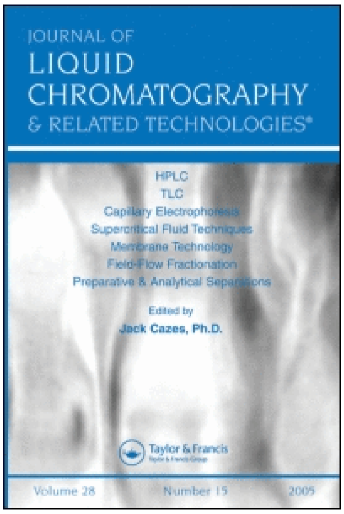

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THIN-LAYER CHROMATOGRAPHY OF METAL IONS IN OXALIC ACID - OXALATE SYSTEMS

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ABSTRACT

The adsorption behaviour of 48 metal ions has been studied in Oxalic acid - Oxalate systems using silica gel - G layers. The effect of p_H on R_f values was also investigated. A plot of -log Ksp Vs. R_M and R_f shows the dramatic behaviour of Hg^{2+} ion in 0.1 M Potassium Oxalate + 0.1 M Ammonium Oxalate (1:1) system. A number of interesting separations have been achieved e.g., Fe^{3+} - Ti^{4+}, Zr^{4+}- Ti^{4+}, Ce^{4+} - La^{3+}, Zr^{4+} - Th^{4+}, Te^{4+}- Se^{4+} and Zr^{4+} - Y^{3+} - La^{3+}. Ti^{4+} and Nb^{5+} were separated from a mixture of number of ions.

INTRODUCTION

Thin layer chromatography offers an interesting method for the separation of metal ions in microgram quantities. The separation potential of this technique is greatly enhanced if complexation is used. Considering this aspect of the problem, we have tried to use solvents containing Oxalic acid and Potassium or Ammonium Oxalate solutions as eluants using silica gel-G thin layers as

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the stationary phase. As a result of the change in p_H and the concentration of the complexing Oxalate anion, some very interesting separations have been achieved which are presented in the following article.

MATERIALS AND METHODS

Apparatus

Toshniwal (made in India) TLC apparatus was used for the preparation of thin layers on glass plates (20x3 cm). The plates were developed in glass jars (20x6 cm). p_H meter (Toshniwal, India) was used for p_H determination.

Reagents

Silica gel-G, Potassium Oxalate, Ammonium Oxalate and Oxalic acid used were all of analytical grade from B.D.H., England. Other reagents were of AnalaR grade.

Test solutions and Detectors

Test solutions were generally prepared in 0.1 M metal chlorides, sulphates or nitrates. A little amount of the corresponding acid is added to prevent hydrolysis. Conventional spot test reagents were used for detection perposes.

Preparation of Silica gel-G plates

The slurry used was prepared by mixing silica gel-G in D.M.W. in the ratio of 1:3 with constant shaking for about 5 min. This slurry was immediately coated on clean glass plates with the help of an applicator and uniform thin layers (~ 0.15 mm Thick) were obtained. The plates were first allowed to dry at room temperature and then in an electric oven at 100 ± 5°C for 2 hrs. These were then stored in an oven at room temperature.

Procedure

Test solutions (1 or 2 spots) were placed on the dry silica gel-G plates with the help of thin glass capillaries. After drying the spots, plates were developed in a chosen solvent and the ascent was fixed at 11 cm in all cases. R_T and R_L values were measured as usual after detection.

Solvent systems

In all, seven solvent systems were used. Their composition and p_H values are given in Table 1.

TABLE 1.

p_H METRIC STUDIES IN OXALIC ACID - OXALATE MEDIA

Solvent	Composition	p_H
S_1	0.1M Oxalic acid	0.7
S_2	0.1M Potassium oxalate + 0.1M Oxalic acid(1:1)	2.2
S_3	0.1M Ammonium oxalate + 0.1M Oxalic acid (1:1)	2.2
S_4	0.1M Potassium oxalate + 0.1M Ammonium oxalate + 0.1M Oxalic acid (1:1:1)	3.2
S_5	0.1M Potassium oxalate + Ammonium oxalate(1:1)	6.8
S_6	0.1M Ammonium oxalate	7.3
S_7	0.1M Potassium oxalate	7.6

RESULTS

The plots given in the figures are only for those metal ions which give compact spots. A number of separations of analytical importance have actually been realised as given in Table 2.

