

## CHROMATOGRAPHY ON ION EXCHANGE PAPERS

## X. SOME DATA FOR CELLULOSE ION-EXCHANGERS WITH ORGANIC SOLVENTS

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The influence of organic solvents on the ion exchange behaviour of several metal ions on cation and anion resin papers and on zirconium phosphate paper was recently reported by us<sup>1</sup>.

Cellulose ion exchange papers have already been employed for two-dimensional chromatography of metal ions using an organic solvent mixture in one direction<sup>2</sup>. However, no systematic work similar to our study with resin papers<sup>1</sup> has been reported so far and this seemed to us of interest both for analytical purposes and for the understanding of the effect of organic solvents on ion exchange.

The work described here was thus undertaken and its aim was to study a large number of ions in some solvent systems where the amount of organic solvent can be increased gradually (*i.e.* systems in which the solvents are completely miscible). For this purpose 2*N* HCl containing varying quantities of either ethanol or acetone was selected.

The following four papers were chromatographed together in one container by the technique already described<sup>1</sup>:

- Whatman No. 1 pure cellulose paper,
- Whatman cellulose phosphate paper P 20,
- Whatman diethylaminoethyl-cellulose (DEAE) paper DE 20,
- Whatman aminoethyl-cellulose paper AE 30.

The results are given in Fig. 1-4 where the metal ions are grouped roughly according to their complexing properties.

## DISCUSSION

Fig. 1 shows the behaviour of Ni(II), Al(III), La(III) and Th(IV) which all are known not to form complexes with 2*N* HCl in any of the mixtures examined.

Al, La and Th adsorb to some extent on cellulose phosphate probably due to the formation of phosphate complexes, otherwise the  $R_F$  curves for the metal ions on the exchange papers are almost identical with that on Whatman No. 1 paper *i.e.* a partition mechanism seems to be responsible for the retention on the paper.

