

CHROMATOGRAPHY ON PAPER IMPREGNATED WITH
ION-EXCHANGE RESINS

VII. ION EXCHANGE WITH ORGANIC SOLVENTS

M. LEDERER, V. MOSCATELLI AND C. PADIGLIONE

*Laboratorio di Cromatografia del C.N.R.
e Laboratorio di Chimica delle Radiazioni e Chimica Nucleare del C.N.E.N.,
Istituto di Chimica Generale ed Inorganica,
Rome (Italy)*

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INTRODUCTION

In a previous paper¹ in this series we have shown that the mechanism of adsorption on ion-exchange resins can be studied by chromatography with resin loaded papers, and in particular the comparison of several resins is rendered very simple by chromatographing on several papers simultaneously with the same solvent. The present communication utilises this simple technique for the investigation of several problems. Firstly no work with organic solvents on the inorganic ion exchangers (except ref.²) such as zirconium phosphate has been reported as far as we know. Secondly the claim was made³ that evidence for an anionic chloro-complex of thorium was obtained by adsorption studies on anion exchangers, although neither solvent extraction nor partition chromatography have given evidence for such a complex. Preliminary results on this question have already been reported in the preceding communication¹ and have indicated that the mechanism of the retention of thorium on anion exchangers seems to be rather a kind of partition chromatography where the resin supports the stationary phase. This work was extended and confirmed with numerous solvents. Finally we believe that with the comparative method used we can present a better picture of the processes involved in the adsorption of inorganic substances on ion exchangers from organic solvents, than has been obtained so far from equilibrium and column experiments.

Ion exchange with organic solvents has already been the topic of numerous publications over the last fifteen years⁴. More detailed studies of analytical interest were recently made by FRITZ AND PIETRZYK⁵ who examined the anion exchange behaviour of numerous metal ions in a number of solvents containing hydrochloric acid and by KORKISCH *et al.*⁶ who studied the behaviour of thorium and uranium in numerous solvents containing various mineral acids at various concentrations.

EXPERIMENTAL AND RESULTS

In all experiments the following four papers were developed in the same solvent at a temperature of $20 \pm 1^\circ$ in tightly closed small volume jars (26 cm \times 15 cm diam.) by the ascending method:

(1) Amberlite SA-2 paper containing 45 % of Amberlite IR-120 (a sulphonic resin).

(2) Amberlite SB-2 paper containing 45 % of Amberlite IRA-400 (a quaternary ammonium resin).

(3) Zirconium phosphate paper prepared according to ALBERTI AND GRASSINI⁷ by precipitating zirconium oxychloride inside the filter paper with phosphoric acid.

(4) Whatman No. 1 cellulose paper.

The solvents examined all contain 1 *N* or 2 *N* acids since intermediate R_F values are obtained on zirconium phosphate paper in this region of acidity. The following organic solvents (of chemically pure grade) were studied: methanol, ethanol, isopropanol and acetone. The main interest of this investigation was centred around the behaviour of thorium and uranium. So as to observe also the behaviour of typical transition and non-transition elements, copper and lanthanum were chromatographed with thorium and uranium. A wider range of ions was studied in acetone mixtures and ethanol since these seemed to yield the most promising results.

The solutions of the ions to be studied were usually made by dissolving the salt (chloride, nitrate or sulphate respectively) in 1 *N* or 2 *N* acid. Thorium nitrate was evaporated 3 times with conc. HCl and then dissolved in 2 *N* HCl as recommended by KORKISCH AND TERA³ to prevent hydrolysis. Nitrate and sulphate solutions of thorium were also made by evaporating with the concentrated acid and subsequent dilution in the cold.

Uranium and copper could be detected on all papers with potassium ferrocyanide.