DISCUSSION

It is surprising that very few studies on silica gel-G thin layers have been done using aqueous Oxalate solutions as eluants. The results in Table 3 show that it is possible to obtain some very interesting separations using these eluants. Thus Ti^{4+} can be separated from Fe^{3+}, Al^{3+}, Th^{4+}, In^{3+}, UO_2^{2+} and La^{3+}. These separations are very neat and the spots are well separated. Ti^{4+} has a R_f value of almost zero and the strong adsorption is due to its high charge. Zr4+ can be separated from Y^{3+}, La^{3+} and Th^{4+}. Zr^{4+} has a R_f value O.D. probably because it is precipitated as confirmed by the results summarized in Table 3.

The R_f values of 48 cations in solvent systems are summarized in Figures 1-4. An analysis of the results tabulated in these figures show that it is possible for one to seperate Ti^{4+}, Ag^+,

TABLE 2.

SEPARATIONS ACHIEVED EXPERIMENTALLY (40 min)

Solvent System	Separations achieved, metal ion (R_T-R_L)				
S_1	Ti^{4+}	(0.00-0.20)	-	Fe^{3+}	(0.88-1.00)
	Ti^{4+}	(0.00-0.19)	-	Al^{3+}	(0.90-1.00)
	Pb^{2+}	(0.00-0.00)	-	Tl^{+}	(0.90-1.00)
S_2	Ti^{4+}	(0.00-0.30)	-	Th^{4+}	(0.80-1.00)
	Ti^{4+}	(0.00-0.40)	-	In^{3+}	(0.85-1.00)
	Ti^{4+}	(0.00-0.30)	-	UO_2^{2+}	(0.85-1.00)
	Ti^{4+}	(0.00-0.35)	-	VO^{2+}	(0.90-1.00)
	Ti^{4+}	(0.00-0.30)	-	Zr^{4+}	(0.80-1.00)
	Ti^{4+}	(0.00-0.35)	-	Cu^{2+}	(0.90-1.00)
	Ti^{4+}	(0.00-0.30)	-	Cd^{2+}	(0.95-1.00)
	Ti^{4+}	(0.00-0.25)	-	Be^{2+}	(0.80-1.00)
	Bi^{3+}	(0.00-0.00)	-	Tl^{+}	(0.65-1.00)
	Ti^{4+}	(0.00-0.30)	-	Co^{2+}	(0.90-1.00)
	Ti^{4+}	(0.00-0.25)	-	Ni^{2+}	(0.95-1.00)
	Ti^{4+}	(0.00-0.20)	-	Pd^{2+}	(o.85-1.00)
	Ti^{4+}	(0.00-0.18)	-	Mg^{2+}	(0.80-1.00)
	Ti^{4+}	(0.00-0.25)	-	A mixture of Th^{4+}, UO_2^{2+}, VO^{2+}, Co^{2+}, Ni^{2+}, Zr^{4+}, Pd^{2+}, Mg^{2+}, Cu^{2+}, Cd^{2+} and Be^{2+}	
S_4	Pb^{2+}	(0.00-0.28)	-	Cd^{2+}	(0.90-1.00)
	Ti^{4+}	(0.00-0.30)	-	La^{3+}	(0.90-1.00)

(continued)

TABLE 2 (continued)

