CHROMATOGRAPHY ON PAPER IMPREGNATED WITH ION EXCHANGE RESINS

IX. THE ADSORPTION OF METAL IONS FROM HCl ON ANION-EXCHANGE RESIN PAPER, DEAE PAPER AND AMINOETHYL-CELLULOSE PAPER

M. LEDERER and L. OSSICINI
Laboratorio di Cromatografia del C.N.R., Istituto di Chimica Generale ed Inorganica, Rome (Italy)

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INTRODUCTION

In recent years it has become increasingly apparent that the adsorption of metal ions on anion-exchange resins of the type of Dowex-1 depends not only on the so-called exchange groups (trimethylbenzylammonium groups) but also on the styrene–divinylbenzene network.

The main evidence for adsorption in which the quarternary ammonium groups are not involved is:

(1) The adsorption of chloro-complexes of the type $AuCl_4^-$ on sulphonic resins[1,2].

(2) The adsorption of neutral organic substances on ion-exchange resins (usually considered under the term "salting-out chromatography")[3].

(3) The adsorption of anions which are held very strongly on Dowex-1, on neutral substances such as cellulose[4].

(4) The desorption of strongly held anions from anion-exchange resins with organic solvents such as acetone[5].

We thought that a better picture of the effect of the resin network could be obtained, if it were possible to study anion exchange in presence and absence of the resin network. Such a comparison is possible at least in part, since anion exchangers of the type of diethylaminoethyl-cellulose and aminoethyl-cellulose exist where the network consists only of cellulose. In HCl solutions these substituted amines must be considered as completely ionised. Since it is possible to correct for adsorption on cellulose, the differences in behaviour between exchangers can thus only be due to the resin network and the substituents on the ammonium group.

In this paper we shall describe an extensive study of adsorption on various anion-exchange papers. Only a few data are at present available for the cellulose–anion exchangers[6–8], although it has been shown that for a few selected ions[9,10] equilibrium data can be used for resin papers and vice-versa. However, more experimental data were desirable both for the resin paper and for analytical applications.

EXPERIMENTAL

Usually four paper strips (each a different paper) were developed simultaneously in tightly closed jars (26 cm × 15 cm diam.) by the ascending method. For this work the concentration of R.P. concentrated HCl (Carlo Erba) was assumed to be 12 N and all dilutions (namely 0.5 N, 1 N, 2 N, 4 N, 6 N and 8 N) were made from this acid.

Table I lists the papers employed and their relevant properties. The ratio A_L/A_S was obtained by weighing the dried and developed paper strips. The capacities are those claimed by the manufacturers. With exception of the Whatman No. 1 paper, the papers were washed twice with 2 N HCl and distilled water and air dried before use.

TABLE I

PROPERTIES OF ANION EXCHANGE PAPERS USED

Paper	*Ion exchange capacity mequiv. per gram*	*Ratio amount of 0.5 N HCl to amount of paper (factor A_L/A_S)*
Whatman No. 1	negligible	about 1.0
Amberlite SB-2 paper	1.13	0.88
Whatman DEAE paper DE 20	0.4	2.5
Whatman aminoethylcellulose paper AE 30	0.6	2.3

Solutions of metal ions were placed on the paper in HCl solution, usually 6 N HCl. The usual reagents such as 8-hydroxyquinoline or ammonium sulphide were used for the detection of most ions. Both cellulose ion exchange papers disintegrated in acid above 8 N and the aminoethylcellulose gave already rather indifferent chromatograms with 8 N HCl.

Fig. 1 shows the R_F values of most of the metal ions which adsorb on anion exchangers. A number of ions were not available at the time (TcO_4^-, $RuCl_6^{2-}$), and some others have a tendency to form double spots (*e.g.* Sb (V)). It is intended to deal with these at a later date.

DISCUSSION

(a) *Correlation between the data on SB-2 papers and data obtained by column and equilibrium experiments*

To obtain the conversion of R_F values to D values (distribution coefficients) the equation

$$D = \left(\frac{1}{R_F} - 1\right) \frac{A_L}{A_S} \qquad (1)$$

may be used as has been shown previously[10]. The factor A_L/A_S was calculated by comparison with equilibrium data[10] and was found to be 1.9; it may also be obtained from the ratio

$$\frac{\text{mg resin/cm}^2}{\text{mg } 0.5\ N\ \text{HCl/cm}^2} \qquad (2)$$

and was found to be 1.95. The agreement is excellent considering the assumptions made and the relative irregularity of the paper.

