CHROMATOGRAPHY ON ION EXCHANGE PAPERS

XIII. THE ADSORPTION OF INORGANIC IONS FROM SULPHATE SOLUTIONS

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(Received December 27th, 1963)

INTRODUCTION

Comparison of the adsorption of ions on various cellulose and resin anion exchangers from HCl and HBr solutions has led us to conclude that not only ion exchange but also adsorption plays a considerable role in the retention of ions on anion exchangers[1].

We now extended these studies to include nitrate and sulphate solutions and encountered several technical difficulties. Nitric acid seemed to attack the cellulose ion exchangers and in neutral lithium nitrate solution hydrolysis occurred with most of the complex ions of interest. In sulphuric acid solutions two fronts were formed, presumably due to the preferential adsorption of SO_4^{2-} over HSO_4^- ions and some ions move with this front making comparisons with for example HCl solutions difficult. However, in sulphate solutions a salting-out effect was observed which adsorbed ions otherwise not adsorbed on resins or paper. It was found that by choosing a suitable salting-out agent, anions such as Cl^-–Br^-–I^- could be separated on cation exchange resins.

EXPERIMENTAL

(i) The adsorption of ions from sulphuric acid solutions on anion exchangers

Fig. 1 shows the R_F values of some ions on Whatman No. 1 paper, amino-ethyl cellulose paper (AE 30), DEAE cellulose paper (DE 20) and strong anion exchange resin paper (SB-2). Fe(III) forms a very narrow zone on the "second front" up to which SO_4^{2-} appears to saturate the paper.

The behaviour of ReO_4^- requires some comment. In Fig. 2 we have plotted the R_F values of ReO_4^- in HCl, HBr and H_2SO_4. If this adsorption were governed by ion exchange, sulphuric acid, being a divalent acid, should desorb perrhenate more than HCl or HBr. We shall show below that this strong adsorption is due to the rather strong salting-out effect of polyvalent acids and salts.

(ii) The adsorption of anions from sulphate solutions on cellulose and cation exchange resin papers

The rather considerable salting-out effect of sulphates was already employed by SARGENT AND RIEMAN[2] in the salting-out chromatography of neutral organic substances on both cation and anion exchange resins.

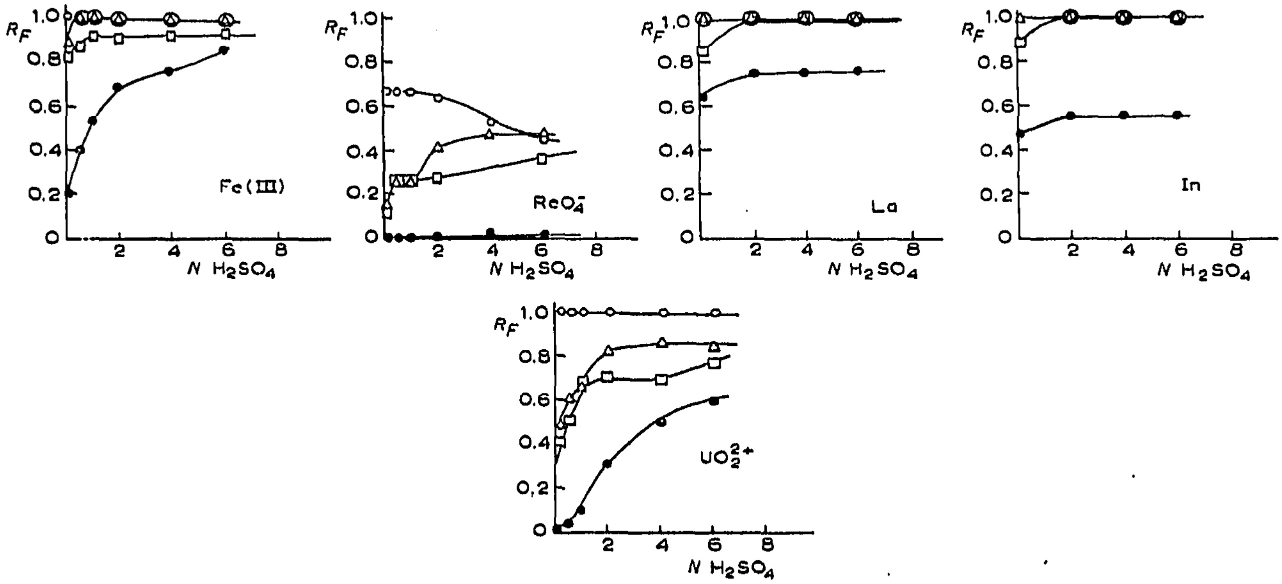

Fig. 1. R_F values of some metal ions plotted against the concentration of H_2SO_4 for various ion exchange papers. ●—● SB-2 (strong base resin) paper; △—△ DEAE (Whatman DE-20) paper; □—□ Aminoethyl (Whatman AE-30) paper; ⊙—⊙ Whatman No. 1 cellulose paper.