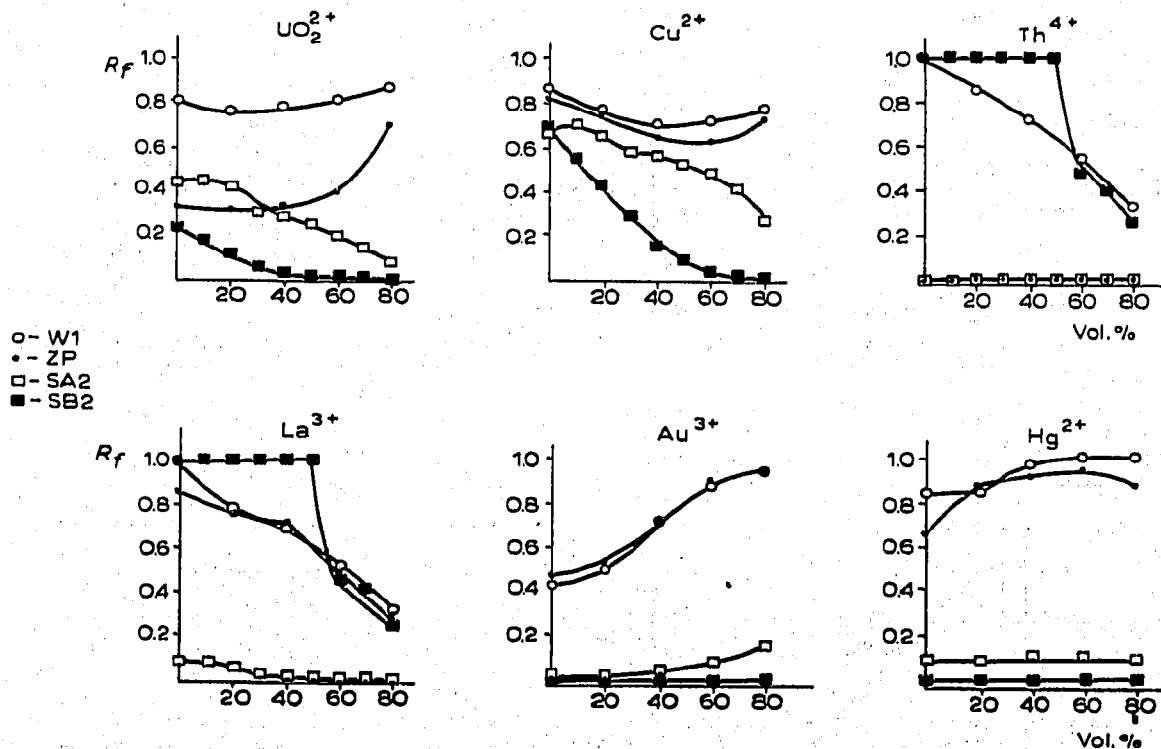
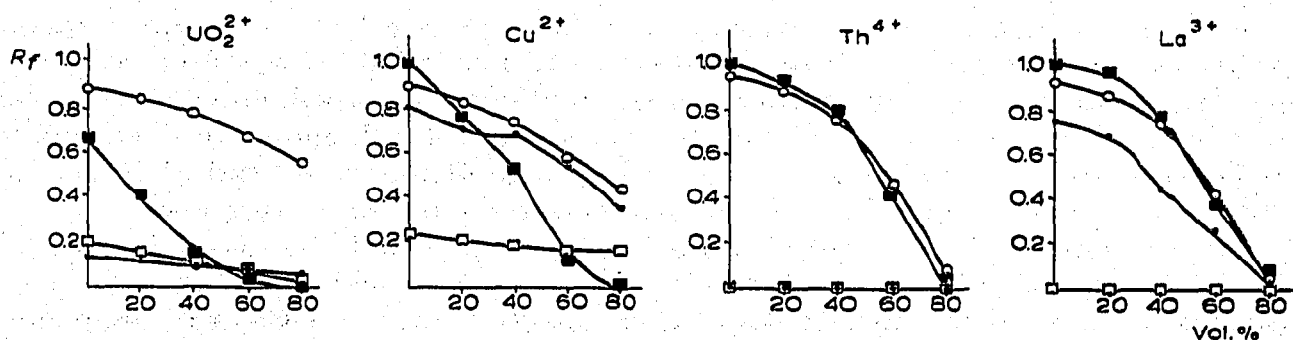


Fig. 1. R_F values of some metal ions in methanol-2 *N* HCl mixtures. Ordinates: R_F values; abscissae: vol. % of methanol in mixtures of methanol-water-HCl all being 2 *N* with respect to HCl. ○ = W1: Whatman No. 1 paper; ● = Z.P.: zirconium phosphate paper; □ = SA-2: Amberlite SA-2 paper (strong acid sulphonic type resin ca. 45 %); ■ = SB-2: Amberlite SB-2 paper (strong base quaternary ammonium type resin ca. 45 %).

Thorium and lanthanum were detected with thoron and in absence of zirconium phosphate also with alcoholic ammoniacal 8-hydroxyquinoline.

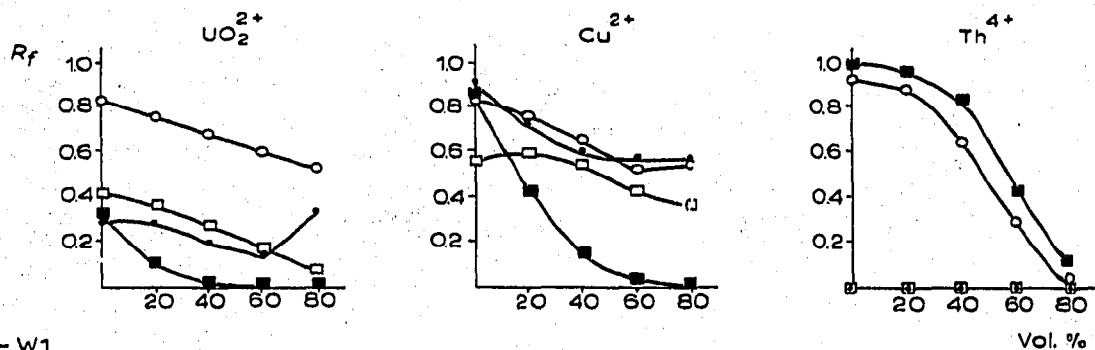
Anion exchange papers usually gave rather elongated spots for Th(IV) and La(III) for intermediate R_F values. However, only the values of the centres of the spots were recorded in the results.

