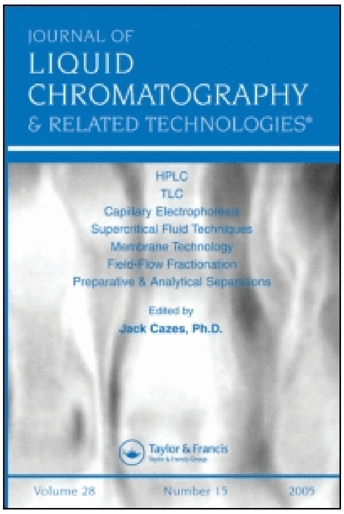

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PREDICTION OF K_{sp} FROM Rf VALUES: THIN LAYER CHROMATOGRAPHY OF 47 METAL IONS ON STANNIC ARSENATE IN AQUEOUS HYDROCHLORIC ACID SYSTEMS.

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Abstract

The adsorption behaviour of 47 metal ions has been studied in aqueous HCl systems using stannic arsenate layers. The effect of solvent pH on R_f alongwith the complexation effect of HCl has been investigated. On the basis of R_f values the K_{sp} of some metal arsenates have been predicted. HCl has been utilized to resolve some binary and ternary mixtures such as Be^{2+} - Mg^{2+}, Zr^{4+} - La^{3+}, Th^{4+} - Ce^{4+}, Th^{4+} - UO_2^{2+}, Cr^{3+} - Mo^{6+} or W^{6+}, Sb^{3+} - Bi^{3+} - Cd^{2+} and Ag^{+} - Cu^{2+} - Cd^{2+}.

INTRODUCTION

The use of inorganic ion-exchangers in thin layer chromatography of metal ions has received some attention in recent years (1-5). In these studies a binder such as silica gel, starch or cellulose, which clouds the interpretaion of the mechanism, is not used. However, the following limitations are noticed:

(a) Numerous ions have not been systematically studied.

(b) The effect of solvent pH on the Rf value has not been investigated and hence the separations can not be put to much practical use.

Stannic arsenate is known to possess some unusual and promising ion exchange properties (6.7). Its analytical utility has been demonstrated im paper chromatography (8-10) and electrochromatography (11) of inorganic ions. The present study summarises our efforts to use thin layers of this material without any binder in aqueous HCl systems. As a result some very important and difficult separations were achieved. HCl has been chosen owing to its complex forming ability. An effort has been made to predict on the basis of Rf values, the Ksp of some metal arsenates.

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EXPERIMENTAL

Apparatus:

Thin layer chromatography applicator of Toshniwal (India) was used to prepare the layers on 20 x 3.5 cm glass plates. Chromatography was performed in 24 x 6 cm glass jars.

Reagents:

Stannic chloride pentahydrate (PPH, Poland) and sodium arsenate heptahydrate (Riedel, Germany) were used. All other chemicals were of AnalaR grade .

Test solutions and Detectors:

Test solutions were generally 0.1 M in the metal nitrate or chloride and were prepared as described earlier (8). Conventional spot test reagents were used for detection purposes (8).

Preparation of Thin Layer Plates:

Stannic arsenate in the H^+ form, prepared according to the procedure described earlier (6) , was powdered and slurried with a little demineralized water in a mortar. Vigorous grinding for a long time proved to be very important for complete adhesion. The slurry was then spread over the clean glass plates with the help of an applicator, and uniform thin layers (~ 0.1 mm. thick) were obtained. The plates were ready for use after drying at room temperature.

Procedure:

One or two drops of the test solution were placed on the plates with thin glass capillaries. After drying the spots, development was made in different solvent systems and the ascent was fixed as 11 cm in all cases. After development , the plates were dried and the cation spots were detected using the appropriate spraying agent.

