

CHROMATOGRAPHY ON ION EXCHANGE PAPERS

XII. THE ADSORPTION OF METAL IONS ON VARIOUS ANION EXCHANGE PAPERS—FURTHER RESULTS

G. BAGLIANO, G. GRASSINI, M. LEDERER AND L. OSSICINI

*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

The adsorption of numerous metal ions on anion exchange resin paper, DEAE cellulose paper, amino-ethyl cellulose paper and Whatman No. 1 paper from HCl solutions was described in a previous communication of this series¹. The differences between the adsorption from HCl and LiCl were considered in a preliminary note² dealing only with two typical anions, ReO_4^- and AuCl_4^- . In this paper we shall describe further investigations on the adsorption of metal ions on various anion exchange papers which enlarge upon the problems already dealt with and add new data for analytical purposes.

The directions in which we extended the previous work were (i) obtaining data of adsorption from HCl solutions of ions which had not been previously studied [As(III), As(V), Ru(III) and U(IV)], (ii) studying Amberlite WB-2 weak anion exchange resin paper with a few typical metal ions, (iii) making an extensive survey of the adsorption of metal ions from LiCl solutions and (iv) studying the adsorption of a number of metal ions from HBr solutions.

The general technique of washing the papers and chromatographing in small jars by the ascending method was employed as described previously¹. When additional operations were performed these are mentioned under the relevant sub-heading.

(i) Further data on the adsorption of metal ions from HCl

Fig. 1. shows the R_F values of As(III), As(V), U(IV) and Ru(III) plotted against the normality of HCl. The R_F values on the strong base resin paper (SB-2) agree well with the data of KRAUS AND NELSON³. The adsorption of Ru(III) (*i.e.* chlororuthenite) on aminoethylcellulose is much higher than may be expected from the adsorption on the DEAE cellulose and is difficult to explain by ion exchange and adsorption phenomena; the latter should be more pronounced for the DEAE paper.

(ii) The adsorption of some metal ions on the Amberlite weak anion exchange paper (WB-2) from HCl or LiCl

The weak base resin paper (WB-2) containing Amberlite IR-4B differs from the strong base resin paper SB-2 (containing Amberlite IRA-400) not only in the type of ion

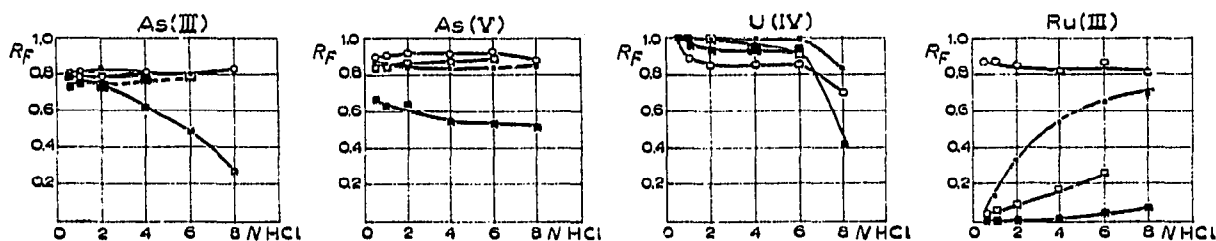


Fig. 1. R_F values of some metal ions plotted against the concentration of HCl. O—O on Whatman No. 1 paper; ■—■ on SB-2 strong base resin paper; ●—● on Whatman DE 20 DEAE paper; □—□ on Whatman AE 30 amino ethyl cellulose paper.

exchange groups but also in the type of polymer, as Amberlite IR-4B is a phenol-formaldehyde resin while Amberlite IRA-400 is a polystyrene resin. It is unlikely that in solutions containing more than 1 N HCl any difference in ionisation exists between the two types of exchange groups, the quaternary ammonium and the amino group. The effect of the substituents on the nitrogen as well as the differences in the polymer network should, however, both produce differences in the non-polar nature of the two resins. In Fig. 2 we have given the R_F values on WB-2 and SB-2 papers both with HCl and with LiCl (containing 1 N HCl) for a few metal ions. The adsorption on the WB-2 paper is consistently lower, the biggest differences occurring in those solutions where equilibria of neutral species seem to be involved e.g. with Fe(III) and $UO_2(II)$ in intermediate concentrations of chloride ions. In the case of Cu(II) there seems to be little difference between the two resins. Strongly adsorbed

