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# THE EFFECT OF SUBSTITUENT GROUPS ON THE MIGRATION OF METAL IONS IN THIN LAYER CHROMATOGRAPHY

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## ABSTRACT

A reverse phase thin layer partition chromatography has been performed on metal ions using silica gel G as an adsorbent. The effect of chlorosubstituent groups on the migration of cations has been studied. The use of aqueous solutions of acetic acid, monochloro, dichloro and trichloro acetic acid in the solvent system revealed profound effect of substituent groups on the  $R_f$  values of metal ions. The effect of concentration and pH of the mobile phases have been studied. Many qualitative ternary separations have been successfully achieved.

## INTRODUCTION

Chromatographic behaviour of metal ions on the thin layers of silica gel G (SGG) has been extensively studied due to its simplicity. The thin layers of impregnated and unimpregnated SGG have been found to be wonderful tool for separating complex mixtures into individual components. SGG impregnated with *S*-butylamine and *t*-butylamine has been used for binary and ternary

separations (1). The use of inorganic salts such as ammonium chloride and barium nitrate for the impregnation on SGG has been reported for many qualitative separations (2). Literature survey reveals the use of several solvent systems including formic acid-sodium formate (3) and oxalic acid-oxalate (4) for separation of cations by thin layer chromatography but it appears that the effect of substituent groups on the migration of cations is not yet reported. In the present paper the effect of chlorosubstituent groups on the migration of cations has been studied, using acetic acid (AA), monochloroacetic acid (MCAA), dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) in the solvent systems. The study is extended to explore the possibility of separation at a lower pH to avoid the hydrolysis of metal ions. The present method has been successfully applied for separation of cations in binary and ternary mixtures within 12-15 minutes.

### EXPERIMENTAL

#### Apparatus

Elico pH meter L1 10T (Elico Private Ltd. Hyderabad, India) was used for adjusting the pH of the solutions. The chromatography was performed in 18x13 cm. glass jars. Ordinary glass plates of 4x13 cm. size were used for coating thin layers of SGG.

#### Reagents

SGG of E.Merck was used for preparation of thin layers. All the required solutions and reagents were made in double distilled water. AA, MCAA, DCAA and TCAA used were of AnalaR grade.

### Test Solutions and Detectors

Test solutions were of 0.05 M metal chloride, nitrate or sulphate. Conventional spot test reagents (5) were used for detection of  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$ .  $\text{Mn}^{2+}$  was detected by 0.1% aqueous solution of 4-(2-Pyridylazo) resorcinol and 3% Potassium ferrocyanide solution was used for detection of  $\text{Cu}^{2+}$ .

### Preparation of Thin Layer Plates

A slurry of SGG was prepared by mixing SGG and double distilled water in the ratio of 1:3 with constant shaking for five minutes. The resultant slurry was then immediately used for coating on clean glass plates by dipping method (6). The plates were allowed to dry over night at room temperature and were used next day for chromatography.

### Solvent Systems

The aqueous solutions of AA, MCAA, DCAA and TCAA with concentration 0.01, 0.05, 0.1, 0.15 and 0.2 M were used as mobile phases.

### Procedure

The test solutions were spotted on the chromatoplates with the help of glass capillaries and the spots were blow dried with hot air. The solutions of AA, MCAA, DCAA and TCAA of desired concentration were adjusted to particular pH using sodium hydroxide and hydrochloric acid solution. Then the plates were developed by ascending technique for 15 minutes in the glass jar containing 25-30 ml of solvent. Approximately 2-3 ml of solvent was required for development of each plate. The plates were then blow dried with hot air, solvent front was marked and cations were detected by spraying

suitable spot test reagents. All the experiments were carried out at room temperature.  $R_f$  value measurements were done in triplicate for each set of determination. Various experiments were carried out using all the four solvent systems to study the effect of their concentration and pH on the  $R_f$  values of cations.

### RESULTS AND DISCUSSION

The present thin layer reverse phase chromatographic method has following interesting features.