RESULTS

The chromatographic behaviour of 47 ions on stannic arsenate layers has been studied using HCl as solvent in the concentration range 10^{-5} M to 5 M. The binary and ternary separations achieved experimentally are given in Tables 1 and 2. The ions investigated were : Ag^+, Tl^+, Hg_2^{2+}, K^+, Rb^+, Cs^+, Hg^{2+}, Pd^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, UO_2^{2+}, VO^{2+}, Ca^{2+}, Be^{2+}, Zn^{2+}, Mn^{2+}, Ba^{2+}, Sr^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Mg^{2+}, Sb^{3+}, Bi^{3+}, Fe^{3+}, Cr^{3+}, Ir^{3+}, Al^{3+}, Ga^{3+}, Au^{3+}, Y^{3+}, La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Ce^{3+}, In^{3+}, Pt^{4+}, Se^{4+}, Te^{4+}, Ce^{4+}, Ti^{4+}, Th^{4+}, Zr^{4+}, Mo^{6+} and W^{6+}.

In order to check the reproducibility of the R_f values, some ions were chromatographed in 1.0 M HCl , 0.1 M HCl and 0.01 M HCl. It was observed that the variations does not exceed 10% of the average R_f value.

DISCUSSION

It is evident from Tables 1 and 2 that HCl in a wide concentration range offers numerous possibilities for analytically difficult separations, which

TABLE 1

Some Binary Separations Achieved On Stannic Arsenate Layers

Solvent	Separations Achieved (R_T-R_L)
0.00001 M HCl	Cu^{2+} (0.00 - 0.16) - Ni^{2+} (0.58 - 0.80)
	Cr^{3+} (0.86 - 0.96) - VO^{2+} (0.00 - 0.08)
	Mn^{2+} (0.70 - 0.80) - VO^{2+} (0.00 - 0.06)
	Ni^{2+} (0.56 - 0.74) - VO^{2+} (0.00 - 0.10)
	Y^{3+} (0.00 - 0.10) - Mg^{2+} (0.72 - 0.98)
	Al^{3+} (0.00 - 0.04) - Mg^{2+} (0.70 - 0.95)
	Be^{2+} (0.00 - 0.05) - Ba^{2+} (0.74 - 0.84)
	Al^{3+} (0.00 - 0.08) - Ba^{2+} (0.75 - 0.86)
	Ti^{4+} (0.00 - 0.05) - Cr^{3+} (0.85 - 0.96)
0.001 M HCl	Cu^{2+}(0.00 - 0.18) - Mn^{2+} (0.73 - 0.91)
	Fe^{3+}(0.00 - 0.20) - Mn^{2+} (0.75 - 0.95)
	Pb^{2+}(0.00 - 0.06) - Mn^{2+} (0.70 - 0.95)
	Ti^{4+}(0.00 - 0.00) - Mn^{2+} (0.75 - 0.92)
	Al^{3+}(0.00 - 0.15) - VO^{2+} (0.51 - 0.60)
	Be^{2+}(0.00 - 0.06) - Ga^{3+} (0.30 - 0.58)
0.1 M HCl	UO_2^{2+} (0.00 - 0.10) - VO^{2+} (0.55 - 0.63)
	Mo^{6+} (0.00 - 0.03) - VO^{2+} (0.53 - 0.65)
	Cu^{2+} (0.00 - 0.16) - Cd^{2+} (0.64 - 0.76)
	Cu^{2+} (0.00 - 0.22) - Cr^{3+} (0.67 - 0.78)
	Cu^{2+} (0.00 - 0.21) - Mg^{2+} (0.70 - 0.98)
	Pb^{2+} (0.00 - 0.08) - Hg^{2+} (0.70 - 0.80)
	Pb^{2+} (0.00 - 0.10) - Cd^{2+} (0.65 - 0.76)
	Bi^{3+} (0.00 - 0.08) - Cd^{2+} (0.64 - 0.77)
	Bi^{3+} (0.00 - 0.05) - Pd^{2+} (0.62 - 0.80)
	Ti^{4+} (0.00 - 0.00) - Au^{3+} (0.82)- 1.00)
	Ti^{4+} (0.00 - 0.00) - VO^{2+} (0.55 - 0.64)
	Mo^{6+} (0.00 - 0.04) - Au^{3+} (0.80 - 1.00)
0.5 M HCl	Fe^{2+} (0.59 - 0.80) - Fe^{3+} (0.00 - 0.20)
	Tl^{+} (0.00 - 0.00) - Tl^{3+} (0.89 - 1.00)
	Fe^{3+} (0.00 - 0.20) - Ni^{2+} (0.72 - 0.87)
	Fe^{3+} (0.00 - 0.21) - VO^{2+} (0.68 - 0.78)
	Bi^{3+} (0.24 - 0.44) - Sb^{3+} (0.00 - 0.00)
	UO_2^{2+} (0.59 - 0.80) - Pb^{2+} (0.00 - 0.16)
	Te^{4+} (0.00 - 0.00) - Pd^{2+} (0.80 - 1.00)

Table 1 (Contd.)

