CHROMATOGRAPHY ON PAPER IMPREGNATED WITH ION-EXCHANGE RESINS

VI. THE ADSORPTION OF UO_2^{2+} AND Th(IV) ON RESIN PAPERS

M. LEDERER AND F. RALLO

Laboratorio di Cromatografia del C.N.R.,
Istituto di Chimica Generale ed Inorganica,
Rome (Italy)

In numerous papers on the chemistry of metal ions in solution, the sign of the charge on an ion has been determined by means of its adsorption on an ion-exchange resin (e.g.[1,2]). Often the solution of the metal ion is examined only with one resin and at one concentration of an electrolyte. It seems to us that such evidence is unsatisfactory, because in addition to actual cation and anion exchange, resins can adsorb ions also by other mechanisms such as adsorption on the organic network[3], or complex formation with the reactive groups, especially the sulphonic group[4,5]; furthermore in solutions of organic solvents partition may occur between the water held on the resin and the solution[6,7].

Recently a range of commercial ion-exchange resin papers has become available, which papers offer the advantage that experiments with several resins (as well as with pure cellulose paper) may be run simultaneously with the same developing solvent. Under these conditions it is possible in most cases to distinguish the various adsorption effects. In the work here described we first confirmed that resin papers produce results identical to those obtained in column or equilibrium experiments, and then studied some of the evidence on the adsorption of UO_2^{2+} and Th(IV) reported in the literature.

MATERIALS AND METHODS

The following commercial papers were employed:

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

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

WA-2 paper (Rohm and Haas) containing 45 % of Amberlite IRC-50 (a carboxylic resin).

Whatman 3 MM paper, which has approximately the same thickness as the above papers, was used to observe whether there was any adsorption on the cellulose.

SA-2 and SB-2 papers, which are originally in the Na^+ and Cl^- forms, were converted to the required form by equilibrating with a 10% solution of the acid for 30 min and washing several times with distilled water, which is also allowed to equilibrate for 30 min after each wash.

Development was carried out by the ascending method in glass jars, which were closed by means of rubber gaskets.

The solution of thorium in HCl was prepared as described by KORKISCH AND TERA[8]. A solution of UO_2^{2+} in $HClO_4$ was prepared by precipitating $UO_2(NO_3)_2$ with NaOH, washing the precipitate and dissolving it in about 4 N $HClO_4$. A solution free of other anions is thus obtained.

Th(IV) was detected with alcoholic ammoniacal 8-hydroxy-quinoline and UO_2^{2+} with aqueous ferrocyanide.

(i) Comparison of equilibrium constants from column and paper experiments

The distribution coefficient D usually measured in equilibrium or column experiments is related to the R_F value on resin papers by the equation:

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

where A_L/A_S is the ratio of the amount of solvent to the amount of resin in a cross-section of the paper.

Since most results for columns are available for Dowex-1 and since the paper contains Amberlite IRA-400 we preferred to determine the value of A_L/A_S by taking D from column experiments and the R_F value from resin papers for a given ion at a given concentration. Thus we correct also for differences in the resin structure, etc.

TABLE I

COMPARISON OF R_F VALUES MEASURED ON SB-2 RESIN PAPER AND
CALCULATED FROM EQUILIBRIUM DATA FROM KRAUS *et al.*[9,10] ON DOWEX-1 RESIN

Concentration of HCl	R_F values of Fe(III)			R_F values of Cu(II)		
	measured	*calculated from D*	*D*	*measured*	*calculated from D*	*D*
2 N	0.49	—	1.92	0.71	0.735	0.6
4 N	0.03	0.027	67	0.29	0.39	2.9
6 N	0.04	0.004	460	0.21	0.17	9.6
8 N	0.0			0.16	0.17	9.6
9 N		0.0003	5900			

Table I shows the R_F values of Fe(III) and Cu(II) as measured on the resin paper (column 1), and the R_F values calculated with equation (1) from the values of D as obtained by KRAUS *et al.*[9,10] on Dowex-1 (column 2). The value for Fe(III) in 2 N HCl was used to calculate A_L/A_S, which was found to be 1.9; this value was used in all subsequent work. The agreement of the results can be considered as very satisfactory considering that two different resins are compared as well as two techniques.