- 1) The study deals with the effect of chlorosubstituent groups on the migration of metal ions. It has been observed that the replacement of hydrogen atoms by chlorine atoms in MCAA, DCAA and TCAA does influence the migration of metal ions and their separation conditions, and hence the attention is also focussed on finding out the optimum conditions for separation of metal ions from their ternary mixtures.
- 2) The present method involves the use of commercially available SGG and avoids the use of costly ion exchangers and hence it is very inexpensive.
- 3) Preparation of chromatoplates by dipping method and use of partition technique simplifies the method.
- 4) The result show excellent reproducibility (variation does not exceed 5% of average  $R_f$  value) in all solvents and for all metal ions detected.
- 5) The time required for the development of chromatoplates is surprisingly little i.e. 12 to 15 minutes for a ternary separation.

The results obtained have been summerized in Fig. 1-4 and Table I. Many ternary separations have been experimentally achieved and are presented in Table I. Fig. 1 and 2 summerizes the variation in  $R_f$

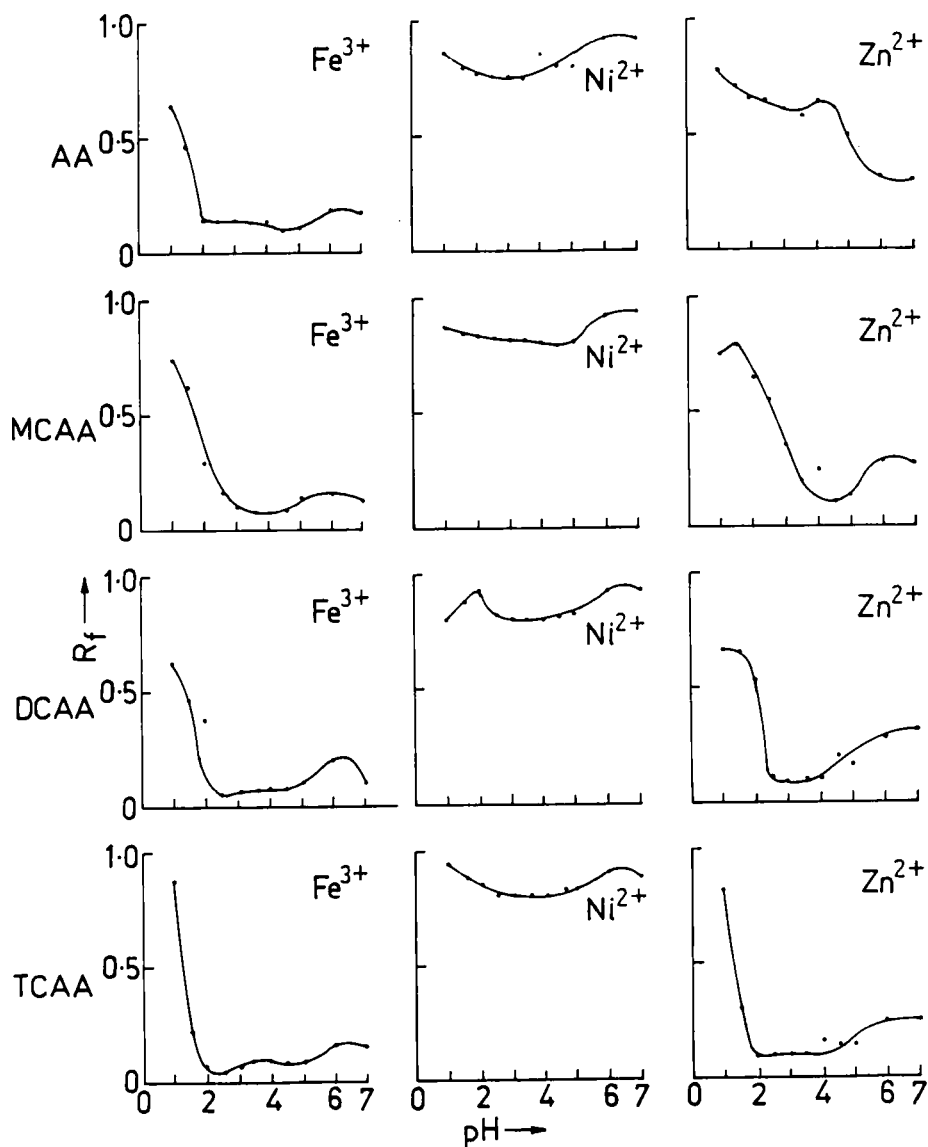


FIGURE 1 -  $R_f$  vs pH at 0.1M concentration of AA, MCAA, DCAA and TCAA.