Solvent	Separations Achieved (R_T-R_L)
1.0 M HCl	Fe^{3+} (0.00 - 0.16) - Cr^{3+} (0.90 - 1.00)
	Cr^{3+} (0.87 - 1.00) - Mo^{6+} (0.00 - 0.12)
	Cr^{3+} (0.90 - 1.00) - W^{6+} (0.00 - 0.08)
	Th^{4+} (0.00 - 0.10) - Ce^{3+} (0.71 - 0.92)
	Th^{4+} (0.00 - 0.12) - Ce^{4+} (0.60 - 0.94)
	Zr^{4+} (0.00 - 0.06) - La^{3+} (0.70 - 0.92)
2.0 M HCl	Zn^{2+} (0.71 - 0.95) - Hg^{2+} (0.48 - 0.60)
	Th^{4+} (0.00 - 0.08) - UO_2^{2+} (0.35 - 0.55)
	Th^{4+} (0.00 - 0.05) - Y^{3+} (0.82 - 0.97)
3.0 M HCl	Hg_2^{2+} (0.00 - 0.00) - Hg^{2+} (0.62 - 0.82)
	Th^{4+} (0.00 - 0.00) - VO^{2+} (0.66 - 0.74)
	Th^{4+} (0.00 - 0.04) - Mg^{2+} (0.90 - 1.00)
0.1 M HNO_3	Cr^{3+} (0.00 - 0.00) - Ni^{2+} (0.55 - 0.71)
	Be^{2+} (0.00 - 0.12) - Mg^{2+} (0.77 - 0.95)

have been actually realised. Some of the more important are Be^{2+} - Mg^{2+}, Zr^{4+} - La^{3+}, Th^{4+} - Ce^{4+}, Th^{4+} - UO_2^{2+}, UO_2^{2+} - VO^{2+}, Cr^{3+} - Mo^{6+} or W^{6+} and Sb^{3+} - Bi^{3+} - Cd^{2+}, Ag^+ - Cu^{2+} - Cd^{2+} etc.

These separation possibilities arise from two effects:

(a) Formation of Chloro-complexes due to the presence of HCl,

(b) Selective adsorption of certain cations by stannic arsenate layers.

In order to bring out the more interesting features of these studies R_f values were plotted against pH (Figs. 1a and 1b). The following trends were noticeable:

(i) For most cations there is no significant change in R_f values with the change in pH. Ag^+, Hg_2^{2+}, Sb^{3+}, Tl^+, Fe^{3+}, Mo^{6+}, W^{6+}, Se^{4+}, Te^{4+}, Th^{4+} and Zr^{4+} have almost zero R_f value at all pH. Ag^+ is strongly adsorbed on stannic arsenate. Tl^+ is probably precipitated as TlCl or Thallous arsenate. Sn^{4+} from stannic arsenate precipitates Se^{4+}, Te^{4+}, Mo^{6+} and W^{6+}. Excessive hydrolysis of Sb^{3+} in acidic solution may be attributed to its very low R_f value. Stannic arsenate is highly selective for Fe^{3+} and even at low pH its R_f is not significant. Zr^{4+} and Th^{4+} form insoluble arsenates