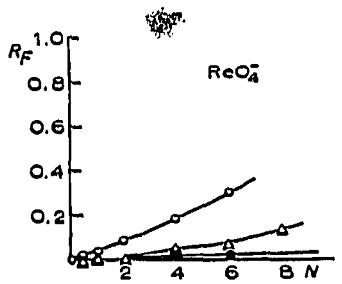

Fig. 2. R_F values of perrhenate plotted against the concentration of the eluant acid on strong base resin (SB-2) paper. ●—● H_2SO_4; ⊙—⊙ HBr; △—△ HCl.

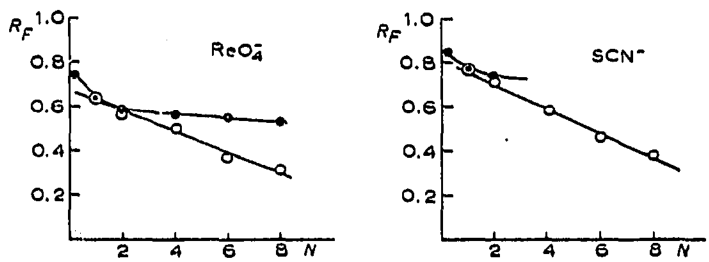

Fig. 3. R_F values of perrhenate (left) and thiocyanate (right) plotted against the normality of H_2SO_4 and $(NH_4)_2SO_4$ on cellulose paper (Whatman No. 3MM). ●—● H_2SO_4; ⊙—⊙ $(NH_4)_2SO_4$.

In order to obtain some indications of salting-out in absence of anion exchange, we examined a range of inorganic anions on pure cellulose paper (the thicker Whatman 3MM paper), on sulphonic resin paper (SA-2) and on carboxylic resin paper (WA-2) with both sulphuric acid and ammonium sulphate solutions.

Numerous anions such as CrO_4^{2-}, MoO_4^{2-}, SeO_4^{2-}, TeO_3^{2-} give comets and double spots and hence we report in Table I only those ions which led to the formation of sharp spots.

As may be expected from the incomplete ionisation of H_2SO_4, its salting-out effect is lower than that of ammonium sulphate (see Fig. 3).

While oxy-anions are adsorbed to a relatively small extent, remarkably good adsorption and separations can be obtained with halides on strong cation exchangers (see for example Fig. 4).

With this kind of adsorption chromatography on ion exchange papers we seem to have arrived at the extreme of adsorption mechanisms on ion exchange resins which do

TABLE I

R_F VALUES OF INORGANIC ANIONS ON CELLULOSE PAPER AND CATION EXCHANGE RESIN PAPERS WITH AMMONIUM SULPHATE AND SULPHURIC SOLUTIONS AS SOLVENTS

W 3MM = Whatman 3MM cellulose paper; SA-2 = sulphonic resin (SA-2) paper; WA-2 = carboxylic resin (WA-2) paper.

Anion	*Paper*	*$(NH_4)_2SO_4$ solution as solvent*				
		1 N	*2 N*	*4 N*	*6 N*	*8 N*
I^-	W 3MM	0.76	0.74	0.67	0.54	0.46
	SA-2	0.87–0.62	0.85–0.59	0.71–0.46	0.59–0.29	0.47–0.27
	WA-2	0.84	0.79	0.71	0.63	0.51
Br^-	W 3MM	0.84	0.81	0.73	0.70	0.64
	SA-2	0.86	0.83	0.75	0.70	0.62
	WA-2	0.89	0.85	0.77	0.74	0.70
Cl^-	W 3MM	0.87	0.80	0.79	0.77	0.74
	SA-2	0.93	0.90	0.87	0.77	0.75
	WA-2	0.92	0.88	0.81	0.80	0.76
IO_3^-	W 3MM	0.86	0.85	0.83	0.82	0.81
	SA-2	0.91	0.86	0.88	0.86	0.85
	WA-2	0.83	0.81	0.79	0.81	0.81
BrO_3^-	W 3MM	0.89	0.85	0.82	0.82	0.81
	SA-2	0.91	0.93	0.80	0.81	0.75
	WA-2	0.85	0.84	0.81	0.82	0.79
ClO_3^-	W 3MM	0.83	0.78	0.77	0.81	0.80
	SA-2	0.83	0.79	0.74	0.75	0.65
	WA-2	0.87	0.85	0.82	0.82	0.81
NO_2^-	W 3MM	0.86	0.87	0.80	0.79	0.74
	SA-2	0.70–0.54	0.59	0.55	0.71–0.46	0.70–0.51
	WA-2	0.02	0.03	0.04	0.07	
NO_3^-	W 3MM	0.85	0.83	0.81	0.74	0.72
	SA-2	0.88	0.83	0.81	0.75	0.64
	WA-2	0.85	0.86	0.82	0.72	0.70
ReO_4^-	W 3MM	0.62	0.57	0.50	0.37	0.32
	SA-2	0–0.10	0–0.09	0–0.08	0–0.06	0–0.05
	WA-2	0.57	0.53	0.43	0.32	0.25
SCN^-	W 3MM	0.76	0.71	0.59	0.47	0.39
	SA-2	0.12–0.40	0.09–0.31	0.06–0.26	0.04–0.22	0–0.18
	WA-2	0.76	0.72	0.63	0.51	0.43