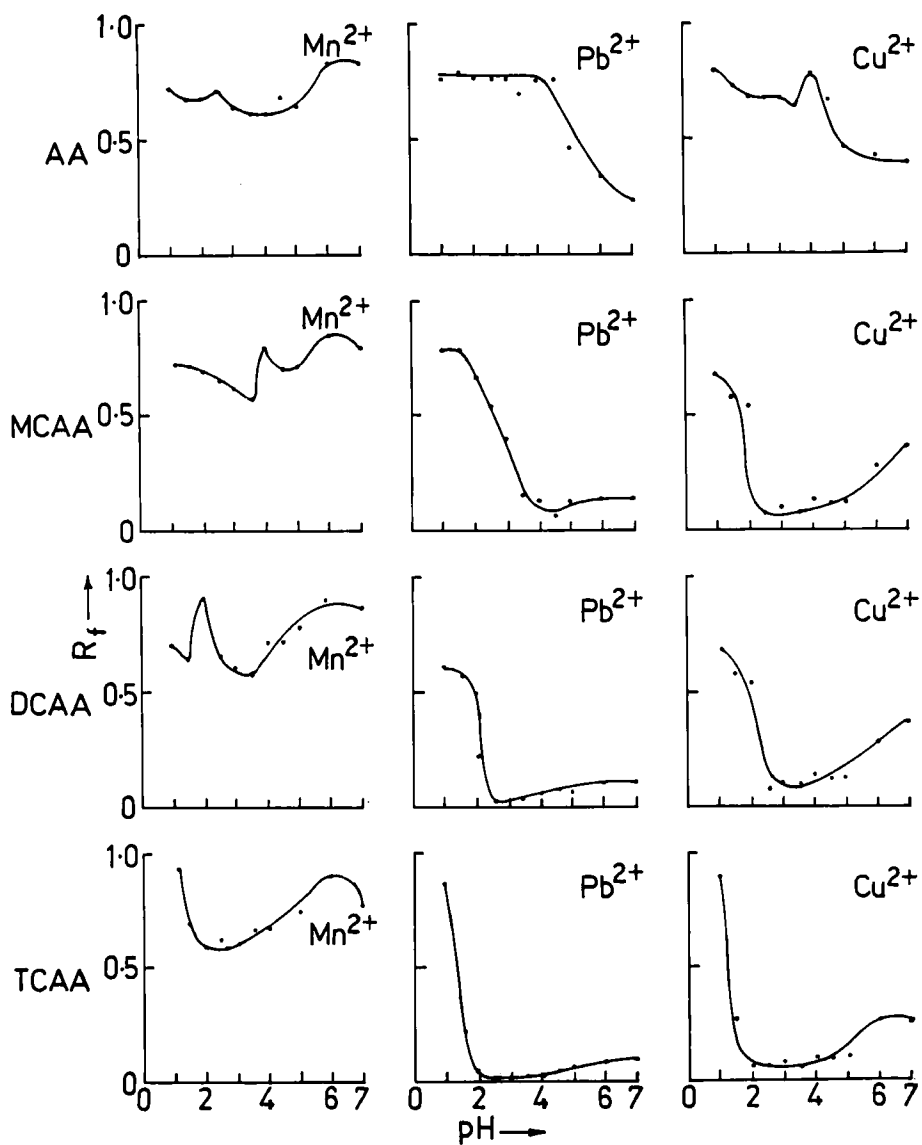


FIGURE 2 -  $R_f$  vs pH at 0.1M concentration of AA, MCAA, DCAA and TCAA.