On the resin paper D values of more than 200 correspond to R_F values below 0.01 and D values below 0.2 correspond to R_F values above 0.90. For practical reasons these are the limits in which comparisons can be made. Although KRAUS AND NELSON[11] carried out their work with Dowex-1 and the SB-2 paper does not contain the same

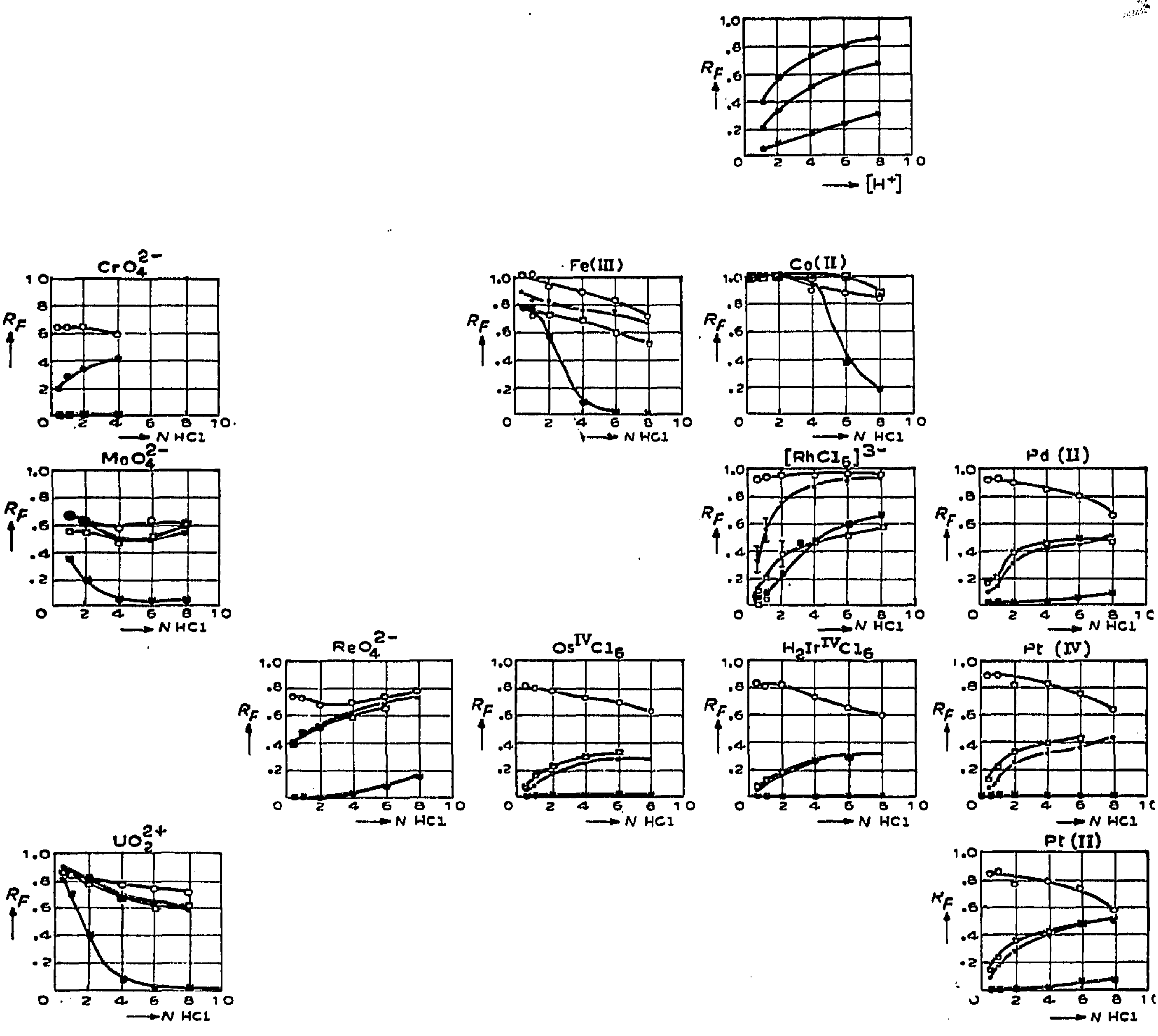
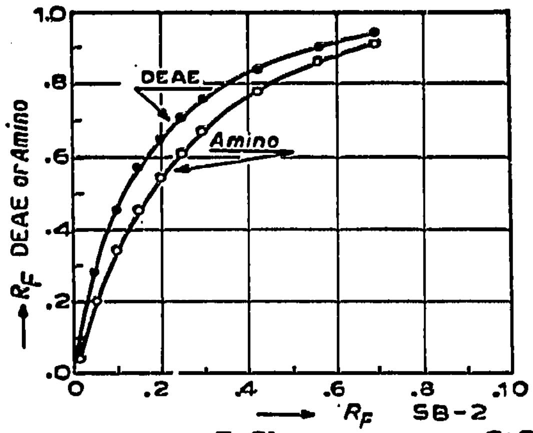
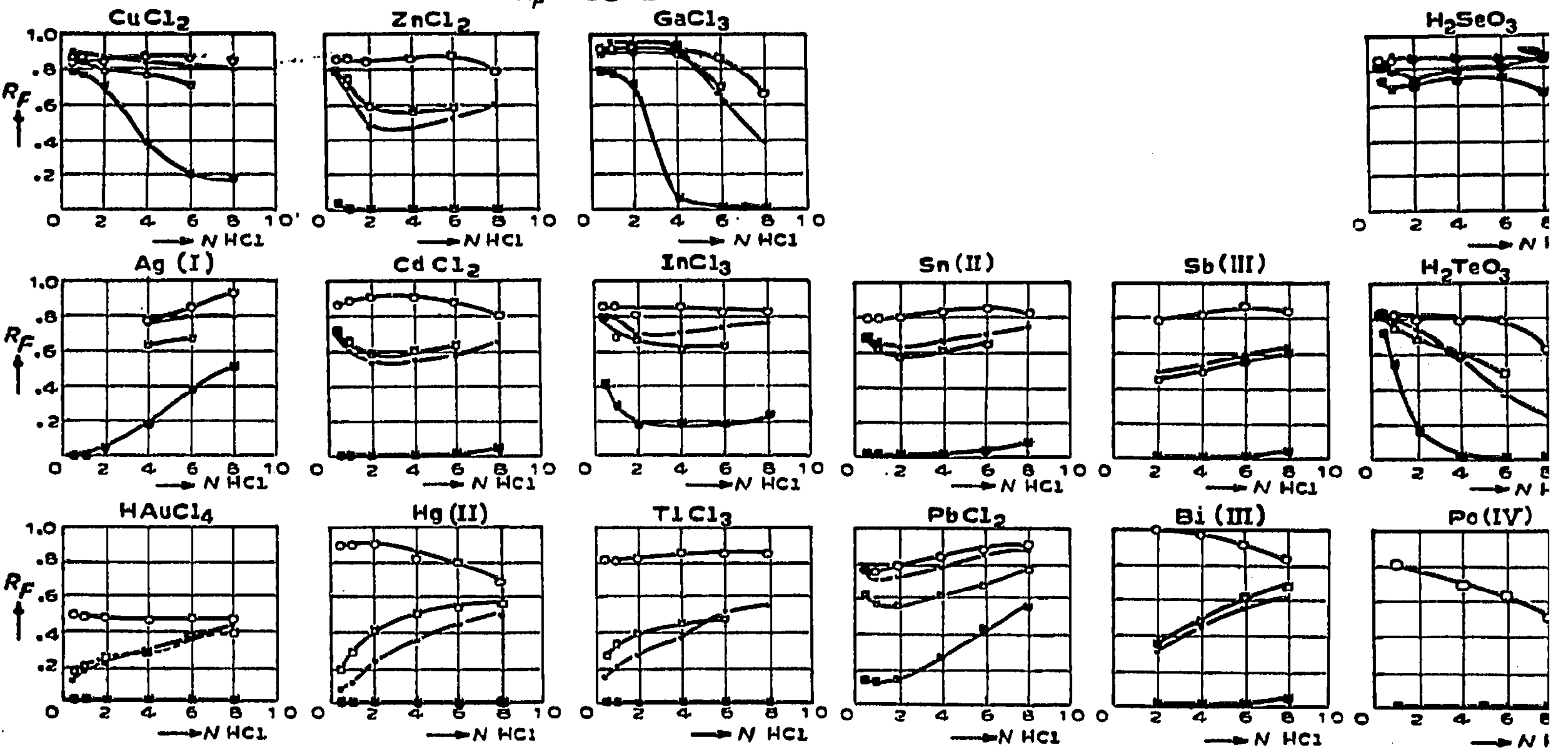


