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POTENTIOMETRIC DETERMINATION OF STABILITY CONSTANTS OF TRANSITION METAL COMPLEXES WITH p-AMINOBENZOIC ACID

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ABSTRACT

The stability constants of complexes of metals (Mg, Ni and Co) with p – aminobenzoic acid was determined by potentiometric methods by keeping 1 : 1, 1 : 2, 1 : 5 and 2 : 3 molar ratios. The results are analysed for their stabilities.

Key words: Metal complex, p-Amino benzoic acid, Potentiometric studies.

INTRODUCTION

Stability constants of metals complexes have been determined by different methods such as spectroscopy and potentiometry. It is well known that the simplest electroanalytical technique for determination of stability constants is potentiometric titration system using glass electrode.

The accurate determination of acidity and stability constants values are fundamental to understand the behaviour of ligands and their interaction with metal ions in aqueous solution. Such an understanding is important in a wide variety of areas like metal ions in biology, in biomedical applications, metal ions in the environment, extraction metallurgy, food chemistry and metal ions in many industrial process. One specific application is the use of chelating agents in heavy metal ion in toxication treatment.

For monobasic acids, pK_a values are simply determined by potentiometric titration of a known weight of the acid against standard sodium hydroxide solution. The method of calculation is also simple. The link between acid dissociation and stability constant is

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based on the fact that those ionic species, which combine with a hydrogen cation have an affinity for the cations of metals also. The principal difference is that ionisation is commonly regarded as dissociation, where as metal binding is seen as an association.

EXPERIMENTAL

All chemicals used were of the A. R. or extra pure grade. Determination of the pK_a values of the 1 : 1 and 1 : 2 and M^{II} complexes were carried out by potentiometric titration against standard 0.1N sodium hydroxide solution using pH meter as follows: The metal nitrate and p-aminobenzoic acid in the molar ratios 1 : 1, 1 : 2, 1 : 5 and 2 : 3 were mixed together in a beaker. 5 mL of HNO_3 (0.1N) and 5 mL of 1M $KNO_{3,}$ was added the solution was made to 50 mL and titrated against 0.1N NaOH. The pK_a values were than calculated using computer programme.

All the other solutions were also prepared in doubly distilled water. The pH measurements were carried out on ELICO digital model LI-122 pH meter (accuracy $\pm$ 0,01 pH unit) with a combined electrode type CL-51 having pH range 0 –14 and temperature range 20 –100 ^{0}C. The method of Calvin-Bjerrum as modified by Irving and Rossotti was used to obtain log K_l^H and log K_l^M values.

RESULTS AND DISCUSSION

There are different approaches to study the interaction of a metal ion with an organic ligand. Each method may require different experimental conditions, which may in turn, create differences in the interpretation of complexation reactions and the stability constants.

When a ligand and acid (HNO_3) solution is titrated with standard, NaOH, and after each addition of NaOH, the pH of solution was measured. In such solutions, several conditions must hold, such as:

$$[H^+] + [Na^+] = [^-OH] + [L^-] \qquad \text{…… (1)}$$

for electrical neutrality

Total concentration of ligand

$$L_{Total} = [HL] + [L^-] \qquad \text{…(2)}$$

We can represent the protonation of ligand as –

$$HL \rightleftarrows H^{+} + L^{-}$$

$$\therefore \ Ka = \frac{[H^{+}]\,[L]}{[HL]} \qquad \ldots(3)$$

Combining equation (1), (2) and (3), we get –

$$pK_{a} = - \log [H^{+}] + \log \left(\frac{L_{Total} - \{[Na^{+}] + [H^{+}] - [^{-}OH]\}}{[Na^{+}] + [H^{+}] - [^{-}OH]} \right) \qquad \ldots(4)$$

At the near neutral solution, $[^{-}OH]$ and $[H^{+}]$ are very small as compared to $[Na^{+}]$. Hence, equation (4) becomes

$$pK_{a} = - \log [H^{+}] + \log \left(\frac{L_{Total} - [Na^{+}]}{[Na^{+}]} \right) \qquad \ldots(5)$$

This equation is used to calculate the pK_a of ligand, but in our experiments, we calculate $\eta^{-}{}_{A}$ from the pH titration curve and pK_a is determined from $\bar{\eta}_{A}$ values.

Formation curve for $\bar{\eta}_{A}$ against pH was constructed and the value of log K_1H was found out for the pH at $\bar{\eta}_{A} = 0.0$ and the stability constant value obtained by least squares method were in good agreement with half integral method and pointwise calculation method.

When a solution containing M^{n+} ion and an equivalent amount of H^{+} (as HNO_3) is titrated it gives a solution containing an equlibrium mixture of H^{+}, ^{-}OH, HL, L^{-}, M^{n+}, $M^{(n-1)+}L$, $M^{(n-2)+}L_2$ etc. From pH measurements and a knowledge of the quantities of M^{n+}, H^{+}, HL etc., it is possible to calculate the stepwise stability constants K_1, K_2, $K_{3,}$ etc.

In most equilibrium studies of metal complexes formation, the equilibrium constant will be evaluated from measurements on solutions containing various concentration of M^{2+} and L^{-}. Such concentration changes will produce changes in the ionic strength of the solutions. To keep the ionic strength constant, a large excess of an unreactive ionic salt is added to the solutions. Then any change in ionic strength owing to changes in the position of equilibrium will be negligible as compared with the high concentration of the added salt.

The salt is added only to maintain the ionic strength of the medium and should not interact directly with M^{2+} or L^{-}. Salts such as KNO_3 and $NaClO_4$ have been used extensively because of the low affinity of the NO_3^{-} and ClO_4^{-} ions for M^{2+}. In this experiment, KNO_3 has been used.

For the present work the value of pK_a for p-aminobenzoic acid was found to be 5.9153. The p-aminobenzoic acid has two binding sites, N of amino group and COO^{-} group. The values for stability constants for Ni, Mg, and Co complexes are given in the Table 1.

Table 1. Stability constants

Metals	M : L Ratio			
	1 : 1	1 : 2	1 : 5	2 : 3
Ni	8.492	14.8593	8.3598	3.4649
Mg	8.4664	8.3392	7.0794	11.1943
Co	8.590	5.3186	8.6337	6.2330

We observed that the stability constant values for Ni shows the trend 2 : 3 < 1 : 5 < 1 : 1< 1 : 2 while the trend for Co is 1 : 2 < 2 : 3 < 1 : 1< 1 : 5 for Mg 1 : 5 < 1 : 2 < 1 : 1 < 2 : 3. These values suggests that 1 : 2 complex of Ni complex is more stable where as 1 : 5 of Co and 2 : 3 of magnesium complex is were stable.

The stability constant value varies with the ionic size of metal ion. The smaller is the ionic radius of the central metal, the more stable is the complex formed. It also depends upon the experimental conditions used.

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