Figs. 1-7 show the variation of the R_F value when the water in 1 N or 2 N acids is gradually replaced with organic solvents from 0% to 80%.

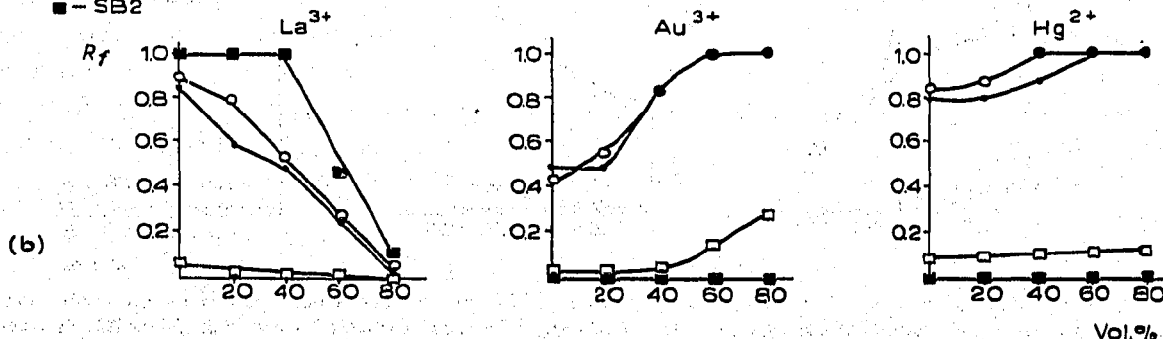


(a)

- - W1
- - ZP
- - SA2
- - SB



○ - W1
● - ZP
□ - SA2
■ - SB2



(b)

Fig. 2. R_F values of some metal ions in (a) ethanol-1 N HCl and (b) ethanol-2 N HCl mixtures. Symbols etc. as in Fig. 1.

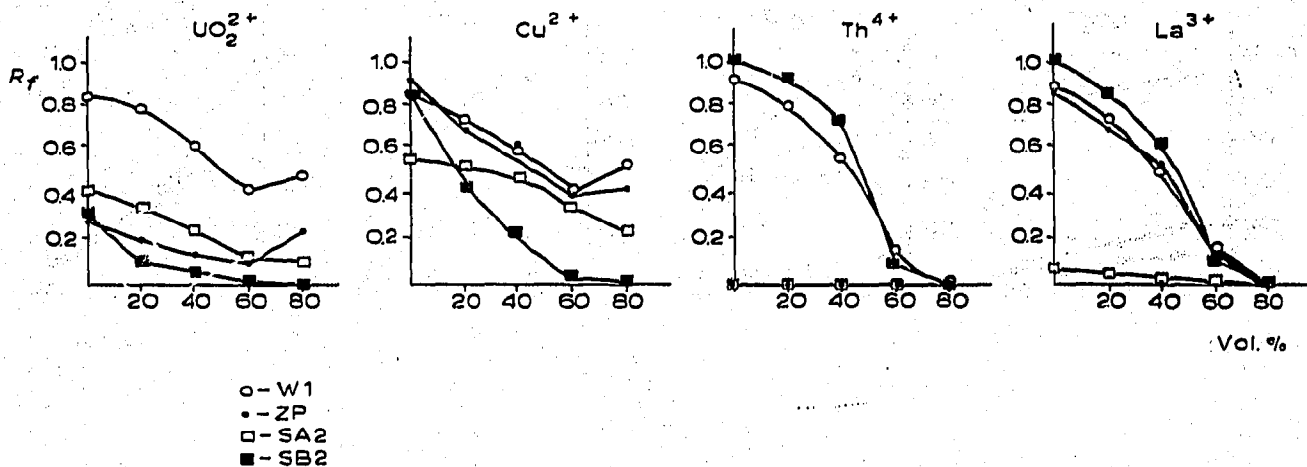


Fig. 3. R_f values of some metal ions in isopropanol-2 N HCl mixtures. Symbols etc. as in Fig. 1.