TABLE 2

Some Ternary Separations Achieved On Stannic Arsenate Layers

Solvent	Separations Achieved (R_T - R_L)
0.00001 M HCl	Ag^+ or Bi^{3+} or Pb^{2+} (0.00 - 0.06) - Cd^{2+} (0.48 - 0.60) - Pd^{2+} (0.80 - 0.98)
0.1 M HCl	Ag^+ or Se^{4+} or Te^{4+} (0.00 - 0.00) - Au^{3+} (0.80 - 0.96) - Ni^{2+} (0.50 - 0.68)
0.5 M HCl	Ag^+ (0.00 - 0.00) - Cu^{2+} (0.75 - 1.00) - Cd^{2+} (0.48 - 0.58)
1.0 M HCl	Fe^{3+} or Mo^{6+} (0.00 - 0.16) - UO_2^{2+} (0.30 - 0.49) - VO^{2+} (0.68 - 0.78)
3.0 M HCl	Ag^+ (0.00 - 0.04) - Cu^{2+} (0.50 - 0.68) - Au^{3+} (0.80 - 1.00)
5.0 M HCl	Ag^+ (0.00 - 0.05) - Pb^{2+} (0.33 - 0.45) - Cu^{2+} (0.70 - 0.75)
	Sb^{3+} (0.00 - 0.00) - Bi^{3+} (0.53 - 0.61) - Cd^{2+} (0.80 - 0.98)

resulting in almost zero R_f value. Hg_2^{2+} precipitates as its chloride and thus there is no movement. Hg^{2+}, Cd^{2+}, Zn^{2+}, Mn^{2+}, Ir^{3+}, Au^{3+}, Pt^{4+}, Fe^{2+}, Mg^{2+}, Ca^{2+} and Pr^{3+} have high and constant R_f values. This is due to the solvation of the cations or their chloro complexes. Au^{3+} and Pt^{4+} exist as their anionic complexes which are not sorbed significantly. Hg^{2+} exists almost exclusively as $HgCl_2$ which is largely covalent in character and hence it has R_f value of approximately 1. Zn^{2+} and Mn^{2+} form anionic complexes like $[ZnCl_4^{--}]^{2-}$ and $[MnCl_4^{--}]^{2-}$ resulting into a higher R_f.

(ii) For K^+, Rb^+ and Cs^+, the R_f value slightly decreases from pH 0 to 1. Further increase in pH has no effect on the R_f values of these cations. These metals are not known to form complexes and the decrease in R_f is due to strong adsorption on the stannic arsenate layers.

(iii) Cations such as Bi^{3+}, Pb^{2+}, Cu^{2+}, UO_2^{2+}, Al^{3+}, Be^{3+}, In^{3+}, Ce^{4+} and Ti^{4+} show a sharp decrease in R_f values between pH 0 and 1. At pH $>$ 1 Bi^{3+} has zero R_f value owi-ng to hydrolysis but at lower pH there is an increase in R_f value due to the formation of anionic complexes such as $BiCl_4^-$. Similarly in the case of Pb^{2+}, at lower pH i.e. at higher Cl^-

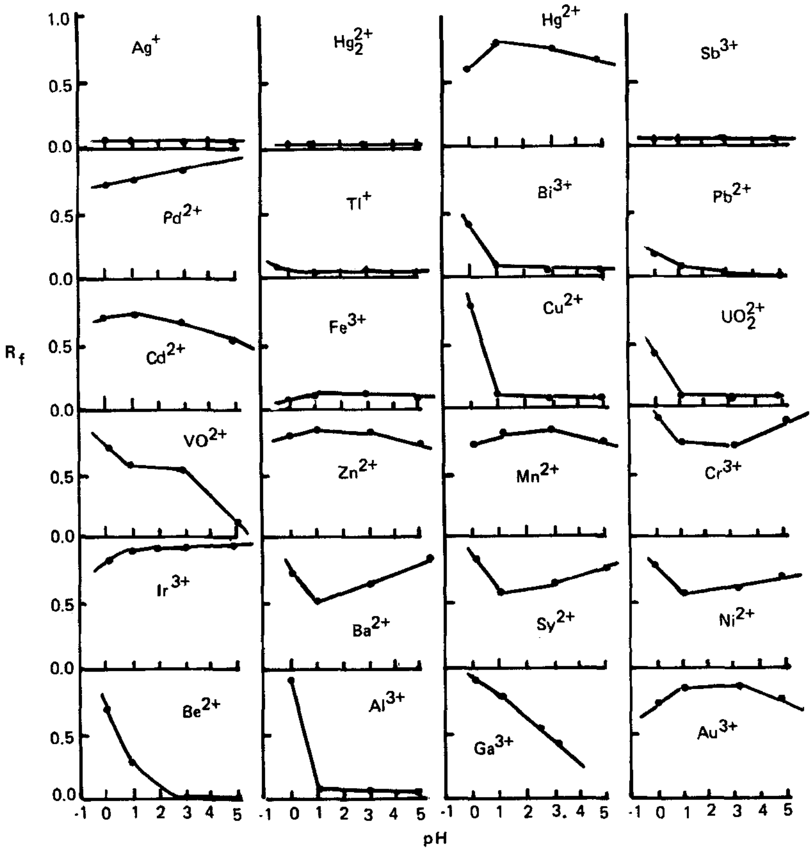

Fig. 1a & b: Plots of R_f vs. pH.