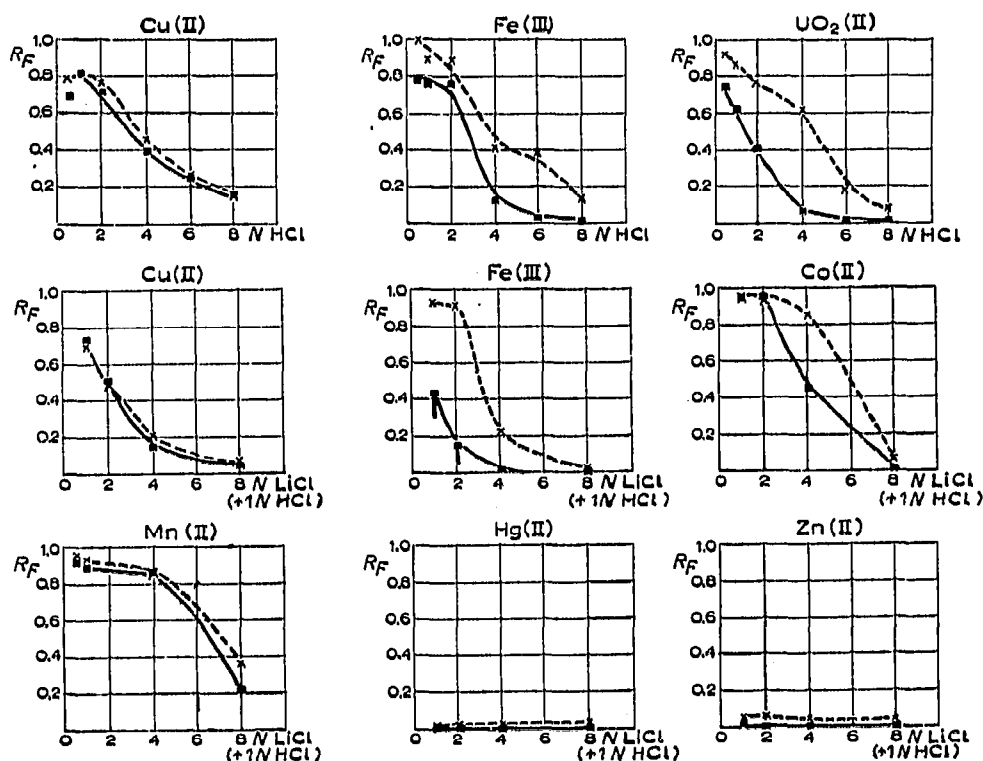
