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# Spectrophotometric Studies on the Stability Constant of $Al^{3+}$, $In^{3+}$ and $Ga^{3+}$ Chelates with Erichrome Cyanin-R

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The interaction of metal ion ($Al^{3+}$, $In^{3+}$ and $Ga^{3+}$) with Erichrome Cyanin-R (ECR) has been investigated by spectrophotometric technique. Light purple and purple coloured chelate having 1 : 2 metal to ligand ratio are formed over the pH range of 3.5 to 5.5 with $\lambda_{max}$ 515 nm for ECR, 540 for $Al^{3+}$, $In^{3+}$ and 530 nm for $Ga^{3+}$. Their stability constants have been determined by applying mole ratio method, Job's method of continuous variation and Dey and Coworkerrs' method. The values of log K for $Al^{3+}$, $In^{3+}$ and $Ga^{3+}$ were found to be 10.05, 7.77 and 8.5 respectively. The analytical applications of the colour reaction have also been investigated.

**Key Words: $Al^{3+}$, $In^{3+}$, $Ga^{3+}$, Chelates, Erichrome Cyanin-R, Stability constant.**

## INTRODUCTION

From the survey of chemical literature[1–6] it has been found that there are very few references regarding spectrophotometric studies on the composition and stability of metal-erichrome cyanin-R (ECR) complex. In this communication the composition, stability and characteristics of the chelate formed by erichrome cyanin-R with aluminium(III), indium(III) and gallium(III) have been reported.

## EXPERIMENTAL

An ECIL made PC based double beam UV-Vis spectrophotometer UV 5704 SS was used for absorbance measurement using matched quartz cells. Erichrome cyanin-R and $AlCl_3$, $InCl_3$ and $GaCl_3$ were obtained from BDH. All the other reagents were of analytical grade. The solutions were prepared in doubly distilled water. pH was measured on EC made L 1612 microprocessor based pH-meter. All experiments were performed at 25 ± 0.1°C. The total volume of the mixture prepared for the measurement was kept at 25 mL. The requisite amounts of buffer solutions were added to maintain the desired pH as shown in Table-1.

TABLE-1
ABSORBANCES OF REAGENTS AND MIXTURES

| System | pH | Colour | Reagent $\lambda_{max}$ (nm) | Chelate $\lambda_{max}$ (nm) |
|---|---|---|---|---|
| ECR-Al | 4.0 | Light purple | 515 | 540 |
| ECR-In | 5.5 | Light purple | 515 | 540 |
| ECR-Ga | 4.0 | Purple | 515 | 530 |

## RESULTS AND DISCUSSION

In view of the observations of Dey and coworkers[7], the organic chelating agents behave as colloidal electrolytes; dilute solutions of the order of $10^{-4}$ M and $10^{-5}$ M of erichrome cyanin-R were employed to avoid complications in absorptiometric measurements. With variation in hydrogen ion concentration erichrome cyanin-R changes its colour and its region of maximum absorption is found to shift. From Table-2 it is concluded that erichrome cyanin-R exists in three different forms depending upon the pH of the solution.

TABLE-2
SHIFT OF $\lambda_{max}$ WITH CHANGE IN pH

| pH | Region of maximum absorption (nm) |
|---|---|
| 2 | 480 |
| 3–7 | 515 |
| 7–above | 430 |

The method of Vosburgh and Cooper[8] was employed to determine the nature of the complexes formed in the solutions. Mixtures containing different ratios of metal-ECR were prepared at desired pH and absorbances were measured. It was found that only one complex having wavelength of maximum absorbance 530–540 nm is formed under the condition of study.

For determining the empirical formula of the chelates formed under the experimental conditions, mole-ratio method (Figs. 1–3), method of continuous variation (Figs. 4–6) and Jobs method of non-equimolar concentration (Figs. 7–9) were used. It was found that the combining ratio of metal-ECR was 1 : 2 at particular pH suggesting the formation of $M(ECR)_2$.