Anion	*Paper*	*H_2SO_4 solution as solvent*					
		0.1 N	*1 N*	*2 N*	*4 N*	*6 N*	*8 N*
ReO_4^-	W 3MM	0.74	0.63	0.59	0.56	0.55	0.53
SCN^-	W 3MM	0.84	0.77	0.75	—	—	—

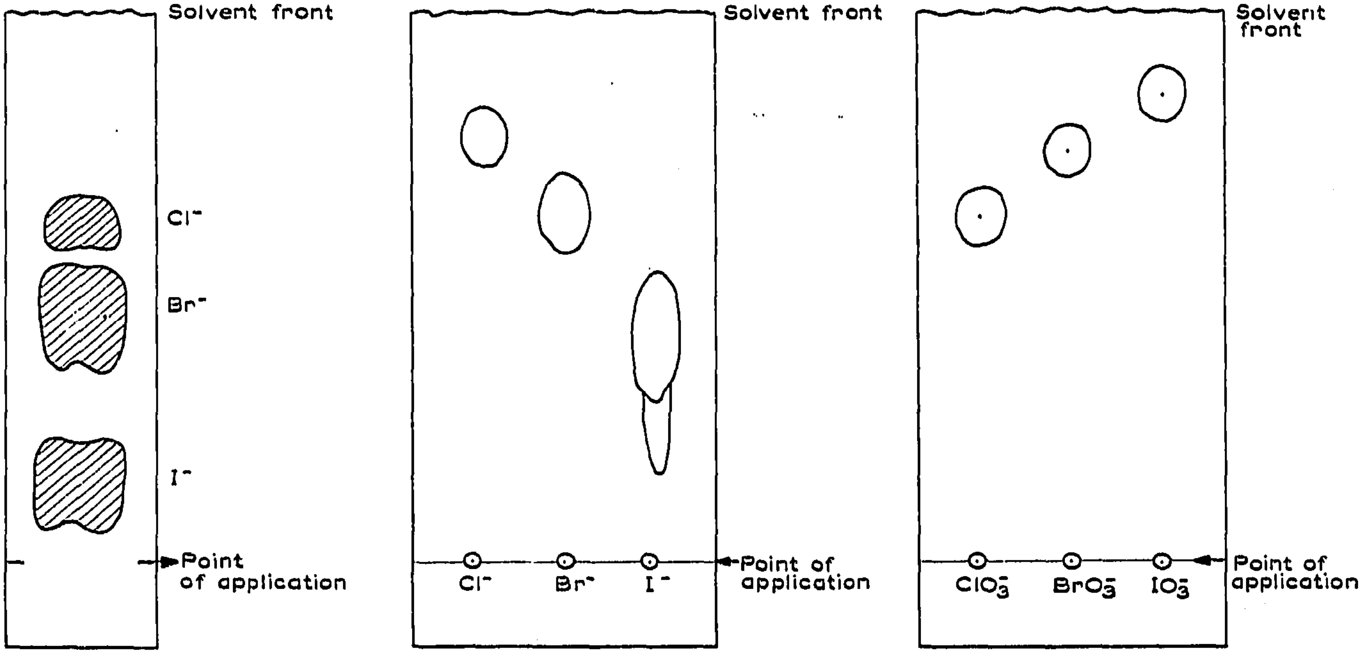

Fig. 4. Some chromatograms of inorganic anions on sulphonic resin (SA-2) paper with 8 *N* $(NH_4)_2SO_4$ as solvent. Left: separation of Cl^-–Br^-–I^-. Centre: movement of Cl^-, Br^- and I^- when run side by side. Right: movement of ClO_3^-, BrO_3^- and IO_3^- when run side by side on one sheet.

not involve the functional groups of the resin. It is not likely that there will be any analytical advantages in a halide separation on cation exchangers. We believe, however, that it is an excellent illustration of the possible factors involved in adsorption on resins and cellulose exchangers.

SUMMARY

The adsorption of inorganic anions on cation exchange resins from sulphate solutions was studied and could be shown to be governed by a salting-out mechanism.

REFERENCES

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