Solvent System	Separations achieved, metal ion (R_T-R_L)				
	Fe^{3+}	(0.50-0.70)	-	Mn^{2+}	(0.90-1.00)
	Pb^{2+}	(0.00-0.30)	-	Mn^{2+}	(0.85-1.00)
	Ce^{4+}	(0.00-0.27)	-	Pr^{3+}	(0.80-1.00)
	Ce^{4+}	(0.00-0.25)	-	La^{3+}	(0.83-1.00)
	Ce^{4+}	(0.00-0.08)	-	Sm^{3+}	(0.50-0.85)
	Nb^{5+}	(0.00-0.10)	-	VO^{2+}	(0.92-1.00)
	Nb^{5+}	(0.00-0.07)	-	Se^{4+}	(0.85-1.00)
	Nb^{5+}	(0.00-0.08)	-	Mo^{6+}	(0.85-1.00)
	Nb^{5+}	(0.00-0.07)	-	Cr^{3+}	(0.82-1.00)
	Nb^{5+}	(0.00-0.00)	-	Zn^{2+}	(0.78-1.00)
	Nb^{5+}	(0.00-0.00)	-	Mn^{2+}	(0.80-1.00)
	Nb^{5+}	(0.00-0.08)	-	In^{3+}	(0.80-1.00)
	Nb^{5+}	(0.00-0.08)	-	Ir^{3+}	(0.80-1.00)
	Nb^{5+}	(0.00-0.08)	-	Cd^{2+}	(0.85-1.00)
	Nb^{5+}	(0.00-0.08)	-	Pd^{2+}	(0.85-1.00)
	Nb^{5+}	(0.00-0.10)	-	Pr^{3+}	(o.82-1.00)
	Nb^{5+}	(0.00-0.08)	-	A mixture of VO^{2+}, Cd^{2+}, Pr^{3+}, In^{3+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}, and Cr^{3+}	
S_6	Zr^{4+}	(0.00-0.08)	-	Y^{3+}	(0.50-0.60)-
				La^{3+}	(0.85-0.95)
	Te^{4+}	(0.00-0.20)	-	Se^{4+}	(0.85-1.00)
	Zr^{4+}	(0.00-0.00)	-	Th^{4+}	(0.70-0.92)
	Fe^{3+}	(0.06-0.16)	-	Ni^{2+}	(0.80-1.00)
	Fe^{3+}	(0.10-0.20)	-	Co^{2+}	(0.87-1.00)

TABLE 3.

PRECIPITATION OF CATIONS WITH THE SOLVENT SYSTEMS USED

	Cations + Solvent	
Solvent	Cations which precipitate	Cations which do not precipitate
S_1	Hg_2^{2+}, Pb^{2+}, Ag^{+}, Zr^{4+}, Te^{4+} Th^{4+}, Co^{2+}, La^{3+}, Cu^{2+}, Bi^{3+}, Hg^{2+}	Tl^{+}, UO_2^{2+}, In^{3+}. Mn^{2+}, Fe^{3+}, Ni^{2+} Se^{4+}, Cd^{2+}, Al^{3+}, VO^{2+}, Be^{2+}, Pd^{2+} Ba^{2+}, Ti^{4+}, Ir^{3+}, Pt^{4+}, Sn^{2+}, Sr^{2+} Ga^{3+}, Cr^{3+}. Mo^{6+}, Au^{3+}, Sn^{4+}, Zn^{2+} W^{6+}, Sb^{3+}, Nb^{5+}, Mg^{2+}
S_2	Hg_2^{2+}, Pb^{2+}, Zr^{4+}, Te^{4+}, Ba^{2+}, Th^{4+}, Co^{2+}, La^{3+}, Cu^{2+}, Bi^{3+}, Ag^{+}, Sr^{2+}	Tl^{+}, UO_2^{2+}, In^{3+}, Mn^{2+}, Fe^{3+}, Ni^{2+} Se^{4+}, Cd^{2+}, Al^{3+}, VO^{2+}, Be^{2+}, Pd^{2+} Ti^{4+}, Ir^{3+}. Pt^{4+}. Sn^{2+}, Ga^{3+}, Cr^{3+} Mo^{6+}, Au^{3+}, Sn^{4+}, Zn^{2+}, W^{6+}, Sb^{3+} Nb^{5+}. Mg^{2+}
S_3	Hg_2^{2+}, Pb^{2+}, Zr^{4+}, Te^{4+}, Th^{4+}, La^{3+}, Al^{3+}, Cu^{2+}, Bi^{3+}, Ag^{+}, Ba^{2+}, Sr^{2+}	Ti^{4+}, Tl^{+}, UO_2^{2+}, In^{3+}, Fe^{3+}, Ni^{2+} Se^{4+}. Cd^{2+}, VO^{2+} Be^{2+}, Pd^{2+}, Mn^{2+} Ir^{3+}, Pt^{4+}, Sn^{2+}, Ga^{3+}, Cr^{3+}. Mo^{6+} Au^{3+}, Sn^{4+}, Zn^{2+}, W^{6+}, Sb^{3+}, Nb^{5+} Al^{3+}, Mg^{2+}
S_4	Pb^{2+}, Hg_2^{2+}, Zr^{4+}, Te^{4+}, Th^{4+}, Co^{2+}, La^{3+}, Bi^{3+}, Ag^{+}, Ba^{2+}, Sr^{2+},	Nb^{5+}, Tl^{+}. UO_2^{2+}, In^{3+}, Fe^{3+}, Ni^{2+} Se^{4+}, Cd^{2+}, Al^{3+}, Cu^{2+}, Be^{2+}. Ga^{3+} Mg^{2+}, Pd^{2+}, Ti^{4+}, Mn^{2+}, Ir^{3+}, Pt^{4+} Sn^{2+}, Cr^{3+}, Mo^{6+}, Au^{3+}, Sn^{4+}, Zn^{2+} W^{6+}, Sb^{3+}
S_5	Hg^{2+}, Pb^{2+}, Zr^{4+}, Th^{4+}, Co^{2+}, La^{3+}, Bi^{3+}, Ag^{+}, Ba^{2+}, Sr^{2+}	Sb^{3+}, Ti^{4+}, Nb^{5+}, Te^{4+}, Tl^{+}, UO_2^{2+} In^{3+}, Fe^{3+}, Ni^{2+}, Se^{4+}, Cd^{2+} Al^{3+}. VO^{2+}. Cu^{2+}, Be^{2+}. Pd^{2+}, Mn^{2+} Ir^{3+}. Mg^{2+}, Pt^{4+}, Sn^{2+}, Ga^{3+}, Cr^{3+} Mo^{6+}. Au^{3+}, Sn^{4+}, Zn^{2+}, W^{6+}