Fig. 1. Top, left: the theoretical R_F–H^+ curve of a monovalent anion obeying the law of mass action (calculated for three different R_F values at 1N H^+). Top, right: an alignment chart for converting R_F values on SB-2 paper to R_F values on AE-30 or DE-20 paper (or vice-versa). In this alignment chart only the differences in water/paper ratios and exchange capacities were considered.





Below: R_F values of metal ions on Whatman No. 1 paper (○——○), SB-2 resin paper (■——■), DE-20 cellulose anion-exchange paper (●——●), and AE-30 cellulose anion-exchange paper (□——□) are plotted against the concentration of HCl. With the exception of Pt (II) which was placed below Pt (IV) the metal ions are placed in their positions in the periodic table.

but only a similar resin, namely Amberlite IR-400, the agreement between D values calculated from Fig. 1 with those of KRAUS AND NELSON[11] is very satisfactory except for H_2TeO_4, which had already been studied and corrected by KLEEMANN AND HERRMANN[12]. Our results agree with those of KLEEMANN AND HERRMANN[12] and the adsorption of Te (IV) on Dowex-1 was further checked by DR. DOBICI of this Institute and found to agree essentially with these authors.

(b) *Comparison of the adsorption on resin and cellulose exchangers*

Fig. 1 (top, right) gives an alignment chart for converting R_F values on SB-2 paper to R_F values on DE 20 and AE 30 papers. In this chart only the differences in exchange capacity and water/paper ratios were taken into account (conversion factors for equation (1) being 7.75 for DE 20 and 4.9 for AE 30 paper). Thus the R_F value obtained by converting either way assumes that no interaction between the polymer (resin or cellulose) and the metal ion occurs. Rather good correlations are obtained with Pb (II) and Ag (I) where the R_F values are all of the right order of magnitude as shown for Pb (II) in Table II. We also want to emphasise that since the A_L/A_S ratios for the two cellulose exchangers are very similar, an ion held merely by ion exchange

TABLE II

R_F VALUES OF Pb (II) ON CELLULOSE EXCHANGERS CALCULATED FROM R_F VALUES ON SB-2 PAPER, AND OBTAINED EXPERIMENTALLY

Conc. of HCl	*R_F value on SB-2 paper*	*R_F value on DE 20 paper*		*R_F value on AE 30 paper*	
		calculated	*measured*	*calculated*	*measured*
2N	0.13	0.54	0.72	0.42	0.55
4N	0.27	0.74	0.78	0.64	0.62
6N	0.43	0.85	0.86	0.79	0.67
8N	0.57	0.91	0.88	0.87	0.79

should always have a higher R_F value on the DE 20 paper than on the AE 30 paper since the capacity of the DE 20 paper is about 30 % higher.

However, if the results for most of the strongly adsorbed anions are examined, it is evident that there is no correlation between the various papers if calculations on the basis of their relative capacities are made and also that, in most instances, there is a stronger adsorption on the DE 20 paper than on the AE 30 paper.

This can be explained if we consider that in addition to ion exchange there is adsorption on the organic network. The resin paper would have the strongest adsorption, then the DE 20 paper which contains two ethyl groups more on each exchange group than the AE 30 paper. Such small differences in the nonpolar nature seem to be sufficient to reverse the order of adsorption but the order of magnitude of the R_F values is essentially the same.

(c) *Some comments on the adsorption of the very strongly adsorbed anions of the type* $AuCl_4^-$

KRAUS AND NELSON[11] noted that a number of anions such as $AuCl_4^-$, $HgCl_4^{2-}$, $TlCl_4^-$, $FeCl_4^-$ and $GaCl_4^-$ have extremely high distribution coefficients on Dowex-1, of the order of 10^5 to 10^6, in contrast to anions such as ReO_4^-, Br^- etc. which have maxima of less than 10^4. These strongly adsorbed anions were also found to adsorb strongly on cation exchangers (such as Dowex-50) and cellulose, and extract into ether and other organic solvents. On cellulose anion exchangers they are adsorbed to the same extent as the less strongly adsorbed anions, such as ReO_4^-. Actually very little difference exists between the R_F value curves of most of the anions. In Fig. 1 (top, left) we have also calculated the type of R_F–[H^+] concentration curve for several R_F values assuming a monovalent anion, the validity of the law of mass action and ignoring the corrections necessary due to the activity coefficient of the acid. It is remarkable that many anions, whether strongly adsorbed or otherwise, follow this "theoretical curve" very closely.

We believe that the above is evidence that on cellulose anion exchangers the adsorption is mainly one of anion exchange with relatively small adsorption effects (except perhaps for $AuCl_4^-$) while for most anions the contrary seems to occur on anion-exchange resins. A similar conclusion was reached by KNIGHT[13] for amino acids in a study of the adsorption behaviour on cationic resin and cellulose exchange papers.

The results given in Fig. 1 also contain numerous analytical possibilities. Several mixtures of analytical interest which showed R_F differences on the cellulose exchange papers were separated and the R_F values in mixtures were identical with those when chromatographed alone.

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SUMMARY

The adsorption of metal ions from HCl onto SB-2 resin paper, DE-20 and AE-30 cellulose anion-exchange papers was studied and the mechanism of adsorption discussed considering the differences observed between the various exchangers.

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