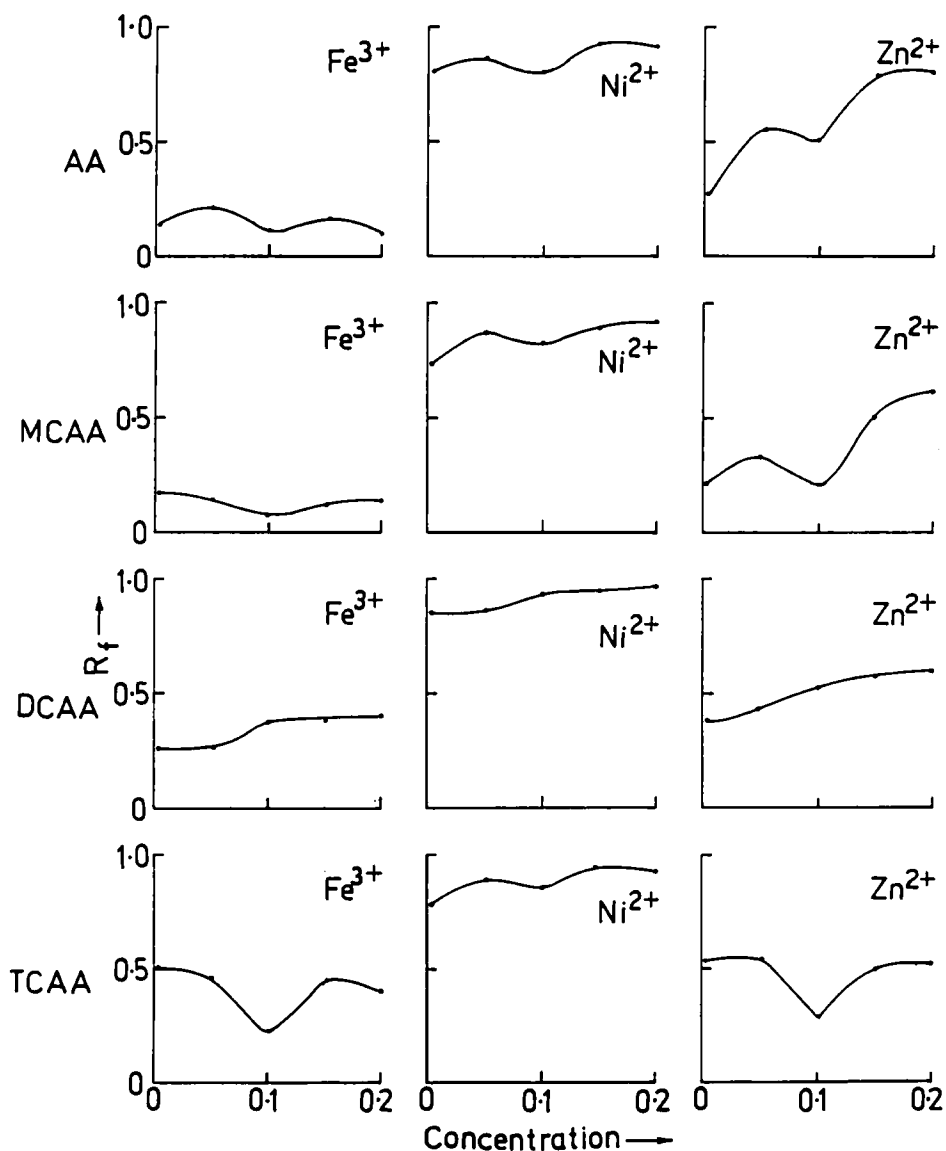


FIGURE 3 - R<sub>f</sub> vs concentration at pH AA(5), MCAA (3.5), DCAA (2) and TCAA (1.5).