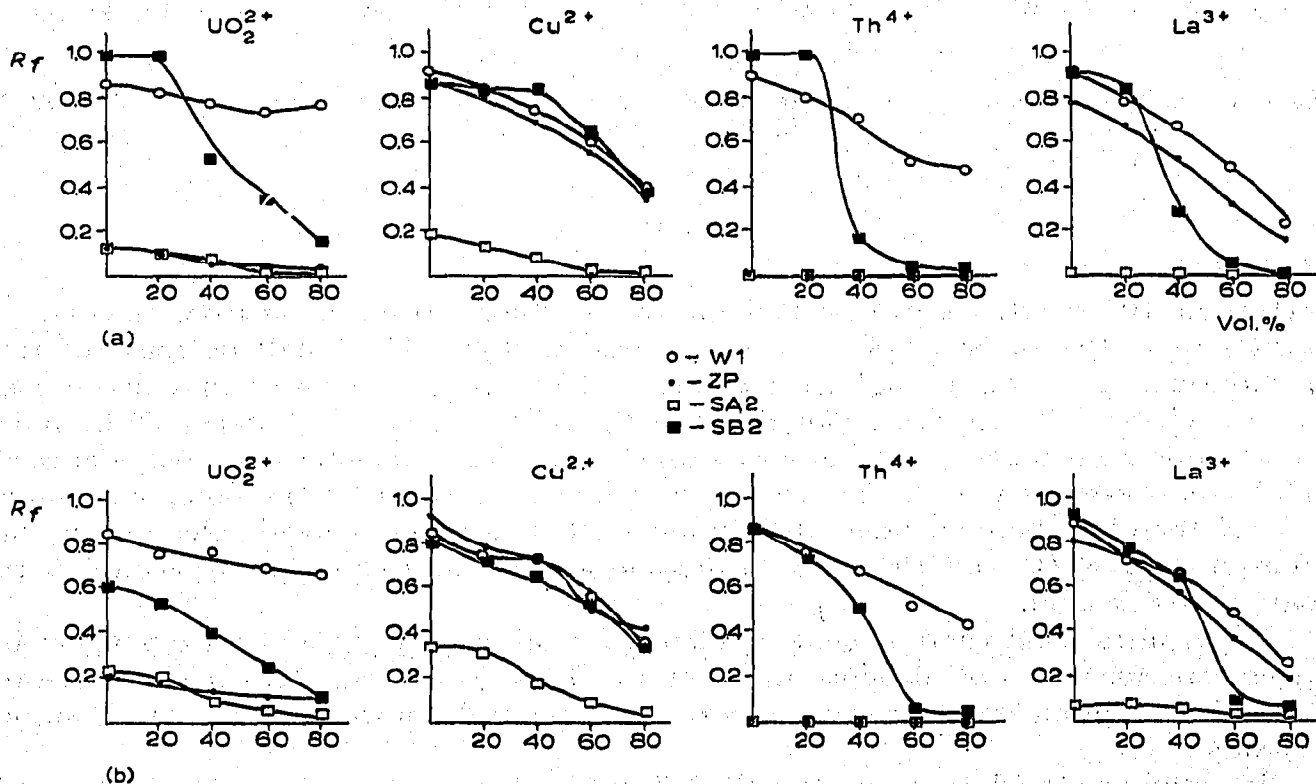


Fig. 4. R_f values of some metal ions in (a) ethanol-1 N HNO₃ and (b) ethanol-2 N HNO₃. Symbols etc. as in Fig. 1.