Fig. 2 shows the behaviour of several metal ions which form anionic complexes

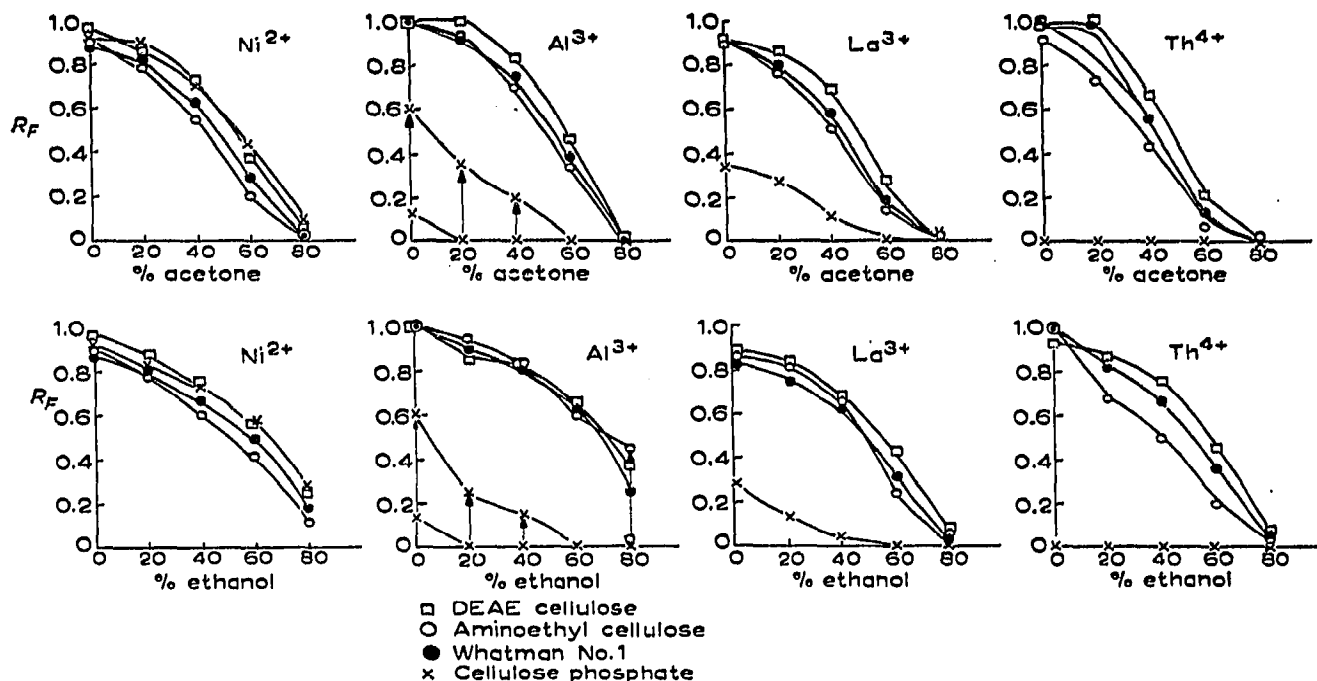


Fig. 1.  $R_F$  values of some non-complexing cations on various cellulose exchangers with acetone-HCl and ethanol-HCl mixtures (the concentration of HCl is maintained constant at 2 *N*).

reversibly with HCl. Again it is best to consider the cellulose phosphate paper separately. Both  $\text{UO}_2^{2+}$  and Fe(III) are adsorbed strongly on P20 paper and only eluted with 80% acetone-2 *N* HCl. It seems worthy of note that the adsorption, which undoubtedly is one due to complex formation, can be reversed by a non-polar organic solvent such as acetone but not by ethanol.

For  $\text{UO}_2^{2+}$ , Cu(II), Co(II) and Fe(III) there is little difference in behaviour between pure cellulose and anion exchange cellulose papers, lowering of  $R_F$  values due to partition effects occurring in most cases.

Zn(II) and Cd(II) both show an increased retention on DEAE and aminoethyl-cellulose papers. Two phenomena are interesting: both ions are more strongly adsorbed on the DEAE paper than on the aminoethyl-cellulose paper although the latter has a higher capacity. This was also discussed when comparing adsorption from various concentrations of HCl<sup>3</sup>, and appears to be due to the more non-polar nature of the DEAE paper, thus suggesting an adsorption mechanism rather than ion exchange proper. The second point of interest is that the adsorption increases with the concentration of ethanol and decreases with the concentration of acetone. This difference between ethanol and acetone was not noted in our study of resin papers<sup>1</sup> because most anions are too strongly held. We would like to suggest the explanation that ethanol decreases the hydration of the complex anion and thus permits stronger adsorption on the paper but is sufficiently polar to permit adsorption, while acetone is sufficiently non-polar to effect a desorption from the more polar cellulose exchanger.

Fig. 3 shows the behaviour of several typical stable chloro-anions. The differences between ethanol and acetone can be explained in the same manner as for Cd(II) and Zn(II) above.