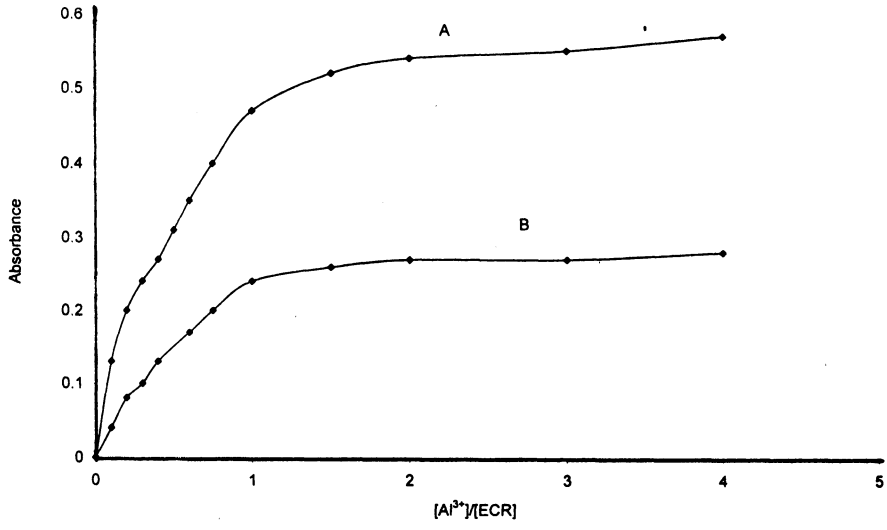


Fig. 1. Composition of Al-ECR chelate by mole ratio method

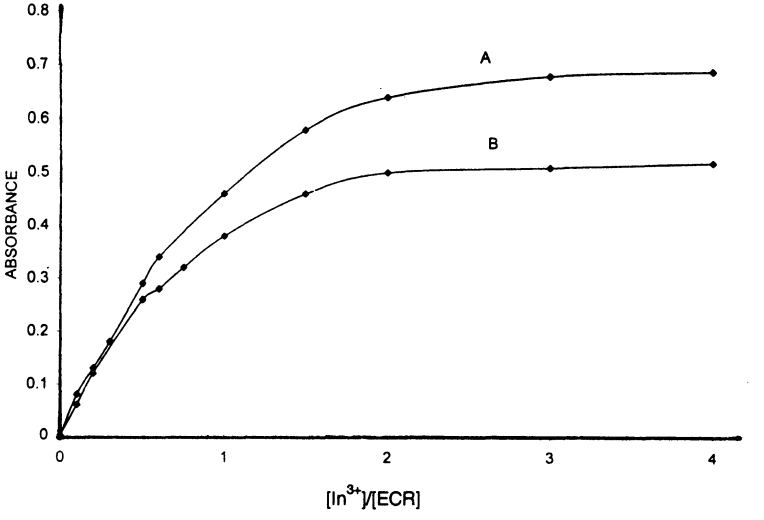


Fig. 2. Composition of In-ECR chelate by mole ratio method

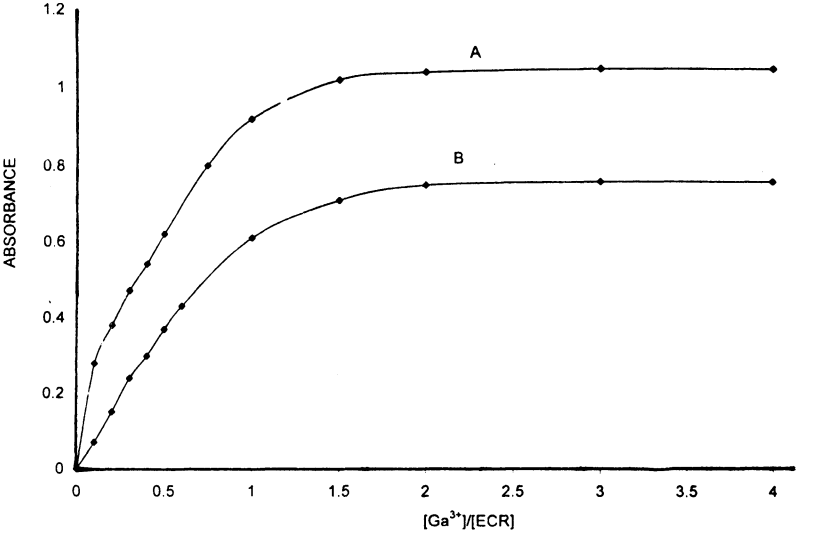


Fig. 3. Composition of Ga-ECR chelate by mole ratio method

TABLE-3
MOLE RATIO METHOD: COMPOSITION OF THE M-ECR CHELATE

Total Vvolume = 25 mL

| | $AlCl_3$ | | $InCl_3$ | | $GaCl_3$ | |
|---|---|---|---|---|---|---|
| Figure | 1 | | 2 | | 3 | |
| Curve | A | B | A | B | A | B |
| Conc. of the ECR in $10^{-5}$ M | 0.133 | 0.1 | 0.166 | 0.1 | 4.0 | 3.33 |