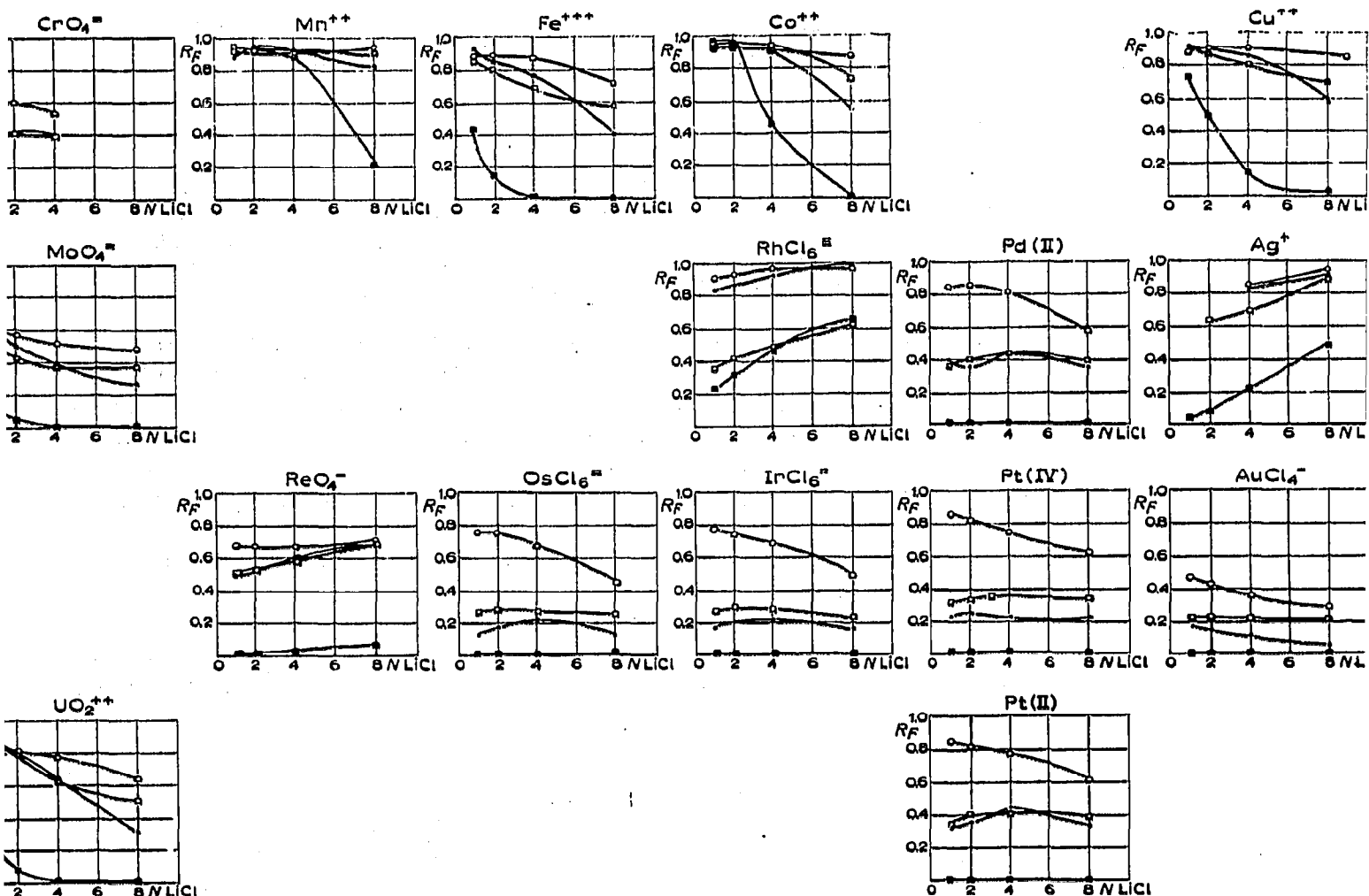