concentration, it forms anionic complexes such as $[PbCl_4^{--}]^{2-}$ which results in an increase in the R_f value of the cation. The same explanation holds good for other cations as well. Ions such as Ba^{2+}, Sr^{2+}, Ni^{2+}, Co^{2+} and Cr^{3+} have minimum R_f at pH 1. This is probably due to the maximum ion-exchange which occurs at this pH.

(iv) Ga^{3+}, VO^{2+}, Y^{3+}, La^{3+}, Nd^{3+}, Sm^{3+} and Ce^{3+} show exceptional behaviour. At pH $>$ 2 Nd^{3+} and Sm^{3+} are almost completely adsorbed on stannic arsenate layers resulting in a very low R_f. The R_f values of VO^{2+}, Ga^{3+} and Ce^{3+} gradually decrease with an increase in pH and become almost zero at pH 5. This is probably due to the formation of stable complexes at higher Cl^- concentration as evidenced by Figure 2.

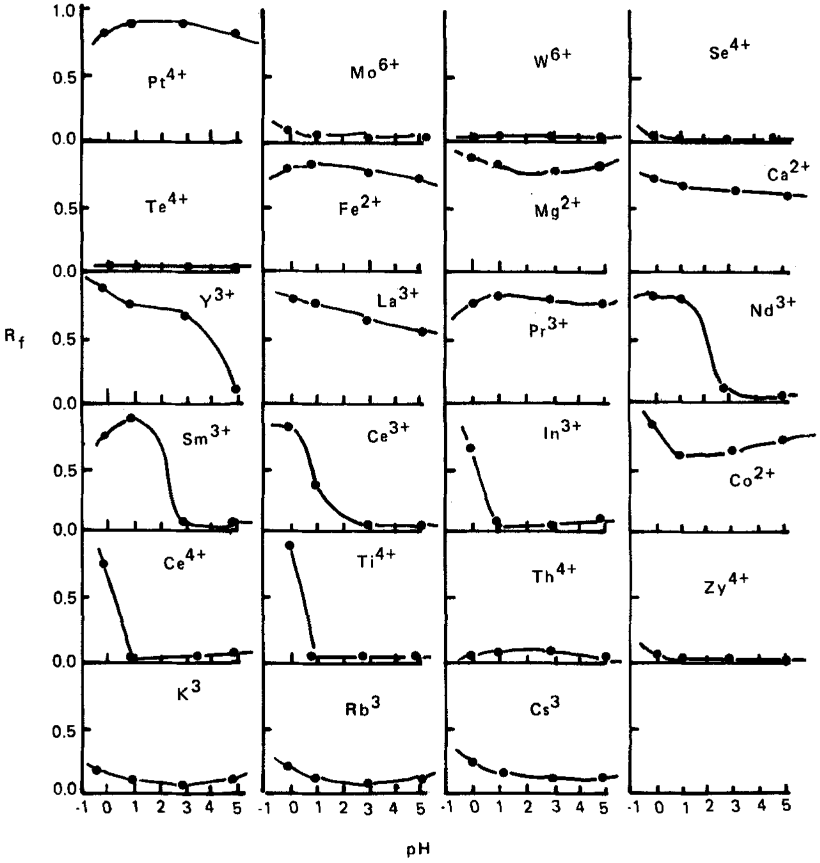

Fig. 1a & b (Contd.)

A survey of the plots (Figs 1a and 1b) reveals that the R_f generally decreases with an increase in pH, the steep fall being between pH 0 and 1. The value further decreases upto pH 2 and then becomes almost constant. This shows that pH 1 to 2 is the most favourable acidity for ion-exchange. This observation is in conformity to our earlier experience on stannic arsenate papers (9).