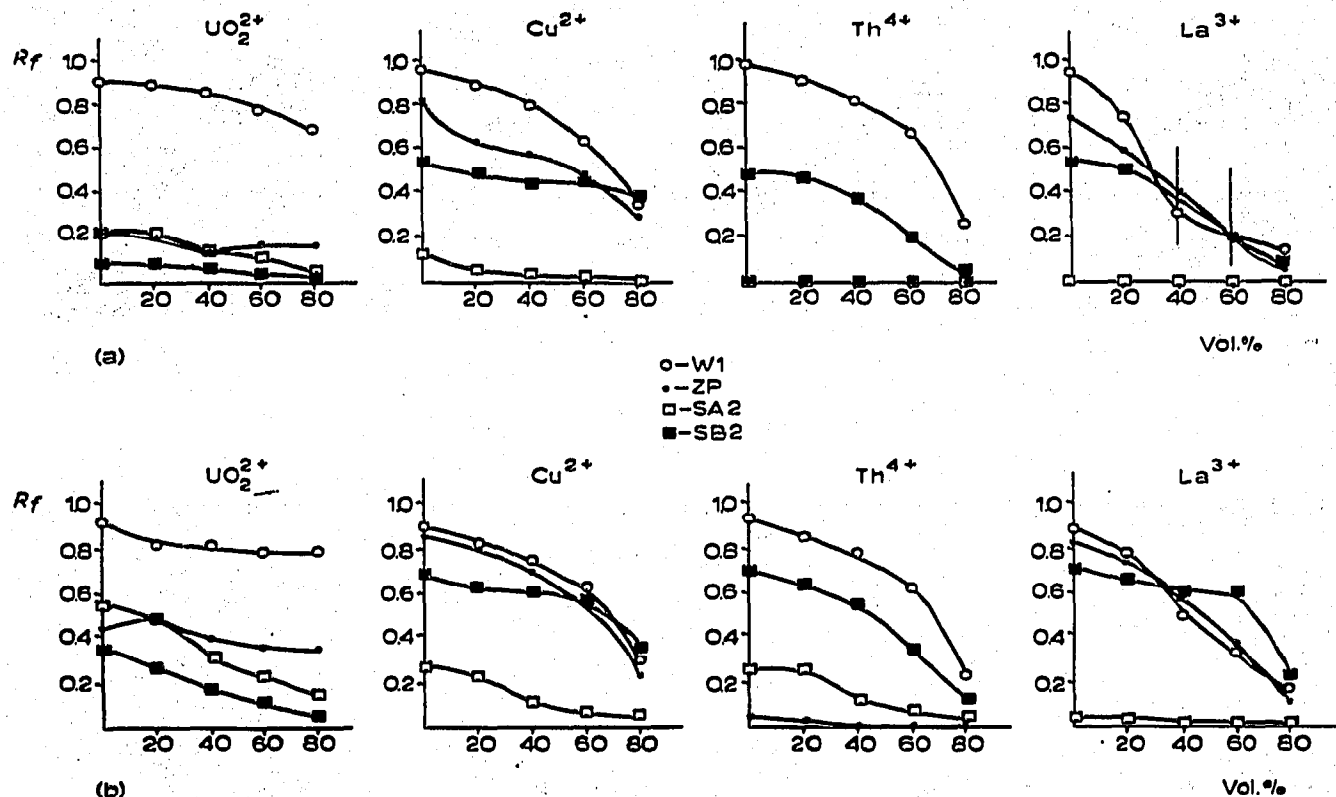


Fig. 5. R_F values of some metal ions in (a) ethanol-1 N H_2SO_4 and (b) ethanol-2 N H_2SO_4 . Symbols etc. as in Fig. 1.

DISCUSSION

Lanthanum

La(III) in HCl is strongly adsorbed on the sulphonic resin paper from all concentrations of methanol, ethanol, isopropanol and acetone. The small decrease of the R_F values may be attributed to a small "partition effect" superimposed on the cation exchange adsorption. From HCl the R_F values on cellulose paper (Whatman No. 1), anion exchange paper and zirconium phosphate paper are almost identical and decrease regularly with the increase in the concentration of the organic solvent. It must therefore be concluded that anion exchange plays a negligible role in the retention of La(III) and that the adsorption on zirconium phosphate is also very small in 1-2 N acid.

From nitric acid there is some evidence for adsorption on anion exchangers in higher concentrations of alcohols and acetone (Figs. 4a, 4b, 7a). This may be due to physical adsorption on the resin network by a neutral complex or to actual anion exchange.

In sulphuric acid there are small differences between anion resin papers and cellulose papers. However, they seem to be negligible as are also those for the zirconium phosphate paper. Thus with the exception of nitric acid there seems to be no anion exchange of La(III) from organic solvents and little retention by zirconium phosphate, the main phenomena being cation exchange with sulphonic groups and partition.