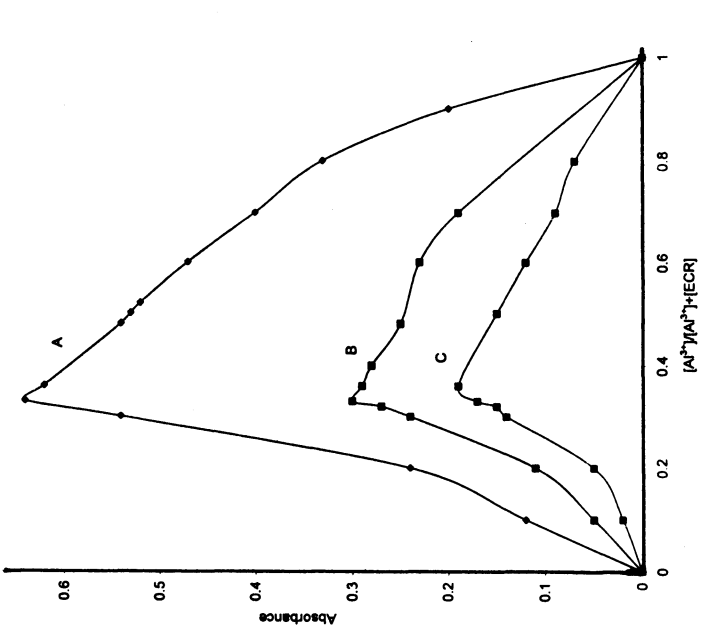


Fig. 4. Composition of Al-ECR chelate by method of continuous variation

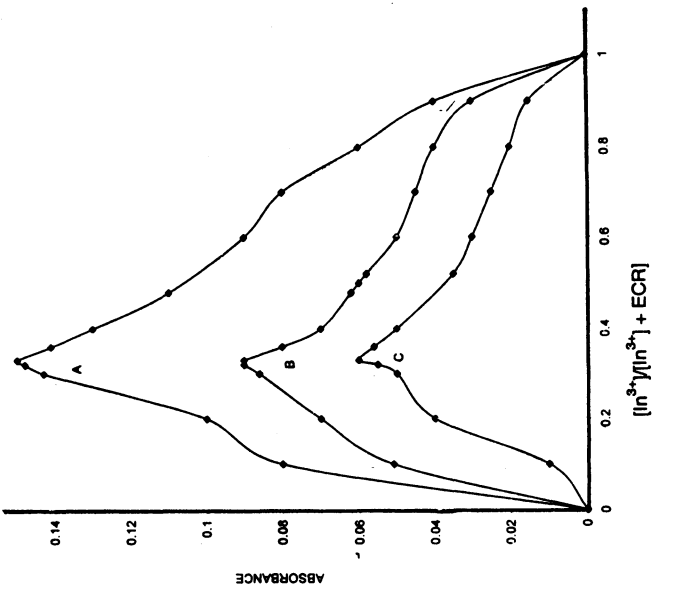


Fig. 5. Composition of In-ECR chelate by method of continuous variation

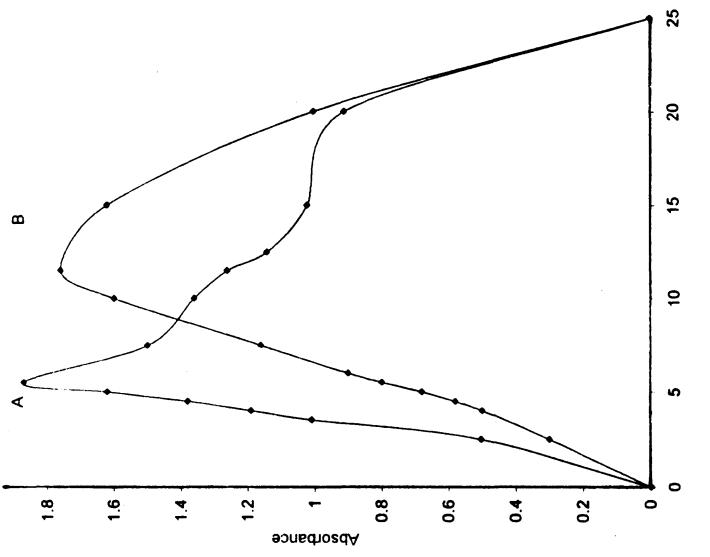