A comparison of R_f values in 0.1 M HNO_3 on stannic arsenate layers and stannic arsenate impregnated papers (9) prepared under similar conditions suggests that there is a decrease in the R_f value on layers for almost all cations probably due to the higher adsorption. Greater total ion-exchange capacity of the thin layer plates than that of the papers may be responsible

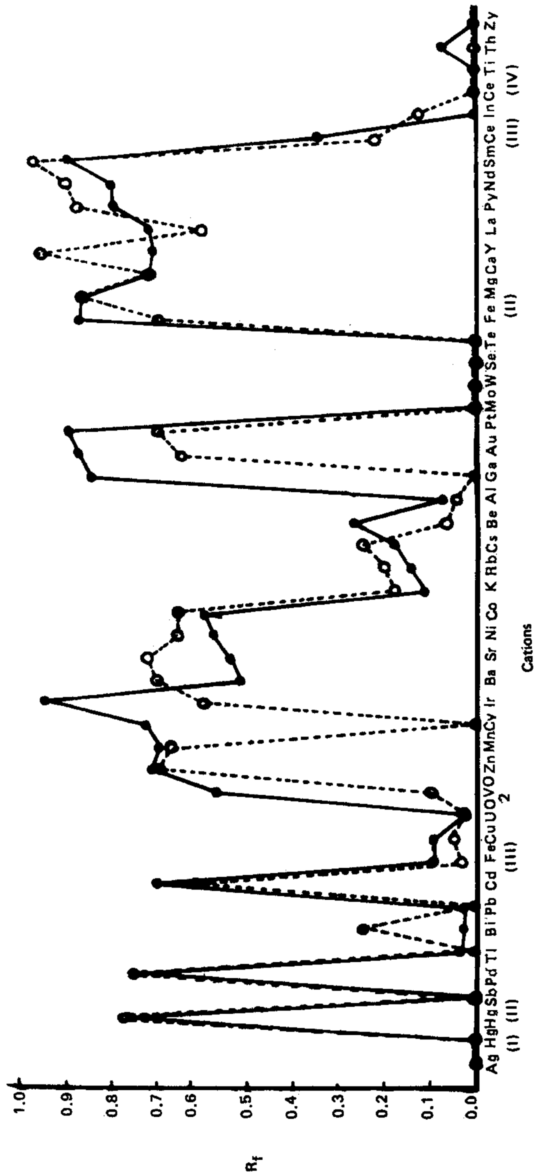

Fig. 2 : Comparison of R_f values in 0.1 M HCl and 0.1 M HNO_3 on stannic arsenate layers.

TABLE 3

Precipitation of Cations in the Mixture of Solvent and Impregnating Material

Solvent	Cation + Sodium arsenate + Solvent	
	Cations which precipitate	Cations which do not precipitate
1.0 M HCl	Hg_2^{2+}, Te^{4+}, Tl^+, Ag^+, Zr^{4+}	Fe^{3+}, Se^{4+}, Mo^{6+}, W^{6+}, Th^{4+}, Sb^{3+}

for this decrease. The decrease is more pronounced in case of Tl^+, Cu^{2+}, VO^{2+}, Cr^{3+}, Y^{3+} and La^{3+}. This is due to the fact that stannic arsenate is more selective for these cations and thus there is a greater exchange resulting in much lower R_f value.

Ions which have zero R_f values may do so owing to (a) precipitation, (b) ion-exchange and (c) strong adsorption due to high charge. In order to similate conditions on thin layers, sodium arsenate was added to the cation solution followed by the solvent. A number of ions precipitate under these conditions (Table 3). In these cases the precipitation mechanism hol-ds good. For other ions, Fe^{3+} is selectively adsorb-ed by stannic arsenate, Sb^{3+} hydrolyses and Se^{4+}, Th^{4+}, Mo^{6+} and W^{6+} are strongly adsorpted owing to their high charge.

To study the effect of complexation, R_f values were determined in 0.1 M HNO_3. A plot of R_f versus cations for 0.1 M HCl and 0.1 M HNO_3 as solvent (Fig.2) indicates the increase in the R_f value of certain cations such as VO^{2+}, Cr^{3+}, Ga^{3+}, Ir^{3+}, Be^{2+} and Th^{4+} due to the formation of anionic chloride complexes. A higher R_f value of Au^{3+} and Pt^{4+} in HCl media can be explained on the same basis.

