

NOTES

**Complexation Behaviour of Some 3d Metals Ions
with Aminobenzoic Acids**

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The formation of binary complexes of 2-aminobenzoic acid, 3-amino-benzoic acid and 4-aminobenzoic acid with Co(II), Nd(II), Cu(II) and Zn(II) has been studied electrophoretically at $25 \pm 1^\circ\text{C}$ and constant ionic strength ($\mu = 0.1 \text{ M HClO}_4$) in aqueous medium. The stability order was found to be $\text{Cu(II)} > \text{Co(II)} > \text{Zn(II)}$.

Aminosubstituted benzoic acids are known to play an important role in biological systems^{1,2}. 3-Aminobenzoic acid (3-ABA) and its derivatives show anti-inflammatory action³ in guinea pigs and are used as local anaesthetics⁴. 2-Aminobenzoic acid (2-ABA) and 3-ABA are used in the manufacture of indigotin and azo dyes⁴. In the present paper the formation of 1 : 1 Co(II)-, Ni(II)-, Cu(II)-, Zn(II)-2ABA, -3ABA and 4-ABA complexes along with their stability constant values has been reported. These laboratories have published number of papers in which a new approach has been made for the study of complexation reaction in solution with the help of paper electrophoresis⁵⁻⁷.

All the chemicals used were of A. R. grade and their solutions were prepared in double distilled water. Metal perchlorates were prepared by the precipitation of metal carbonates from metal sulphates or nitrates or oxides (as the case may be) with appropriate reagents. Precipitates were thoroughly washed with boiling water and treated with calculate amount of 10% perchloric acid. These were boiled on a water bath, filtered and standardized⁸. The final concentrations of metal and ligand solutions were kept at $5.0 \times 10^{-3}\text{M}$ and $1.0 \times 10^{-2}\text{M}$ respectively. The metal ion spots were detected by ethanolic solution of 1-(2-pyridylazo)-2-naphthol (PAN).

Systronics paper electrophoresis equipment horizontal cum vertical type No. 604 (India) and two types of pH indicator and accessories (Leeds and Northrup, and Elico), having glass and calomel electrode assembly and working on 220 volts/50 cycles stabilized a.c. mains were employed after calibrating it with the help of buffer solutions of pH 4 and pH 9.2. After each experiment the calibration was checked.

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Suitable arrangements⁹ were made for controlling the temperature at $25 \pm 1^\circ\text{C}$.

Electrophoretic observations at various pH values of the background electrolyte obtained by adding NaOH solution to it were recorded and electrophoresis was carried out for 30 minutes at 200 volts, ionic strength being maintained at 0.1.

Mobility was calculated by earlier reported method⁹. Stability constants were found out using the pH vs. mobility curve⁹ and dissociation constants of the pH ligands¹⁰. The values are presented in Table 1.

TABLE 1
STABILITY CONSTANTS OF COMPLEXES
Temp. = $25 \pm 1^\circ\text{C}$, Ionic Strength 0.1 HClO₄

Cations/Ligands	Co(II)	Ni(II)	Cu(II)	Zn(II)
2-ABA	2.53	2.60	2.68	2.46
3-ABA	3.21	3.31	3.40	3.12
4-ABA	2.88	2.96	3.05	2.71

In all the metal (II)-2-ABA, -3ABA and -4ABA systems, two plateaus are obtained in the pH vs. mobility curve. The first plateau is attributed to the uncomplexed metal ion. Thereafter, a decrease in mobility is observed with increase of pH giving another plateau and indicating formation of 1 : 1 species. The studies showed that complexation of all the three ligands takes place between pH 2.92 and 5.40. The constant values of mobility after the second plateau indicate that no further complexation is taking place.

The stability constant values are in accordance with Irving and Williams¹¹ series.

Further, with the comparison of stability constant in view of ligands, the order is found to be 3-ABA > 4-ABA > 2-ABA, which can be explained on the basis of ability of the deprotonation of the ligands.

Amino group is an electron releasing group and this is greater from *para* than from the *meta* position. Due to effect of electron release, the electron density at the carbon atom attached to the carboxyl group will cause an increase of electron density at the O atom of the OH group and consequently, proton release will be rendered difficult, decreasing the acid strength. Since electron releasing effect is more pronounced from the *para* position in comparison to *meta*, proton release in the *para* isomer will be more difficult than in the *meta* isomer and hence, 3-ABA will be stronger than 4-ABA. In 2-ABA the amino group causes more electron

release than either of the *meta* or *para* isomers due to resonance effect. Simultaneous operation of positive inductive effect and resonance effect make the proton release difficult. Consequently, 2-ABA is weaker than the 3-ABA and 4-ABA.

From the above discussion, it is evident that 3-ABA is stronger than 2-ABA and 4-ABA which is responsible for the higher values of stability constant of M-(3-ABA) complexes than M-(2-ABA) and M-(4-ABA) complexes. On the same line as 4-ABA is stronger than 2-ABA, the metal complexes of 4-ABA are more stable than the metal complexes of 2-ABA.

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