) and Ni(II) with IMDA as primary ligand and ODAA as secondary ligand have not been studied so far. In view of this it was, therefore, considered of interest to study the formation constants of the following systems:

Co(II) and Ni(II)-IMDA (1:1 complexes), Co(II) and Ni(II)-ODAA (1:1 complexes), Co(II) and Ni(II)-IMDA-ODAA (1:1:1 complexes).

2. Experimental

2.1 Materials

The chemicals used were of BDA (AR) grade. Solutions of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ were prepared in conductivity water and stock solutions were standardized by known methods. Solutions of the ligands IMDA (A) ODAA (B) were prepared by direct weighing. Perchloric acid (0.025 M) was prepared from stock solution and the solution was standardized against standard sodium hydroxide solution.

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2.2 Apparatus

The pH titrations were carried out at $25 \pm 0.5^\circ\text{C}$ (maintained thermostatically) with the help of Philips pH-meter (PR 9405 M). The instrument was calibrated using buffer tablets of pH 4.0 and 9.2.

2.3 Conditions of study

The experiments were performed in a specially designed double-walled beaker of capacity 250 ml made of pyrex glass. The total volume of the solution (50 ml), ionic strength ($\mu = 0.10 \text{ M NaClO}_4$) and concentration of metal ions and ligands ($5 \times 10^{-4} \text{ M}$) were kept constant at the beginning of the titration. All the titrations were performed in duplicate in order to establish the reproducibility of the measurements. The following sets of solutions were prepared and titrated against alkali (0.25 M):

(i) *Acid and ligand*

(a) $2.5 \times 10^{-3} \text{ M HClO}_4$

(b) $2.5 \times 10^{-3} \text{ M HClO}_4 + 5 \times 10^{-4} \text{ M IMDA/ODAA}$

(ii) *1:1 Binary system*

(c) $b + 5 \times 10^{-4} \text{ M metal ion}$

(iii) *1:1:1 Ternary system*

(d) $a + 5 \times 10^{-4} \text{ M IMDA} + 5 \times 10^{-4} \text{ M ODAA} + 5 \times 10^{-4} \text{ M metal ion}$

2.4 Calculations

The pK_1 and pK_2 values determined by the method of Irving and Rossotti (1954) for the acids agree well with the literature values. The values were further refined by computational techniques (Irving and Rossotti 1953; Dubey and Mehrotra 1967): (i) the interpolation at half \bar{n} values, (ii) the pointwise method, (iii) the curve fitting method, and (iv) the correction term method. The formation constants $\log K_{MA}$, $\log K_{MB}$ and $\log K_{MAB}$ of the binary and ternary systems were calculated by the method of Ramamoorthy and Santapa (1970, 1971). The following expressions were utilized for calculations:

$$K_{MA} = \frac{T_M - [A] \cdot X}{[A]^2 \cdot X} \quad (1)$$

$$K_{MAB} = \frac{T_M - \left\{ \frac{1}{2} [A] \cdot X \right\}}{\left(\frac{1}{2} \right)^3 \cdot A^3 \cdot X} \quad (2)$$

where T_M , A and X have their usual meanings. These calculations were carried out with the help of ECIL TDC 316 Computer using FORTRAN IV and COBOL languages in the various programs. Free energies of formations were determined by using the following expressions:

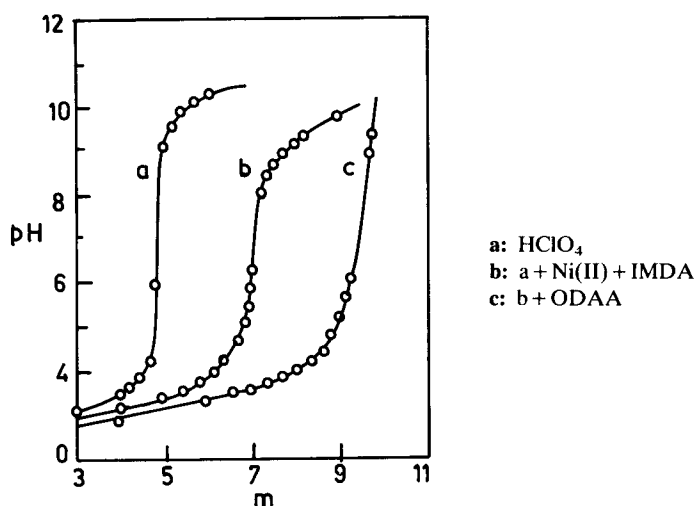
$$\Delta F^0 = -2.303 RT \log K_{MA} / \log K_{MB} / \log K_{MAB}$$

for binary and ternary complexes (table 1).

Table 1. Formation constants and free energy of formation of the complexes.

System	Stoichiometry	pH range investigated	log K	$-\Delta F^0$ (kcal mole ⁻¹)
Co(II)-IMDA	1:1	5.20–6.58	7.08 ± 0.04 (6.95) ^a	9.659 ± 0.055
Ni(II)-IMDA	1:1	3.50–5.25	8.35 ± 0.17 (8.21) ^a	11.392 ± 0.232
Co(II)-ODAA	1:1	3.85–4.23	3.24 ± 0.35	4.420 ± 0.477
Ni(II)-ODAA	1:1	4.20–5.55	3.32 ± 0.21	4.529 ± 0.286
Co(II)-IMDA-ODAA	1:1:1	3.65–4.20	6.69 ± 0.22	9.127 ± 0.300
Ni(II)-IMDA-ODAA	1:1:1	3.80–4.20	7.73 ± 0.01	10.546 ± 0.014

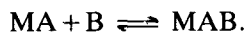
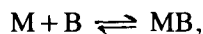
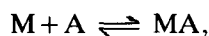
^a Literature value: Chaberek and Martell (1952)

**Figure 1.**

3. Results and discussion

The potentiometric curves of both the metals involved were found to be very similar in nature. Therefore, the curves of different systems for only one metal, viz. Ni(II)-IMDA and Ni(II)-IMDA-ODAA systems, are shown (i.e. b and c respectively) in figure 1 for the sake of brevity. Curve a represents the acid titration curve. For curve a, $m \approx 5.0$, therefore, for curve b, the inflection is assumed to take place at $m \approx 2$ [$\approx 7.0 - 5.0$] which indicates the formation of the 1:1 complex in Ni(II)-IMDA system (m being the number of moles of base added per mole of the metal ion or ligand). The 1:1:1 ternary complex system, Ni(II)-IMDA-ODAA, is represented by curve c, the inflection of which takes place at $m \approx 4$ [$\approx 9.0 - 5.0$]. It may be attributed to the stepwise addition of ligands to the metal ion resulting in the formation of 1:1:1 ternary complex.

The equilibria for M(II)-binary and M(II)-ternary systems can be represented by the following equations:



The formation of heteroligand-metal-complexes in these systems is further evidenced by (i) lowering in pH in comparison with the binary versus ternary systems, (ii) non-appearance of solid phase during the titration.

The stability constant values of all the systems are given in table 1. A perusal of these indicates that the values of $\log K_{MAB}$ (Ni(II)/Co(II)-IMDA-ODAA) are lower than those of $\log K_{MA}$ (Ni(II)/Co(II)-IMDA) systems. Lowering in the stability of ternary complexes in comparison to binary complexes has also been reported by other workers (Limaye and Saxena 1985).

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