It is known that R_f value amongst other factors, depend-s upon the solubility product of the metal salt. On co-relating the R_f values of the metal ions with the K_{sp} of their arsenates, the following linear relationship is obtained:

$$R_f = 0.325 + 0.011 \frac{10^3}{-\log K_{sp}}$$

Figure 3 shows this linear relationship. With the help of this equation it is possible to predict the K_{sp} values of different metal arsenates (Table 4). The K_{sp} values of the various arsenates which have been used in plotting figure 3 are given in Table 5. In our earlier communication (8), we have predicted the K_{sp} of metal arsenates from the R_f value of metal ions on stannic arsenate papers. The only difference in the two

TABLE 4

Predicted Values of K_{sp} for Different Metal Arsenates

Metal arsenate	K_{sp}
Hg^{2+}	2.5×10^{-39}
Pd^{2+}	4.6×10^{-30}
Ir^{3+}	2.8×10^{-21}
Be^{2+}	6.9×10^{-28}
Ga^{3+}	2.2×10^{-17}
Fe^{2+}	5.2×10^{-26}
Y^{3+}	1.7×10^{-22}
La^{3+}	2.1×10^{-23}
Ce^{3+}	2.1×10^{-23}
Ce^{4+}	1.9×10^{-25}

TABLE 5

Experimental Values of K_{sp} for Some Metal Arsenates

Metal arsenate	K_{sp}
Pb^{2+}	4.1×10^{-36}
Cu^{2+}	7.6×10^{-36}
Cd^{2+}	2.2×10^{-33}
Mn^{2+}	$(1.9) \times 10^{-29}$
Cr^{3+}	$(7.8) \times 10^{-21}$
Zn^{2+}	1.3×10^{-28}
Co^{2+}	$(7.6) \times 10^{-29}$
Sr^{2+}	8.1×10^{-19}
Ca^{2+}	6.8×10^{-19}
Al^{3+}	$(1.6) \times 10^{-16}$
Ni^{2+}	$(3.1) \times 10^{-26}$
Mg^{2+}	2.1×10^{-20}

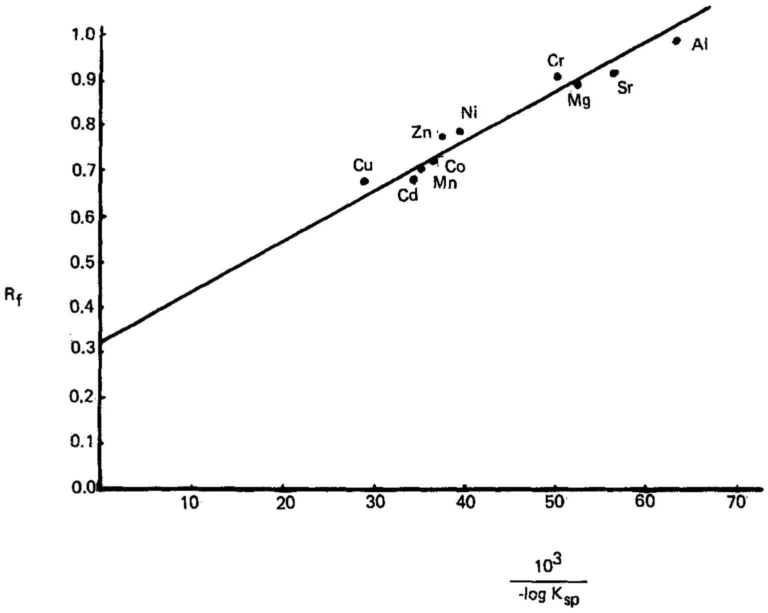

Fig. 3 : Plot of R_f vs. $\frac{10^3}{-\log K_{sp}}$ for metal ions in 1M HCl.

linear relationships obtained for impregnated papers and thin layer plates is that in the latter case, the charge on the ion and the bare ion radii has little effect on the R_f value and only the K_{sp} of metal arsenate is the deciding factor.

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