(continued)

TABLE 3 (continued)

	Cations +	Solvent
Solvent	Cations which precipitate	Cations which do not precipitate
S_6	Ag^+, Pb^{2+}, Ba^{2+}, Sr^{2+}, Zr^{4+}, Ba^{2+}, Th^{4+}, Co^{2+}, La^{3+}, Bi^{3+}, Hg_2^{2+}	Ti^{4+}, Nb^{5+}, Te^{4+}, Tl^+, UO_2^{2+}. Cu^{2+}, Fe^{3+}, Ni^{2+}, Se^{4+}, Cd^{2+}, Al^{3+}, VO^{2+}, Be^{2+}, Pd^{2+}, Mn^{2+}, Ir^{3+}, Pt^{4+}, Sn^{2+}, Sb^{3+}, Mg^{2+}, Ga^{3+}, Cr^{3+}, Mo^{6+}, Au^{3+}, Sn^{4+}, Zn^{2+}, W^{6+}
S_7	Hg_2^{2+}, Pb^{2+}, Ba^{2+}, Sr^{2+}, Zr^{4+}, Th^{4+}, Co^{2+}, La^{3+}, Bi^{3+}, Ag^+, Ba^{2+}	Fe^{3+}, Ti^{4+}, Nb^{5+}, W^{6+}, Te^{4+}, Tl^+, Sb^{3+}, UO_2^{2+}, In^{3+}, Ni^{2+}, Se^{4+}, Cd^{2+}, Al^{3+}, VO^{2+}, Cu^{2+}, Be^{2+}, Pd^{2+}, Mn^{2+}, Ir^{3+}, Cr^{3+}, Ga^{3+}, Pt^{4+}, Sn^{2+}, Mo^{6+}, Au^{3+}, Sn^{4+}, Zn^{2+}, Mg^{2+}

Sn^{2+}, Pb^{2+}, Sb^{3+} and Ce^{4+} from numerous metal ions. In addition to the separations already achieved and presented in Table 2. Other separations are also possible which are analytically very important e.g., separation of Ce^{4+} from Pr^{3+}, Sm^{3+}, Nd^{3+}, La^{3+} and Ba^{2+} ; separation of Y^{3+} from Sr^{2+} and of Tl^+ from Pb^{2+} . Nb^{5+} can also be separated from numerous metal ions such as Zr^{4+}, Y^{3+}, Sr^{2+}, Se^{4+}, Ga^{3+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, VO^{2+} Cr^{3+}, Mo^{6+}, Bi^{3+}, Pb^{2+}, Pd^{2+}, Cd2 In^{3+}, La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Ir^{3+}, Mg^{2+} and Tl^+ (See Figs. 3 and 4)

In order to understand the chromatographic behaviour of the ions, the R_f values were determined at different p_H values and the results are plotted in Figs. 5a and 5b. This behaviour may be divided into the following types:

(i) Those ions whose R_f values are high and independent of p_H i.e., Co^{2+}, Ni^{2+}, Mn^{2+}, VO^{2+}, Be^{2+}, Cd^{2+}, Nd^{3+}, Sm^{3+}, Ir^{3+} and Pt^{4+} .