Fig. 7. Composition of Al-ECR chelate by job's method of non equimolar concentration

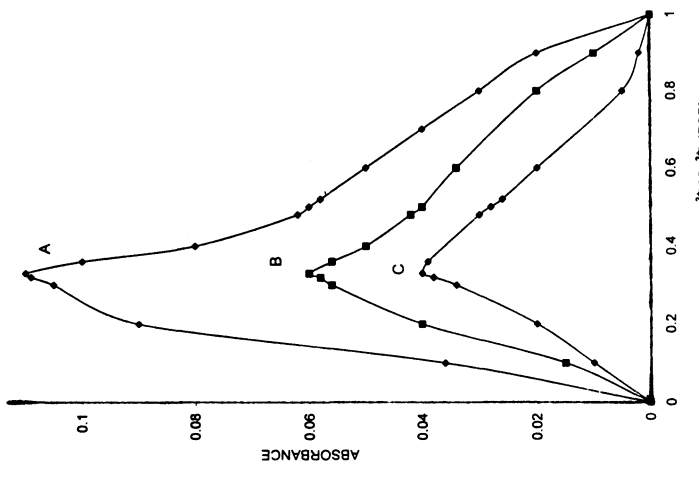


Fig. 6. Composition of Ga-ECR chelate by method of continuous variation

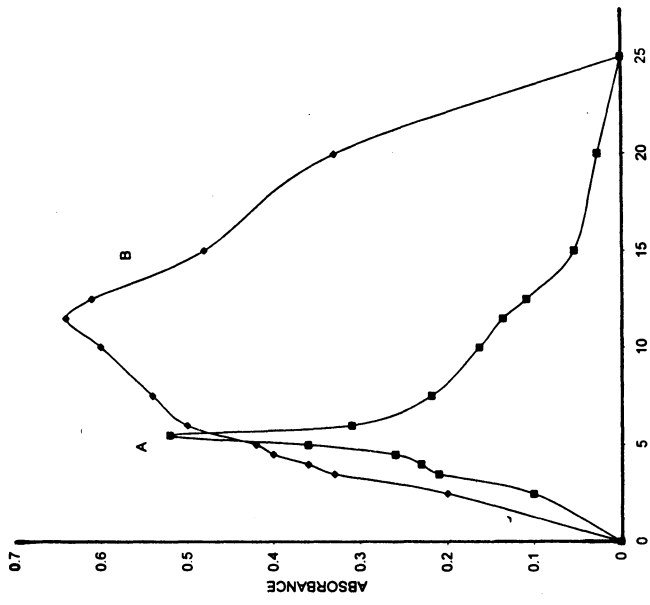


Fig. 9. Composition of Ga-ECR chelate by Job's method of Non equimolar concentration