Fig. 1 shows the R_F values of Fe (III) and Cu (II) in HCl on SB-2 and SA-2 papers. The decrease of the R_F values of Fe (III) on SA-2 paper has already been observed in column experiments by KRAUS *et al.*[3]; it is due to adsorption of $HFeCl_4$ on the
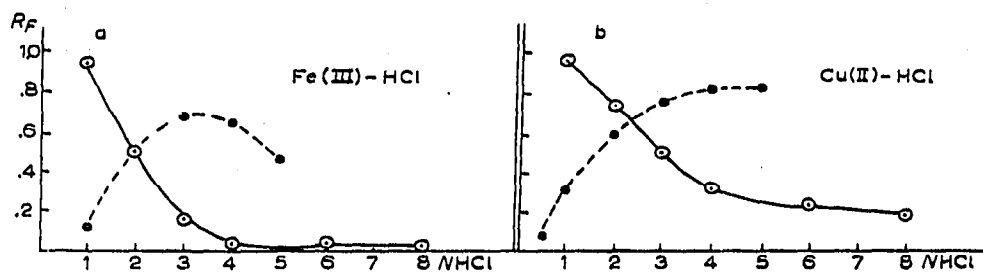

Fig. 1. (a). R_F–HCl concentration plot for Fe (III). (b). R_F–HCl concentration plot for Cu (II). ⊙——⊙ on SB-2 paper; ● – – – ● on SA-2 paper; □——□ on WA-2 paper; ×——× on Whatman No. 3 MM paper (pure cellulose).

organic network. In lower concentrations of HCl both Fe (III) and Cu (II) seem to be adsorbed mainly by ion exchange: adsorption on one resin implies no adsorption on the oppositely charged resin and vice versa.

The intersection of the two R_F curves occurs in the region of $R_F = 0.5$. In this region an uncharged complex should predominate and/or both anionic and cationic species should exist in approximately equal amounts. We should like to emphasise that this behaviour seems to us essential for true ion exchange, and that the electrostatic picture of ion exchange does not permit ions to be strongly adsorbed on both cation and anion exchangers.

(ii) The adsorption of Th (IV) from nitric acid

Fig. 2 shows the R_F values of Th (IV) nitrate on SB-2 and SA-2 paper with nitric acid as solvent. The anion exchange of Th (IV) has also been studied by equilibrium
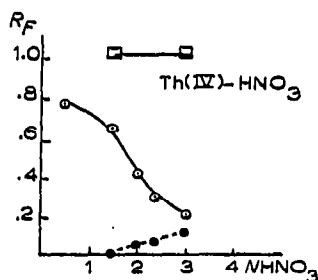

Fig. 2. R_F–HNO$_3$ concentration plot for Th (IV). Symbols as in Fig. 1.

methods by CARSWELL[11] and his results agree well with those on the SB-2 paper as shown in Table II.

We have, however, here a case where Th (IV) is adsorbed strongly both on anion and cation resins. It is evident that a single experiment with only one resin can yield a result which is in contradiction with that obtained with the oppositely charged resin. There is evidence from solvent extraction studies with ether–HNO$_3$ that Th (IV) forms

TABLE II

COMPARISON OF D FROM PAPER AND EQUILIBRIUM EXPERIMENTS FOR Th (IV) IN NITRIC ACID

Normality of HNO₃	R_F value on SB-2 paper	D calculated from R_F values	D from CARSWELL[11]
0.5	0.75		
1.5	0.62	1.2	1.5
2.0	0.39	2.9	2.0
2.4	0.28	4.9	4
3.0	0.18	8.7	7

uncharged or even anionic complexes in HNO_3. The adsorption on the anion-exchange resin may thus be anion exchange or adsorption on the organic network. The latter is, however, unlikely because Th (IV) does not adsorb on the carboxylic resin paper WA-2 under the same conditions. The strong adsorption of Th(IV) on the SA-2 paper thus seems to be due to complexing with sulphonic groups (see also results with UO_2^{2+}).

(iii) The adsorption of Th(IV) from alcoholic solutions of HCl

The adsorption of Th (IV) on anion exchangers from mixtures of conc. HCl with various alcohols was studied by KORKISCH AND TERA[8], who inferred an anionic Th (IV) complex from the results.

In Table III the R_F values are given of the Th (IV) both on SB-2 paper and on Whatman 3 MM in three of the solvents used by KORKISCH AND TERA[8] selected at random. It seems most likely that partition is the predominant factor in this adsorption.

TABLE III

R_F VALUES OF Th (IV) ON SB-2 PAPER AND ON WHATMAN NO. 3MM PAPER

Solvent	R_F value on SB-2 paper	R_F value on Whatman 3MM (pure cellulose) paper
Isopropanol–HCl (96:4)	0.0	0.0
Isopropanol–HCl (40:60)	0.105	0.098
Methanol–HCl (30–70)	0.465	0.48