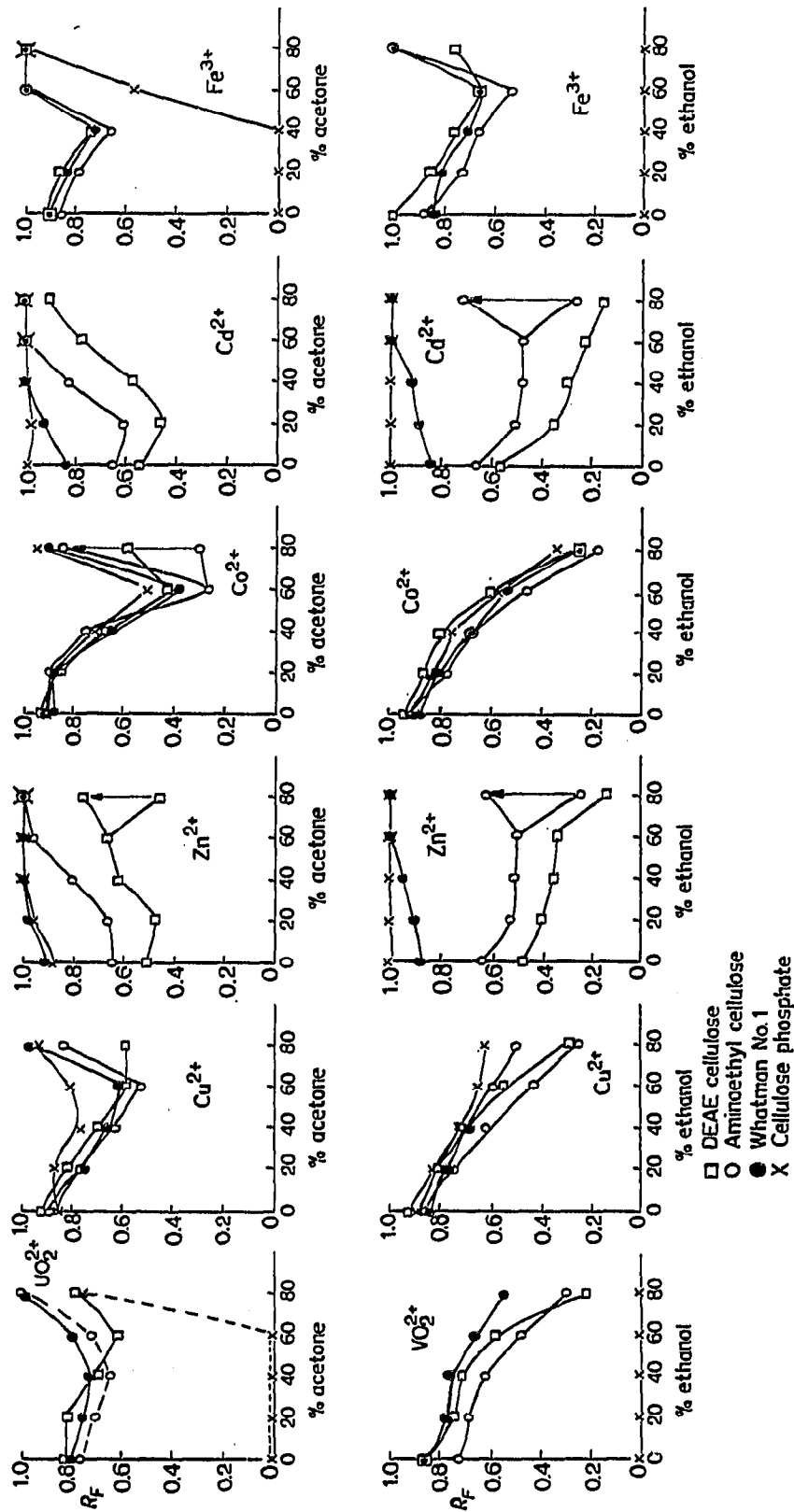


Fig. 2.  $R_F$  values of some transition elements on various cellulose exchangers with acetone-HCl and ethanol-HCl mixtures (as in Fig. 1).