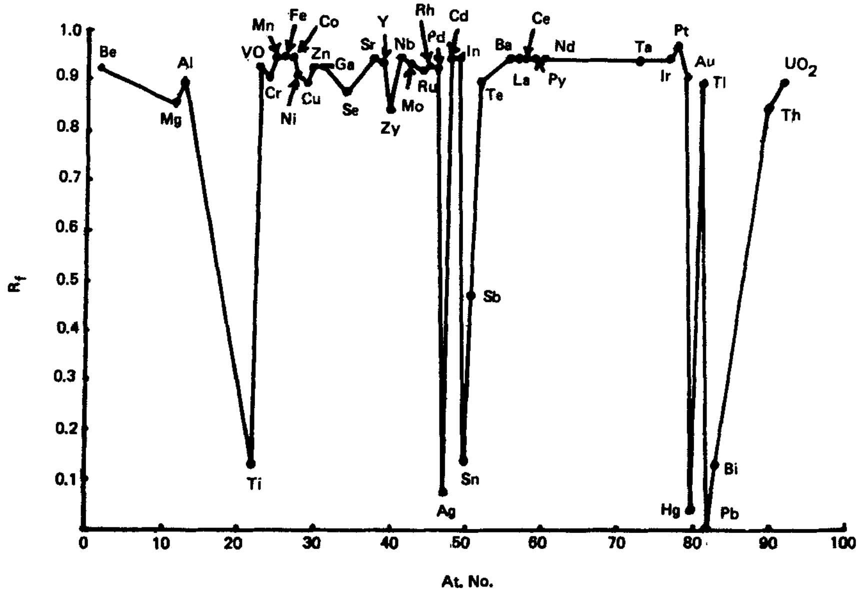

FIG. 1 A Plot of R_f vs Atomic Number in 0.1M Oxalic Acid

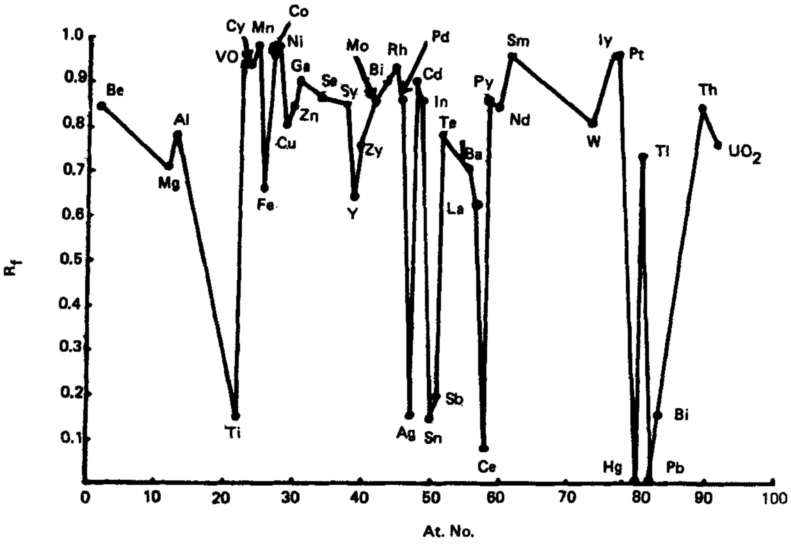

FIG. 2 A Plot of R_f vs Atomic Number in 0.1M Potassium Oxalate + 0.1M Oxalic Acid (1:1)