Fig. 2. R_F values of some metal ions plotted against (a) the concentration of HCl, (b) the concentration of LiCl (containing 1 N HCl throughout). ■—■ on SB-2 strong base resin paper; ×—× on WB-2 weak base resin paper.



anions such as HgCl_4^{2-} and ZnCl_4^{2-} have slightly higher R_F values on the weak base resin paper. The results obtained indicate that an extensive study of resins other than polystyrene resins may produce still more interesting differences in the sequence of separations. Cu(II) for example moves faster than Fe(III) on the SB-2 paper but more slowly on the WB-2 paper (up to 4 N LiCl).

(iii) *A survey of the adsorption of metal ions from LiCl solutions*

In preliminary work with LiCl^2 it was noted that if small amounts of HCl are added to LiCl (e.g. 0.1 N HCl) the H^+ front moves much more slowly than the liquid front. As this would have a considerable influence in work with some hydrolysable metal ions, we increased the HCl concentration to 1 N throughout in this work. The ions were chromatographed with solutions 1 N with respect to HCl and 1, 2, 4 and 8 N with respect to LiCl. The total chloride concentration in these cases is thus the sum of LiCl and HCl concentrations.

In Fig. 3, R_F values have been plotted against LiCl concentration for four papers (Whatman No. 1, Whatman DE 20, Whatman AE 30 and Amberlite SB-2 papers) and the ions are arranged according to their positions in the periodic table. The results

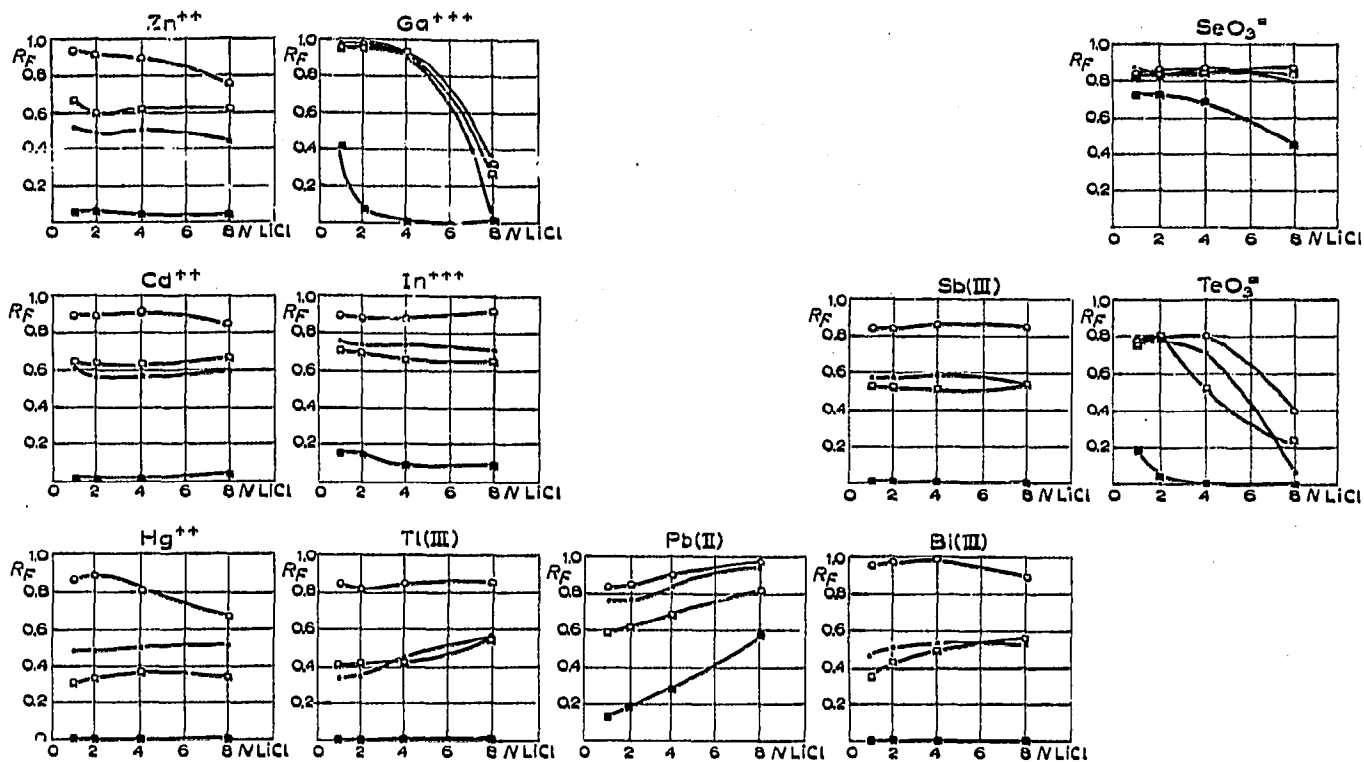


Fig. 3. R_F values of metal ions on various anion exchange papers plotted against the concentration of LiCl (containing 1 N HCl). Symbols as in Fig. 1.

with LiCl must be discussed by comparing them with the results with HCl published previously¹.