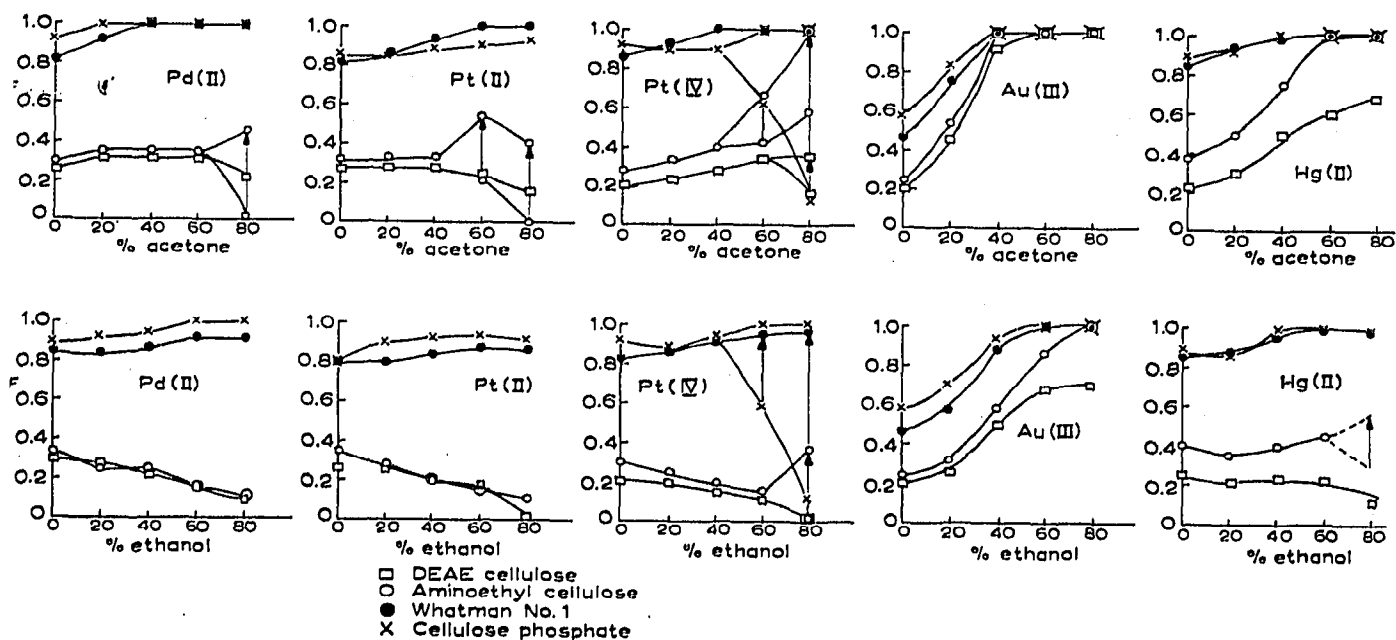


Fig. 3.  $R_F$  values of some anionic chloro-complexes on various cellulose exchangers with acetone-HCl and ethanol-HCl mixtures (as in Fig. 1).