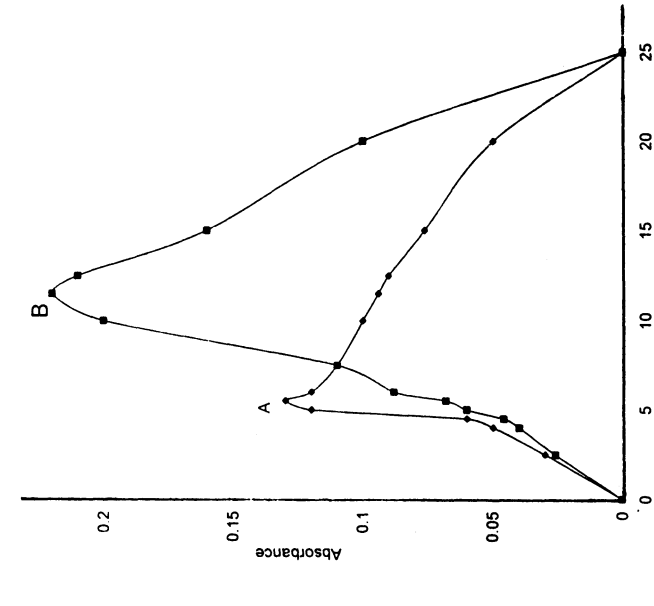


Fig. 8. Composition of In-ECR chelate by Job's method of Non equimolar concentration

TABLE-4
METHOD OF CONTINUOUS VARIATION: COMPOSITION OF THE M-ECR CHELATE

Total volume = 25 mL

| | $AlCl_3$ | | | $InCl_3$ | | | $GaCl_3$ | | |
|---|---|---|---|---|---|---|---|---|---|
| Figure | 4 | | | 5 | | | 6 | | |
| Curve | A | B | C | A | B | C | A | B | A |
| Conc. of the reactants in $10^{-5}$ M | 1 | 0.50 | 0.25 | 0.13 | 0.10 | 0.05 | 6 | 4 | 2 |
| Wavelength (nm) | 540 | | | 540 | | | 530 | | |
| Volume of metal at peak (mL) | 8.33 | | | 8.33 | | | 8.33 | | |
| Composition of the chelate metal : ECR | 1 : 2 | | | 1 : 2 | | | 1 : 2 | | |

TABLE-5
JOB'S METHOD OF NON-EQUIMOLAR CONCENTRATION COMPOSITION OF THE M-ECR CHELATE

Total volume = 25 mL

| | Concentration of Reagents in $10^{-5}$ M | | | | | |
|---|---|---|---|---|---|---|
| Figure | 7 | | 8 | | 9 | |
| Curve | A | B | A | B | A | B |
| Value of p | ECR | $AlCl_3$ | ECR | $InCl_3$ | ECR | $GaCl_3$ |
| 0.5 | 0.1 | 0.2 | 0.1 | 0.2 | 1.0 | 2.0 |
| 2 | 0.2 | 0.1 | 0.5 | 0.25 | 6.0 | 3.0 |

The apparent stability constants were calculated by three different methods[9-10] Values of log K are reported in Table-6.

TABLE-6
VALUES OF log K

| Method | Al-ECR | In-ECR | Ga-ECR |
|---|---|---|---|
| Non-equimolar concentration | 10.096 | 7.73 | 8.58 |
| Continuous variation | 9.990 | 7.98 | 8.90 |
| Mole ratio | 10.054 | 7.77 | 8.34 |

The maximum colour formation is only attained when the mixture contains a four-fold concentration of the reagent with the metal ion. The effective pH ranges for the determination of these elements using ECR as a spectrophotometric reagent and where the results are reproducible are 3.0 to 5.0 (for Al, Ga) and 4.0 to 7.0 (for In), which are shown by the constancy of both wavelength and absorbance of the chelates within these ranges of pH. The sensitivity indices of the colour reaction in Sandell notation are 0.005 for aluminium, 0.009 for indium and 0.03 $\mu g/cm^2$ for gallium. The system was found to adhere to Beer's law in the range of 0.28 to 9.57 ppm of metal.

The rate of colour formation does not depend upon reaction time and is almost instantaneous. A mixture of $InCl_3$ and ECR was precipitated after 24 h at room temperature.

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