Ag⁺ and Pb²⁺ have practically identical R_F values in HCl and LiCl. Here it should be remembered that these two ions seem to be retained almost entirely by ion exchange and not by adsorption. The results with LiCl seem to confirm these findings since in ion exchange the cation of the eluant should theoretically have no effect.

With the chloro-anions such as IrCl₆²⁻, PtCl₆²⁻, AuCl₄⁻, HgCl₄²⁻ and also with CrO₄²⁻ etc., there is a marked desorption with an increase in the HCl concentration on the cellulose exchangers. This is not the case (or to a much less extent) in LiCl, there being little variation of the R_F values. The salting-out effect previously observed² with AuCl₄⁻ seems to be a general phenomenon for these chloro-anions.

With Fe(III), Co(II), Cu(II), Ga(III), UO₂(II) and MoO₄²⁻, there is considerable lowering of the R_F values on SB-2 paper in comparison with HCl and noticeable but relatively small effects with the cellulose exchangers. Surprisingly there is little difference between HCl and LiCl for Zn(II) and Cd(II), although larger salting-out effects would be expected from previous work with anion exchange resins.

(iv) The adsorption of metal ions from HBr solutions

The papers (washed with 2 *N* HCl and water as usual) were converted to the bromide form by leaving them for 30 min in *N* KBr, washing with distilled water till free of excess bromide and subsequent drying in air. Since oxidation to bromine in the atmosphere is a risk with the bromide form of the papers, they were always freshly prepared and used within 24 h. The solutions of HBr used were prepared freshly each day from colourless batches of conc. HBr (Carlo Erba). The solutions of the metal ions were prepared in 4 *N* HBr from chlorides in the case of the reversibly complexing metal ions. Chlorauric acid was heated on the water bath for several hours in 4 *N* HBr to convert it to HAuBr_4 .

Fig. 4 shows the R_F values on SB-2 paper, DEAE paper, aminoethylcellulose paper and Whatman No. 1 paper for a number of selected ions.