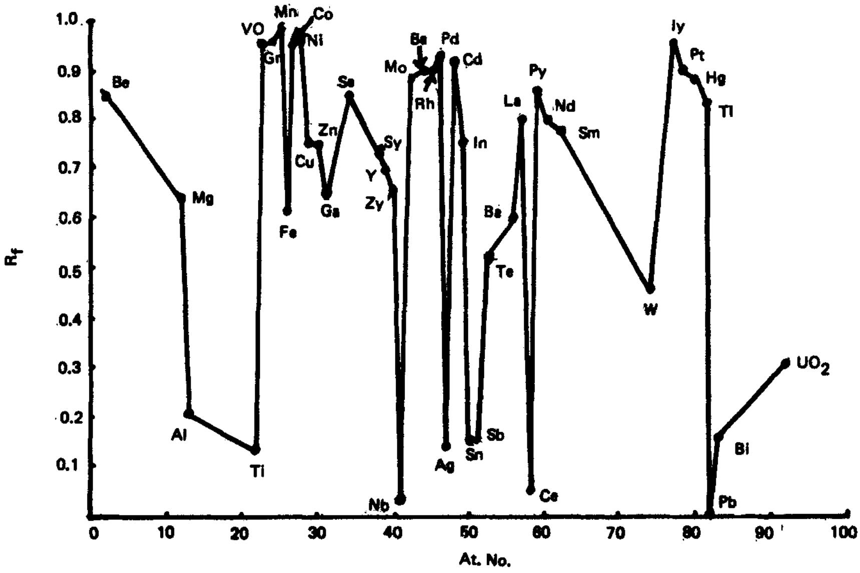

FIG. 3 A Plot of R_f vs Atomic Number in 0.1M Potassium Oxalate + 0.1M Ammonium Oxalate + 0.1M Oxalic Acid (1:1:1)