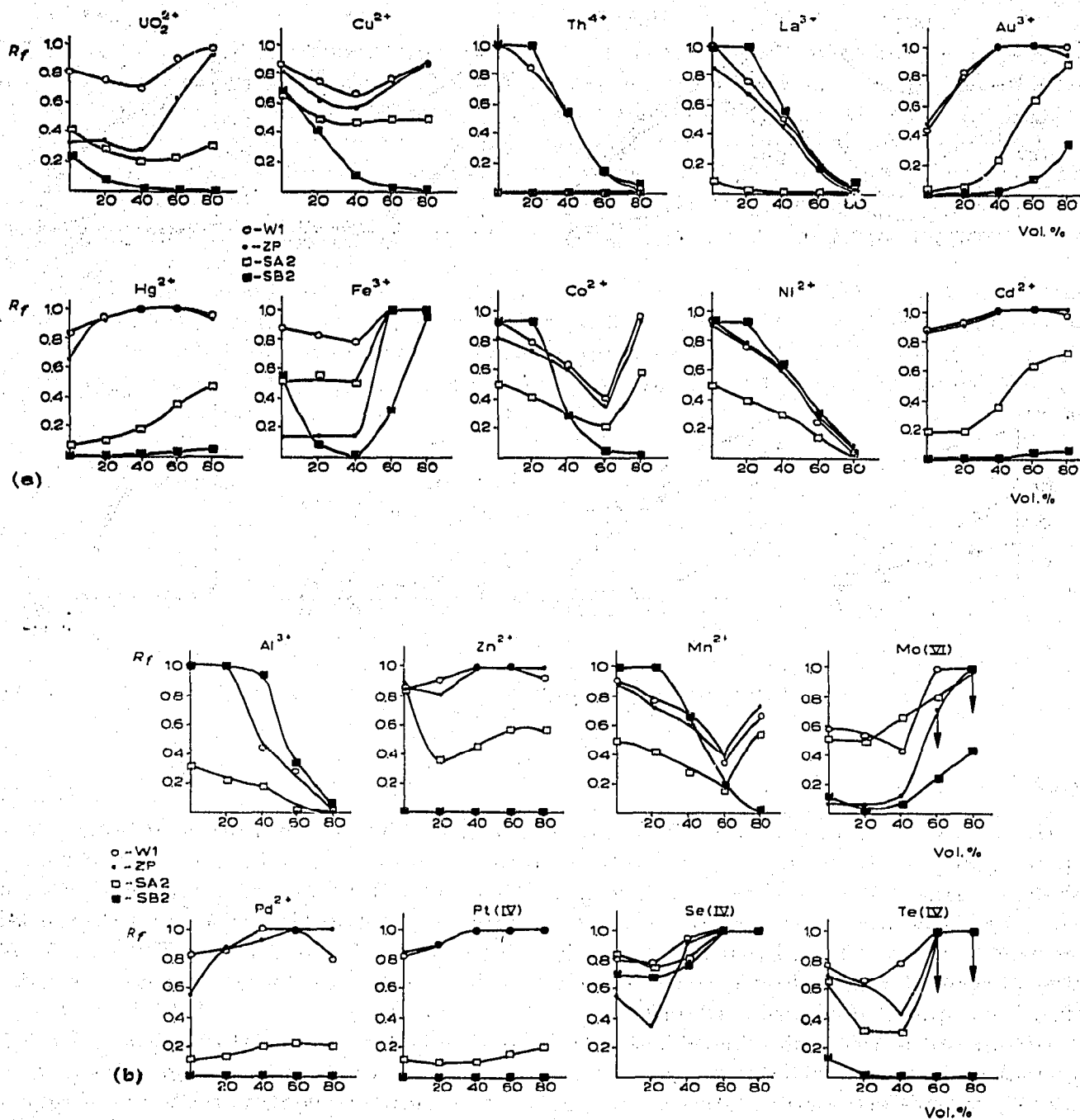


Fig. 6. R_f values of a number of metal ions in acetone-2 N HCl. Symbols etc. as in Fig. 1.

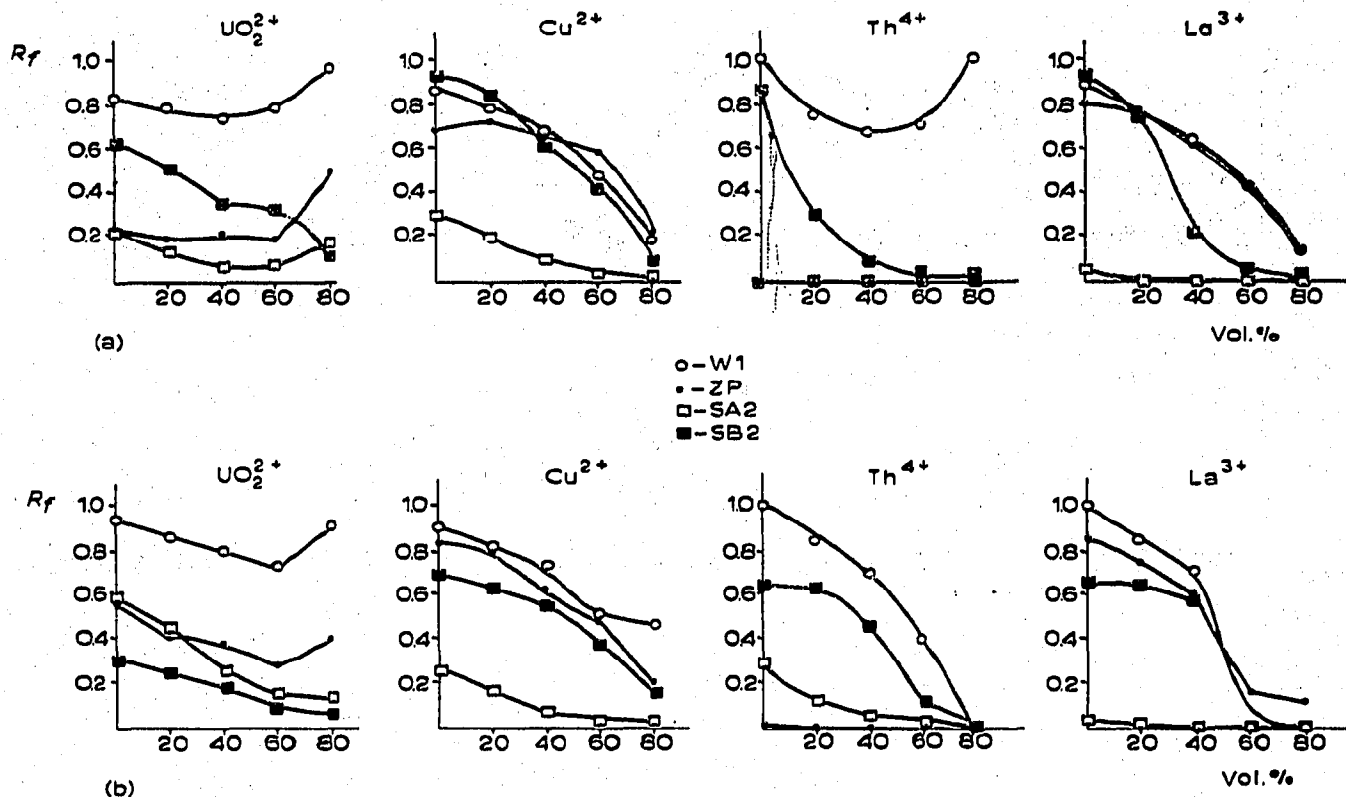


Fig. 7. R_F values of some metal ions in (a) acetone-2 N HNO_3 and (b) acetone-2 N H_2SO_4 . Symbols etc. as in Fig. 1.