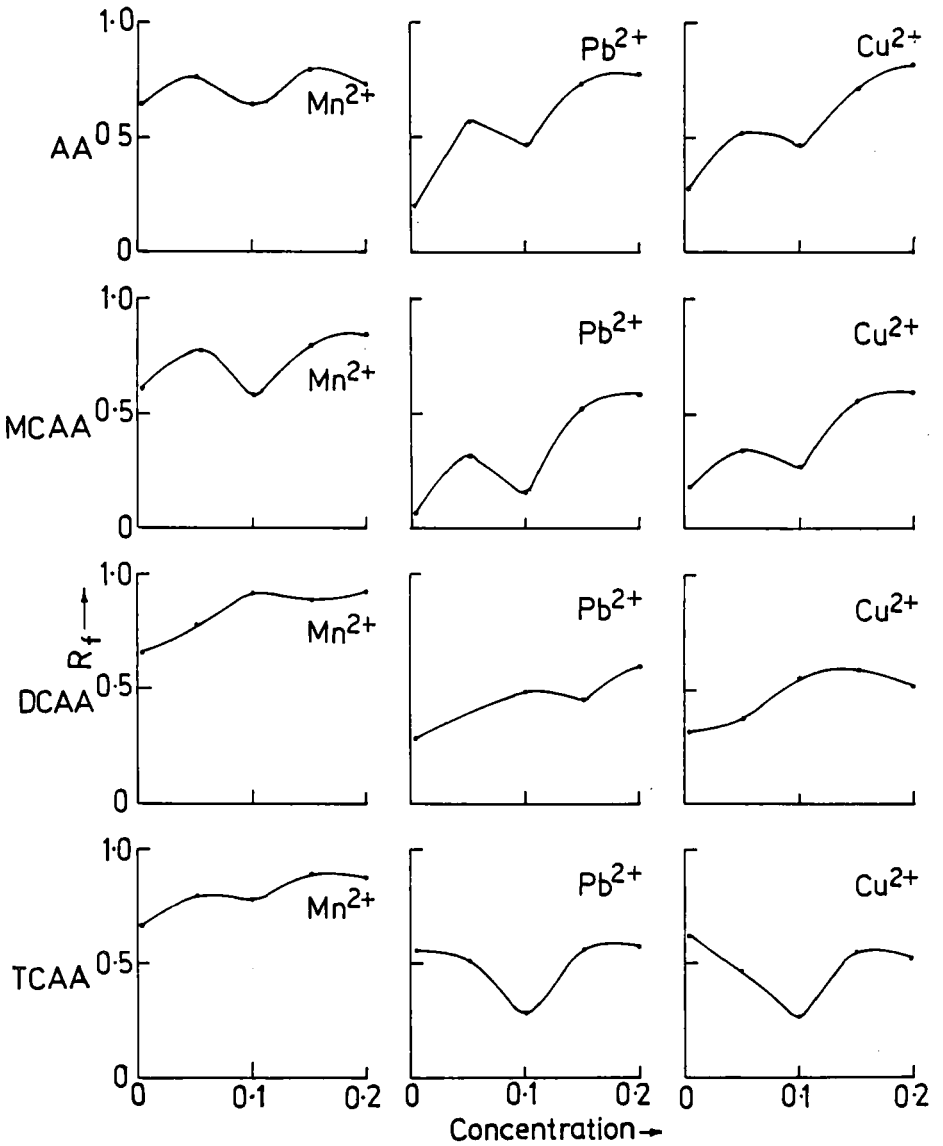


FIGURE 4 - R<sub>f</sub> vs concentration at pH AA (5), MCAA (3.5), DCAA (2) and TCAA (1.5).

TABLE I

Ternary Separations Achieved Experimentally on SGG Thin Layers (Development time = 15 min, Concentration = 0.1M)