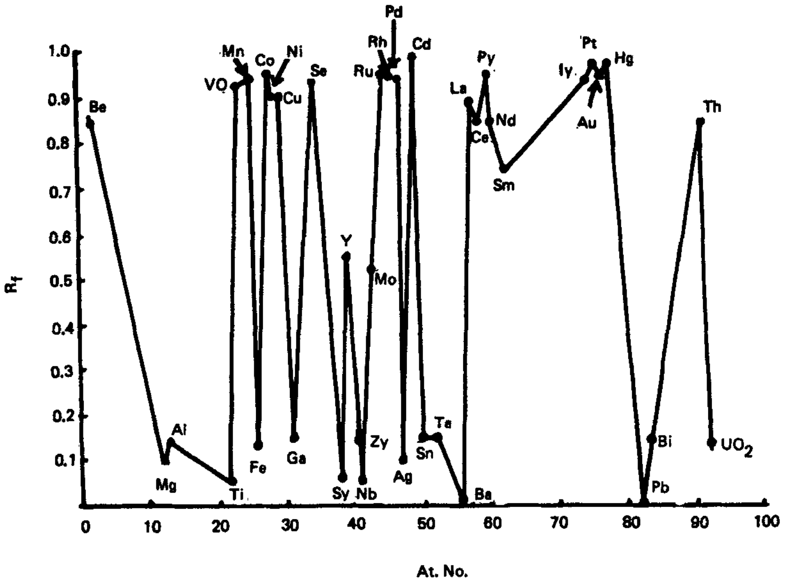

FIG. 4 A Plot of R_f vs Atomic Number in 0.1M Ammonium Oxalate

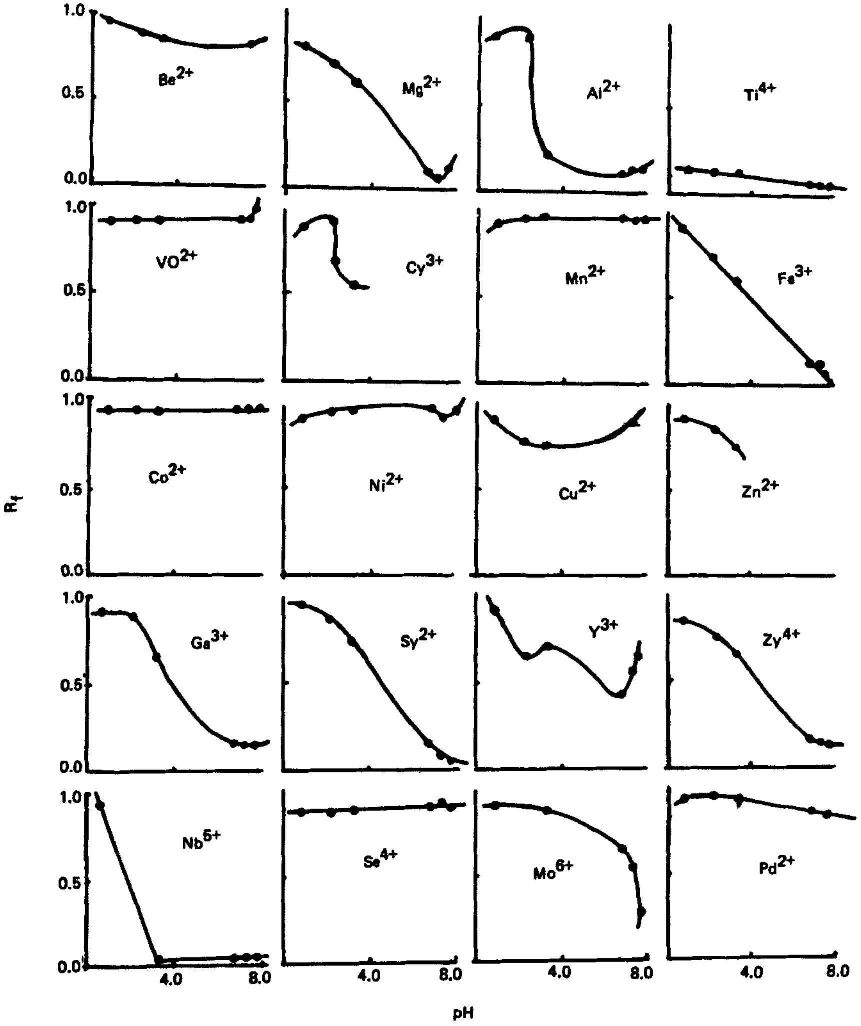

FIG. 5A Plots of R_f vs pH for Various Metal Ions

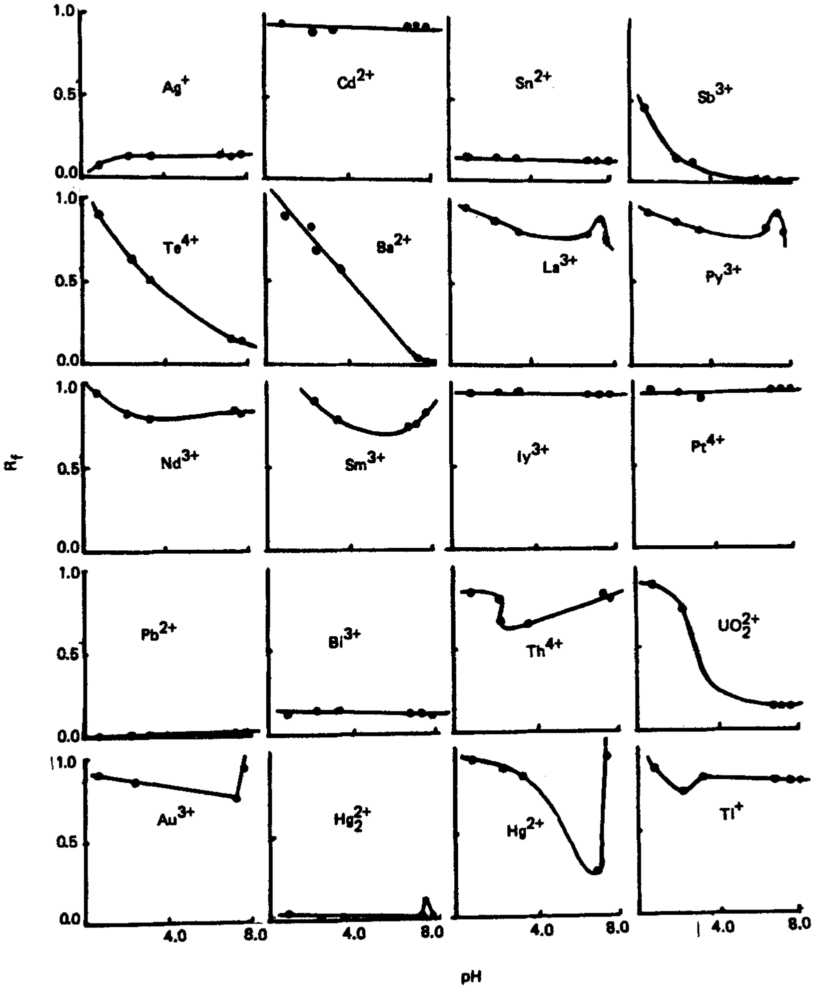

FIG. 5B Plots of R_f vs pH for Various Metal Ions

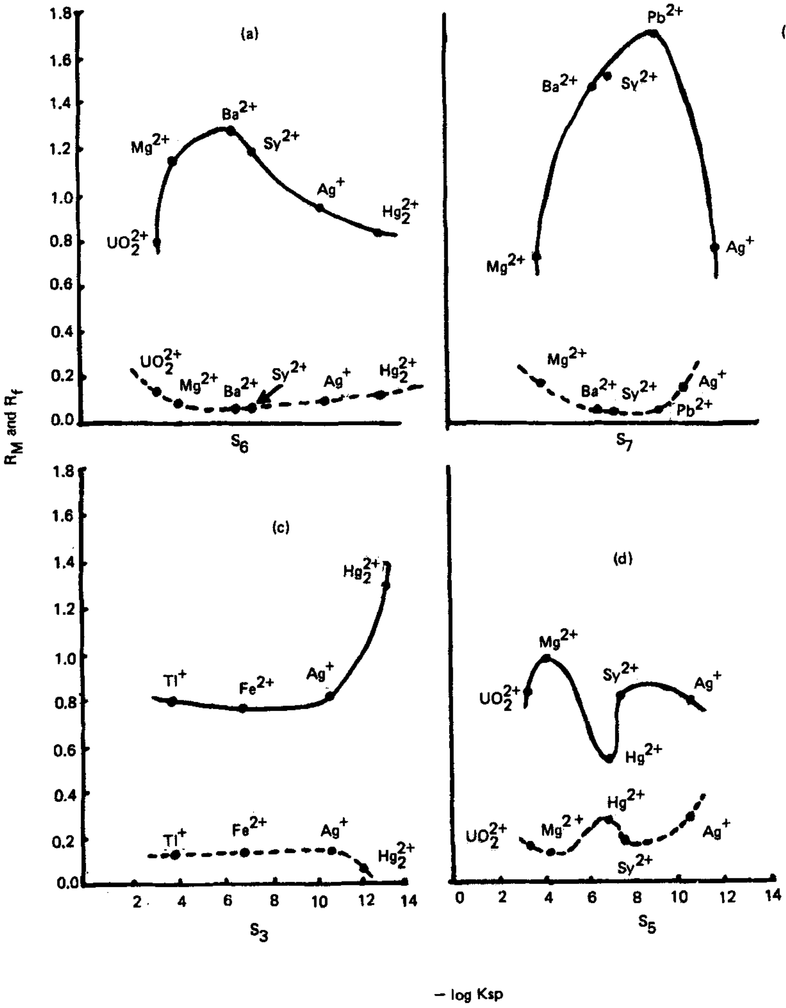

FIG. 6A, B, C, D Plots of -log Ksp vs R_M and R_f of Various Metal Ions

The high values are due to the fact that the oxalates of these ions do not precipitate. The change in R_f value is very small because as the ions do not precipitate, hence change in the oxalate ion concentration or change in H^+ concentration does not affect the mobility of these ions.

(ii) The ions whose R_f values are low but independentof p_H e.g., Ag^+, Sn^{2+}, Bi^{3+}, Hg_2^{2+}, Ti^{4+} and Pb^{2+}. Out of these, all the ions precipitate in the various solvent systems studied except Sn^{2+} and Ti^{4+}. It therefore appears that the low R_f values of these metal ions are due to precipitation and in case of Sn^{2+} and Ti^{4+}, the low R_f value is probably due to the specific interaction of these ions with the silica gel-G.

(iii) The third category is of those ions whose R_f decresses almost linearly with increase in pH. These ions are Ga^{3+}, Sr^{2+}, Fe^{3+}, Mg^{2+}, Zr^{4+}, Te^{4+} and Ba^{2+}. A reference to Table 3 shows that as the p_H is increased, they slowly precipitate and hence there is a decrease in their R_f.

A plot of -log Ksp Vs. R_M and R_f for all those ions whose R_f is less than 0.5 is shown in Fig. 6a, b, c, d. The results show that as the solubility decreases initially there is an increase in the R_M values, as expected. However, on a further decrease in the solubility, there is a decrease in R_M value and the curve passes through a maximum in Figs. 6a and b and even in Fig. 6c there is a tendency towards a maximum. In fig. 6d there is only one point i.e., Hg^{2+} which does not fall in line with this trend. The explanation is, that there are two interactions which are in operation i.e., the solubility effect and the complex formation effect. The decrease in R_f with decrease is solubility is expected. However, the increase in R_f with decrease in solubility is due toccomplex formation. Thus even though, the solubility in an aqueous system decreases, there is an increase in solubility in the complex forming oxalic acid systems.