(iv) The adsorption of UO_2^{2+} from HCl, HNO_3, H_2SO_4 and $HClO_4$

The R_F values on SB-2 and SA-2 papers with HCl, HNO_3, H_2SO_4 and $HClO_4$ are shown in Fig. 3. The adsorption on SB-2 paper follows closely that observed with column experiments by KRAUS AND NELSON[12]. The behaviour on the sulphonic resin paper (SA-2) shows the following peculiarity: after an initial increase, the R_F values at higher acid concentration are constant except in the case of H_2SO_4. This is of course impossible to explain by a law of mass-action type of equilibrium. It could be explained if a reversible complex formation between the sulphonic groups and UO_2^{2+}

were assumed. The R_F values should then be lowest with that acid that has the least tendency to complexation, *i.e.* HClO$_4$, and this is indeed the case. In the case of
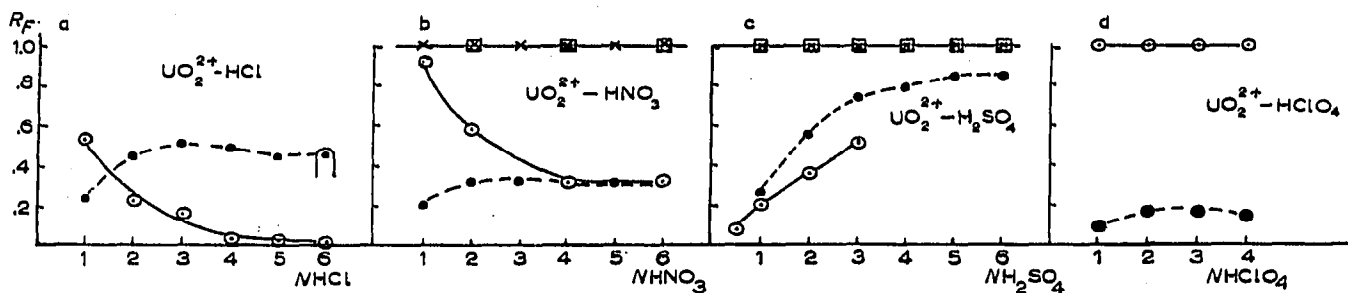

Fig. 3. (a). R_F–HCl concentration plot for UO$_2^{2+}$. (b). R_F–HNO$_3$ concentration plot for UO$_2^{2+}$. (c). R_F–H$_2$SO$_4$ concentration plot for UO$_2^{2+}$. (d). R_F–HClO$_4$ concentration plot for UO$_2^{2+}$. ⊙——⊙ on SB-2 paper; ●– – –● on SA-2 paper; □——□ on WA-2 paper; ×——× on Whatman No. 3 MM paper (pure cellulose).

H$_2$SO$_4$ the UO$_2^{2+}$ may be complexed by sulphate and HSO$_4^-$ ions as well as by the sulphonic groups, hence there is a desorption with an increase of the acid concentration.

We would like to emphasise again that for all acids except HClO$_4$ fallacious conclusions could be drawn if only one resin were examined. With HNO$_3$ R_F values were also measured with WA-2 paper and Whatman 3 MM paper, UO$_2^{2+}$ always being found at the liquid front. It may hence be assumed that the anion-exchange behaviour is due to negatively charged ions. UO$_2^{2+}$ in H$_2$SO$_4$ shows the remarkable property of being strongly adsorbed on both resins from dilute H$_2$SO$_4$ and only little adsorbed on both from higher concentrations.

SUMMARY

The range of ion-exchange resin papers now available permits the study of the mechanism of adsorption on a resin by very simple means. By carrying out chromatography with several resin papers and cellulose paper it is possible to distinguish adsorption on the organic network, complex formation with sulphonic groups and partition (in the case of organic solvents) from real cation and anion exchange.

Examples taken from the literature on Th (IV) and UO$_2^{2+}$ indicate that the above-mentioned side effects contribute considerably to the adsorption observed on ion-exchange resins.

REFERENCES

[1] H. M. NEWMANN, *J. Am. Chem. Soc.*, 76 (1954) 2611.
[2] G. H. AYRES, *Anal. Chem.*, 25 (1953) 1622.
[3] K. A. KRAUS, D. C. MICHELSON AND F. NELSON, *J. Am. Chem. Soc.*, 81 (1959) 3204.
[4] K. H. GUSTAVSON, *The Chemistry of Tanning Processes*, Acad. Press, New York, 1956.
[5] S. K. SHUKLA, *J. Chromatog.*, 1 (1958) 457.
[6] G. CARLESON, *Acta Chem. Scand.*, 8 (1954) 1673.
[7] M. LEDERER, *Anal. Chim. Acta*, 12 (1955) 142.
[8] J. KORKISCH AND F. TERA, *J. Inorg. & Nuclear Chem.*, 15 (1960) 177.
[9] G. E. MOORE AND K. A. KRAUS, *J. Am. Chem. Soc.*, 72 (1950) 5792.
[10] K. A. KRAUS AND G. E. MOORE, *J. Am. Chem. Soc.*, 75 (1953) 1460.
[11] D. J. CARSWELL, *J. Inorg. & Nuclear Chem.*, 3 (1957) 384.
[12] K. A. KRAUS AND F. NELSON. *Proc. Intern. Conf. Peaceful Uses Atomic Energy*, Geneva, 1955, Vol. VII, p. 113.