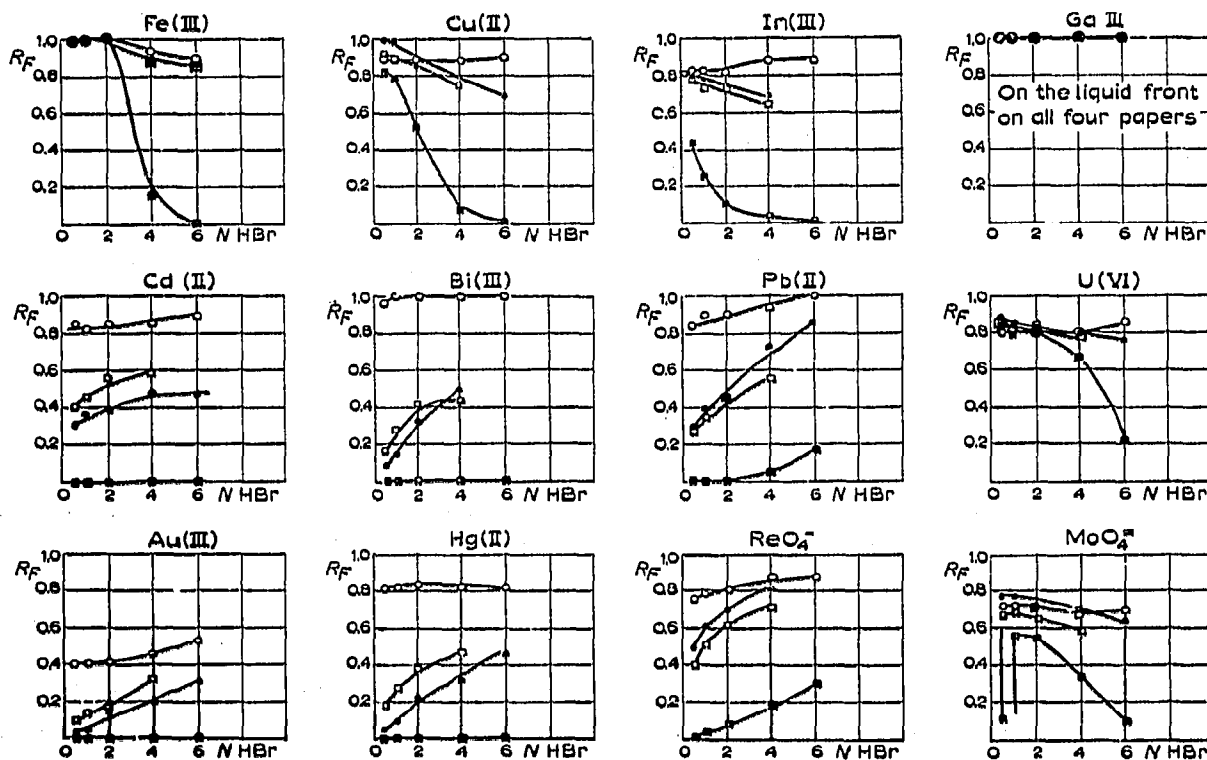


Fig. 4. R_F values of metal ions on various anion exchange papers plotted against the concentration of HBr. Symbols as in Fig. 1.

It is useful to start discussing these results with the perrhenate ion which is neither complexed nor reduced in HBr. Its R_F values are much higher than in the corresponding HCl concentration owing to the stronger affinity of Br^- for the exchanger and the consequent higher displacing action on the ReO_4^- ion. The sequence of the R_F values and the relative values on the various papers indicate that the mechanism of fixation is essentially one of ion exchange with little or no adsorption. Both Pb(II) and In(III) seem to be also retained by ion exchange, while Au(III) (*i.e.* AuBr_4^-), Cd(II) , Bi(III) and Hg(II) seem to be held by adsorption as well as ion exchange; their R_F values on the DEAE paper being considerably lower than on the aminoethyl-cellulose paper.

The retention of Fe(III) and Cu(II) on the SB-2 paper seems to be due to adsorption since there is hardly any fixation on the cellulose exchangers when the R_F values on the SB-2 are near zero. Gallium is practically unadsorbed as could be expected from solvent extraction and paper chromatography results. Molybdate produces long comets on SB-2 paper at concentrations of HBr below 2 *N* and its values then decrease slowly. U(VI) is much less adsorbed than from HCl.

CONCLUSIONS

The results given here confirm on the whole the picture of adsorption on anion exchangers presented in the two previous communications, namely that both adsorption and ion exchange contribute to the retention of ions on the various exchangers and that the differences between HCl and LiCl may be interpreted as a "salting-out effect", affecting those ions which are held by adsorption. A qualitative measure of "adsorption" can be found in the differences in R_F values between the DEAE paper and the aminoethyl cellulose paper where the first will "adsorb" more strongly having two additional ethyl groups, while the latter has a higher ion exchange capacity and should retain ions more strongly by ion exchange. The differences between the adsorption on WB-2 (weak base) and SB-2 (strong base) resin papers can be explained by considering the differences in the polymers rather than in their exchange groups. Preliminary work with a cellulose anion exchanger with quaternary ammonium groups (kindly presented by Macherey-Nagel) showed again that the adsorption of AuCl_4^- from 2 *N* HCl ($R_F = 0.18$) is similar to that on other weak anion cellulose exchangers. It is also very much less than the adsorption on either strong or weak resin paper.

Owing to its simplicity, the method used here for studying ion exchange seems to shed new light on a variety of problems of ion exchange. The results, however, are at best semiquantitative.

Further work is in progress in this laboratory on some of these problems and will be reported here in due course.

SUMMARY

Data on the behaviour of metal ions on various anion exchange papers in HCl, LiCl and HBr are given and the mechanism of the adsorption is discussed.

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