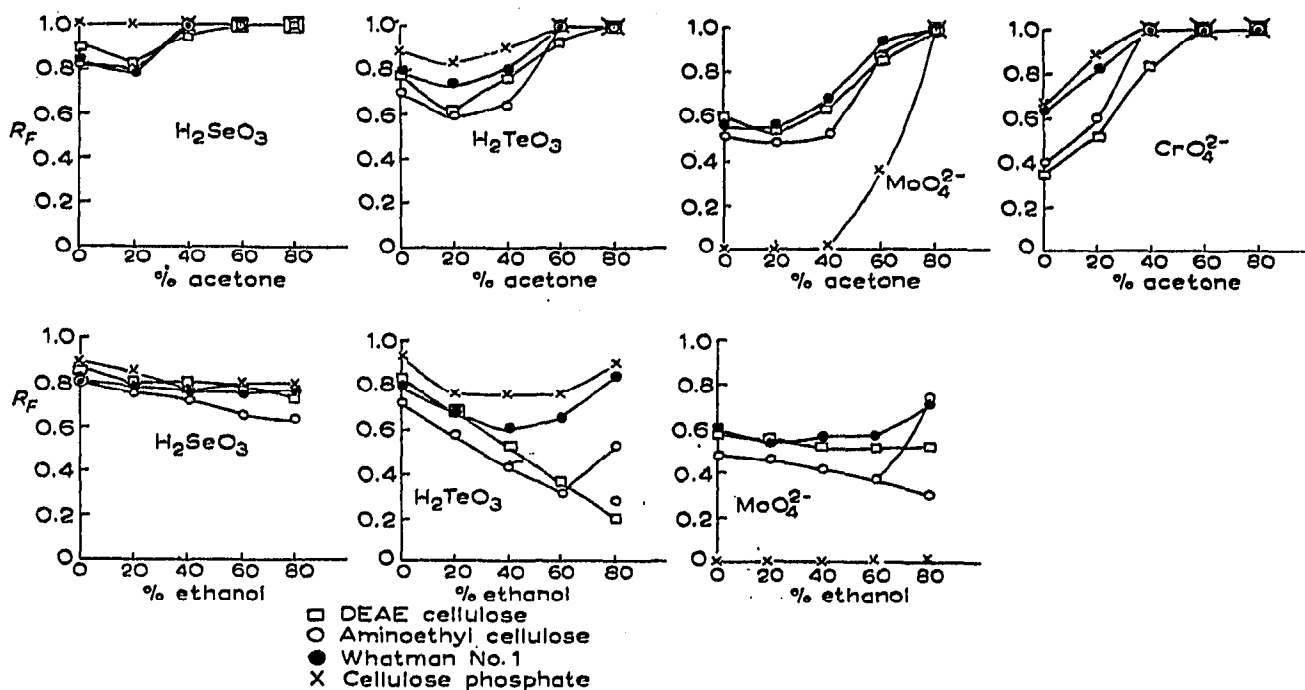


Fig. 4.  $R_F$  values of some oxy-anions on various cellulose exchangers with acetone-HCl and ethanol-HCl (as in Fig. 1).

A discussion on the desorption of  $\text{AuCl}_4^-$  is merited. Cellulose phosphate absorbs it least, then pure cellulose, then ethylamino-cellulose and strongest adsorption is found on the DEAE paper. This sequence is that of the polarities of the various materials, cellulose phosphate naturally being more polar than pure cellulose and it has nothing to do with anion exchange capacities.  $\text{AuCl}_4^-$  is the only anion which is not more strongly absorbed with an increase in the ethanol concentration; perhaps the hydration is already very poor.

The behaviour of a few oxy-anions is shown in Fig. 4. Selenite is little adsorbed on any paper. Tellurite forms an anionic chloro-complex in 2N HCl which is more strongly adsorbed with an increase in the ethanol concentration and desorbed by acetone. Molybdate is strongly adsorbed on cellulose phosphate and it is tempting to attribute this to a formation of a complex of the phosphomolybdate type. If this is correct, such a complex is reversibly decomposed by acetone. Chromate could only be studied in acetone as it is completely reduced in ethanol and shows an adsorption similar to  $\text{AuCl}_4^-$ .

#### CONCLUSIONS

The behaviour of ions on the cellulose exchangers can be explained in a manner analogous to that employed for resin papers<sup>1</sup>. The only new property observed concerns the increased adsorption of some anionic complexes from ethanol solutions on anion exchangers. The use of organic solvents in conjunction with cellulose exchangers can have numerous analytical possibilities as is indicated by the examples studied.

#### SUMMARY

The adsorption of numerous inorganic ions on various cellulose exchangers from mixtures of HCl and organic solvents was studied.

As on ion exchange resins the adsorption depends on various factors and can not be interpreted in terms of true "ion exchange".

#### REFERENCES

- <sup>1</sup> M. LEDERER, V. MOSCATELLI AND C. PADIGLIONE, *J. Chromatog.*, 10 (1963) 82.
- <sup>2</sup> C. S. KNIGHT, *Nature*, 183 (1959) 165.
- <sup>3</sup> M. LEDERER AND L. OSSICINI, *J. Chromatog.*, 13 (1964) 188.

*J. Chromatog.*, 13 (1964) 194-198