Thorium

Thorium(IV) is strongly adsorbed on zirconium phosphate and sulphonic resin papers from all acids and all solvents. From hydrochloric acid the adsorption on anion exchange paper and on cellulose paper is identical except in low concentrations of organic solvents where cellulose adsorbs more than the resin paper. From nitric acid the tendency to adsorption on anion exchangers is very marked and the R_F value curves of the cellulose paper and the anion exchange paper diverge considerably above 40 % of organic solvent.

From sulphuric acid there is an increased adsorption on the anion exchange paper already in the aqueous solution. Both cation and anion exchange papers have lower R_F values with an increase in the organic solvent concentration which suggests a partition effect in addition to the ion exchange effect.

From these results it is evident that anion exchange does not contribute to the adsorption of Th(IV) on the various papers from HCl, while it does from HNO_3 and H_2SO_4 .

In sulphuric acid (Figs. 5b, 7b) another interesting effect may be observed. Th(IV) is more strongly adsorbed on zirconium phosphate than on the sulphonic resin. In 2 N H_2SO_4 a sulphonic resin must be much more ionised than the phosphoric groups of zirconium phosphate. It thus seems that the retention of Th(IV) on the zirconium phosphate is due to complex formation between Th(IV) and the phosphoric acid groups rather than to an electrostatic attraction.

Uranium (VI)

U(VI) is only slightly adsorbed from 2 *N* HCl-methanol on cellulose paper, but quite strongly on both cation and anion resin paper. There seems to be an increased adsorption which does not depend on a partition effect. Since there is an increase on both resin papers we would like to suggest that a neutral species which adsorbs on the organic network of the resin is responsible for this adsorption. This neutral species is formed as the water of hydration is removed from the uranyl ion.

A similar effect is shown in ethanol with 1 *N* or 2 *N* HCl and isopropanol although there is also a slight partition effect as well.

Zirconium phosphate adsorbs U(VI) from aqueous solution but less from organic solvents; in fact acetone-2 *N* HCl may be used to desorb it completely while this is not so easy with high concentrations of aqueous or alcoholic HCl (see Fig. 8). This effect does not seem to have been recorded previously and may have importance in

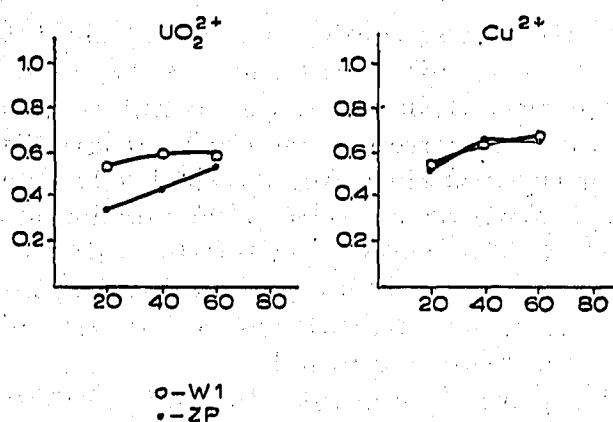


Fig. 8. R_F values of UO_2^{2+} and Cu^{2+} ions on Whatman No. 1 (open circles) and zirconium phosphate (black dots) with mixtures of ethanol-conc. HCl as solvents. Ordinates: R_F values; abscissae: vol. % of conc. HCl in ethanol.

the treatment of uranium solutions. The only organic solvent mentioned for such a desorption in the literature is tributyl phosphate².

From nitric acid (–ethanol or acetone) there is little retention on cellulose paper, a gradual increase of adsorption on anion resin paper and a much greater adsorption on cation resin and zirconium phosphate papers. This seems to be in agreement with solvent extraction studies which suggest an equilibrium of cationic and neutral species. The increase of adsorption on the anionic paper seems to be due to the existence of a neutral species which, however, is not adsorbed on the much more polar cellulose. The fact that the adsorption on zirconium phosphate decreases slightly with increasing acetone concentration seems to confirm this. From sulphuric acid U(VI) is only little retained by cellulose paper and quite strongly on all three exchangers. The existence of anionic sulphato complexes is well-known, and hence the adsorption on the anion resin may be accounted for.