Solvents	pH	Metal ions separated with $R_f$ values
AA	5.0	$\text{Fe}^{3+}$ (0.03) - $\text{Ni}^{2+}$ (0.87) - $\text{Cu}^{2+}$ (0.67)
		$\text{Fe}^{3+}$ (0.03) - $\text{Ni}^{2+}$ (0.89) - $\text{Zn}^{2+}$ (0.69)
		$\text{Fe}^{3+}$ (0.03) - $\text{Ni}^{2+}$ (0.94) - $\text{Pb}^{2+}$ (0.71)
		$\text{Fe}^{3+}$ (0.04) - $\text{Mn}^{2+}$ (0.90) - $\text{Cu}^{2+}$ (0.72)
		$\text{Fe}^{3+}$ (0.04) - $\text{Mn}^{2+}$ (0.90) - $\text{Zn}^{2+}$ (0.68)
		$\text{Fe}^{3+}$ (0.04) - $\text{Mn}^{2+}$ (0.89) - $\text{Pb}^{2+}$ (0.71)
MCAA	3.5	$\text{Fe}^{3+}$ (0.05) - $\text{Ni}^{2+}$ (0.97) - $\text{Cu}^{2+}$ (0.87)
		$\text{Fe}^{3+}$ (0.06) - $\text{Ni}^{2+}$ (0.97) - $\text{Zn}^{2+}$ (0.80)
		$\text{Fe}^{3+}$ (0.06) - $\text{Ni}^{2+}$ (0.94) - $\text{Pb}^{2+}$ (0.69)
		$\text{Fe}^{3+}$ (0.09) - $\text{Mn}^{2+}$ (0.95) - $\text{Cu}^{2+}$ (0.60)
		$\text{Fe}^{3+}$ (0.09) - $\text{Mn}^{2+}$ (0.92) - $\text{Zn}^{2+}$ (0.57)
		$\text{Fe}^{3+}$ (0.10) - $\text{Mn}^{2+}$ (0.91) - $\text{Pb}^{2+}$ (0.56)
DCAA	2.0	$\text{Fe}^{3+}$ (0.47) - $\text{Ni}^{2+}$ (0.96) - $\text{Cu}^{2+}$ (0.71)
		$\text{Fe}^{3+}$ (0.56) - $\text{Ni}^{2+}$ (0.95) - $\text{Zn}^{2+}$ (0.87)
		$\text{Fe}^{3+}$ (0.55) - $\text{Ni}^{2+}$ (0.97) - $\text{Pb}^{2+}$ (0.73)
		$\text{Fe}^{3+}$ (0.40) - $\text{Mn}^{2+}$ (0.90) - $\text{Cu}^{2+}$ (0.60)
		$\text{Fe}^{3+}$ (0.41) - $\text{Mn}^{2+}$ (0.89) - $\text{Zn}^{2+}$ (0.60)
		$\text{Fe}^{3+}$ (0.38) - $\text{Mn}^{2+}$ (0.91) - $\text{Pb}^{2+}$ (0.55)
TCAA	1.5	$\text{Fe}^{3+}$ (0.57) - $\text{Ni}^{2+}$ (0.95) - $\text{Cu}^{2+}$ (0.67)
		$\text{Fe}^{3+}$ (0.55) - $\text{Ni}^{2+}$ (0.92) - $\text{Zn}^{2+}$ (0.68)
		$\text{Fe}^{3+}$ (0.56) - $\text{Ni}^{2+}$ (0.92) - $\text{Pb}^{2+}$ (0.60)
		$\text{Fe}^{3+}$ (0.56) - $\text{Mn}^{2+}$ (0.88) - $\text{Cu}^{2+}$ (0.62)
		$\text{Fe}^{3+}$ (0.57) - $\text{Mn}^{2+}$ (0.92) - $\text{Zn}^{2+}$ (0.71)
		$\text{Fe}^{3+}$ (0.57) - $\text{Mn}^{2+}$ (0.93) - $\text{Pb}^{2+}$ (0.50)

values with pH at 0.1M concentration and 15 minutes development time for all individual metals in four solvent systems i.e. AA, MCAA, DCAA and TCAA. The selection of optimum pH condition for each acid was decided from the study of migration of individual ion. The maximum difference in  $R_f$  values of metal ions has been found to be at pH 5, 3.5, 2, 1.5 for AA, MCAA, DCAA and TCAA respectively and thus these pH values were fixed for further studies.  $Fe^{3+}$ ,  $Cu^{2+}$ ,  $Pb^{2+}$  and  $Zn^{2+}$  (Fig. 1, 2) show high  $R_f$  values at low pH with all solvent systems but after certain pH the  $R_f$  value decreases. Similarly  $Ni^{2+}$  and  $Mn^{2+}$  exhibit 0.59 to 0.95  $R_f$  at mostly all pH. Taking advantage of difference in  $R_f$  values at suitable pH, the metal ions were separated (Table I).

Fig. 3 and 4 illustrates the dependence of  $R_f$  value on concentration of acids (0.01 to 0.2M) at optimum pH as mentioned earlier. It was observed that optimum concentration for better and sharper separation was 0.1M for all solvent systems.

Metal ions in the approximate concentration range of 0.65-3.2  $\mu\text{g}$  of  $Ni^{2+}$ , 0.7-3.5  $\mu\text{g}$  of  $Cu^{2+}$ , 0.5-10  $\mu\text{g}$  of  $Pb^{2+}$ , 2-4  $\mu\text{g}$  of  $Zn^{2+}$ , 6-12  $\mu\text{g}$  of  $Mn^{2+}$  and 4-20  $\mu\text{g}$  of  $Fe^{3+}$  were spotted on the chromatoplates and were separated from their ternary mixtures.

It is revealed from table I that the best separation of metal ions in their ternary mixtures can be achieved at lower pH in TCAA medium in which hydrolysis of metal ions in question is avoided. Although there is a separation of metal ions from their ternary mixtures in other acid medium i.e. AA, MCAA and DCAA, however the metal ions may under go hydrolysis to some extent in these media because of higher pH. Therefore TCAA

has been suggested to be the most suitable solvent amongst all the solvents used for the separation of metal ions from their ternary mixtures.

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