Copper

There is little adsorption on cellulose or zirconium phosphate from alcoholic or acetone–HCl mixtures. The adsorption on the anion resin increases considerably with increase in the organic solvent concentration, more neutral and anionic chloro-com-

plexes being formed, as has been observed in numerous other systems previously. There is also an adsorption on the cationic resin which varies little with the solvent concentration. It is stronger from 1 *N* than from 2 *N* HCl and seems to be due to the cationic chloro-complexes as well as the neutral ones. Thus as the amount of cations decreases with increasing solvent concentration the physical adsorption of neutral complexes increases accordingly.

In nitric acid the curves for anionic resin, cellulose and zirconium phosphate coincide, thus retention on these three seems to be solely due to partition. On cationic resin paper there is strong adsorption which increases in higher solvent concentration due to an additional partition effect. In sulphuric acid the picture is essentially as in nitric acid with a possible slight anion exchange effect which seems to be independent of the organic solvent.

The behaviour of anionic chloro complexes and some anions

Figures 1, 2b, 6 show also the adsorption of chloroauric acid and chloromercuric acid from acetone, methanol and ethanol containing 2 *N* HCl. As has been shown previously⁸ adsorption on the cation resin paper and cellulose paper must be considered as physical adsorption akin to inverted phase chromatography. The effect of organic solvents is studied here for the first time and shows clearly that there is a competition between the tendency to adsorb on one non-polar surface and the tendency to dissolve in a non-polar solvent. The adsorption on the anion exchanger clearly shows that the adsorption is due to anion exchange plus physical adsorption and is always greater than on the cationic resin. No adsorption on zirconium phosphate can be observed from any of the solutions examined.

Fig. 9 shows the adsorption of chloride, bromide, iodide and thiocyanate from ethanol-0.5 *N* LiNO₃ on anion resin paper and cellulose paper. As was previously

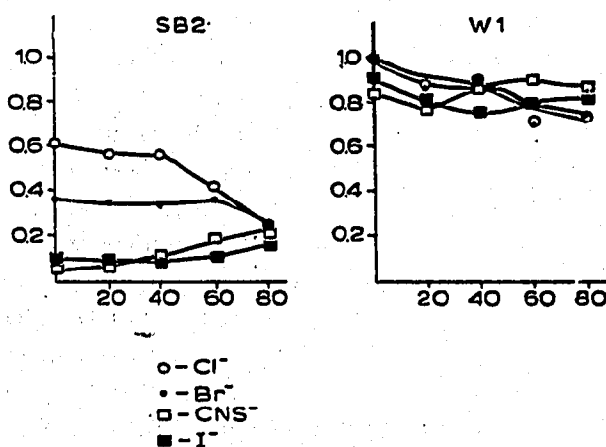


Fig. 9. R_F values of chloride, bromide, iodide and thiocyanate with ethanol-0.5 *N* LiNO₃ as solvent. Ordinates: R_F values; abscissae: vol. % ethanol in ethanol-water-LiNO₃ mixtures which are 0.5 *N* with respect to LiNO₃. \circ = Cl^- ; \bullet = Br^- ; \square = CNS^- ; \blacksquare = I^- . SB-2 = Amberlite SB-2 paper; W1 = Whatman No. 1 paper.

shown⁹ with equilibrium studies, thiocyanate desorbs with increasing ethanol concentration and chloride adsorbs more strongly. This effect seems to be mainly due to the

change in the hydration of the ions on the one hand and their increased solubility in the organic phase on the other.

CONCLUSIONS

The retention of ions on ion-exchange papers from solutions of acids in organic solvents can be due to a variety of mechanisms:

1. Ion exchange, that is, actual electrostatic attraction between ionised groups of the ion exchanger and ionised species in solution.
2. Complex formation with groups such as sulphonic or phosphoric acid groups of the ion exchanger.
3. Partition between the water retained on a polar support, which may be cellulose or also a resin equipped with polar groups.
4. Adsorption on the organic network (either paper or resin) of species which extract readily into organic solvents.
5. Complex formation due to the presence of the organic solvent which changes the water concentration in complexing equilibria as well as changes of hydration of non-complexed ions.

The following effects were observed:

(i) U(VI) can be desorbed from zirconium phosphate with acetone while it is only possible to desorb it with aqueous acids in high concentrations. Fast desorption of U(VI) from organic resins with organic solvents proved equally impossible.

(ii) Chloroauric acid and similar strongly adsorbed halo-complexes may be desorbed from organic resins with organic solvents, the effect depending on the nature of the solvent.

(iii) No evidence for an anionic Th(IV) chloro-complex could be obtained, although complexing with nitric acid and sulphuric acid may be observed readily.

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SUMMARY

The adsorption of a number of metal ions from organic solvents (such as methanol, ethanol, isopropanol, acetone) mixed with acids (such as HCl, HNO₃ or H₂SO₄) was studied on cellulose paper, zirconium phosphate impregnated paper, sulphonic resin paper and quaternary ammonium resin paper. As the mechanisms responsible for the adsorption the following were suggested: ion exchange, complex formation with the groups of the exchangers, partition with the water held on the paper, adsorption on the organic network of the paper or resin and change of the complex equilibria due to the presence of the organic solvent.

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