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Ion-exchange paper chromatography of inorganic ions

XXVII. The adsorption of chlorauric acid on various exchangers from organic solvents

A new method for separating gold from platinum has recently been proposed by DYBCZYNSKI AND MALESZEWSKA¹ which is based on the adsorption of bromoauric acid on Dowex 50 and its subsequent elution with acetylacetone. These authors

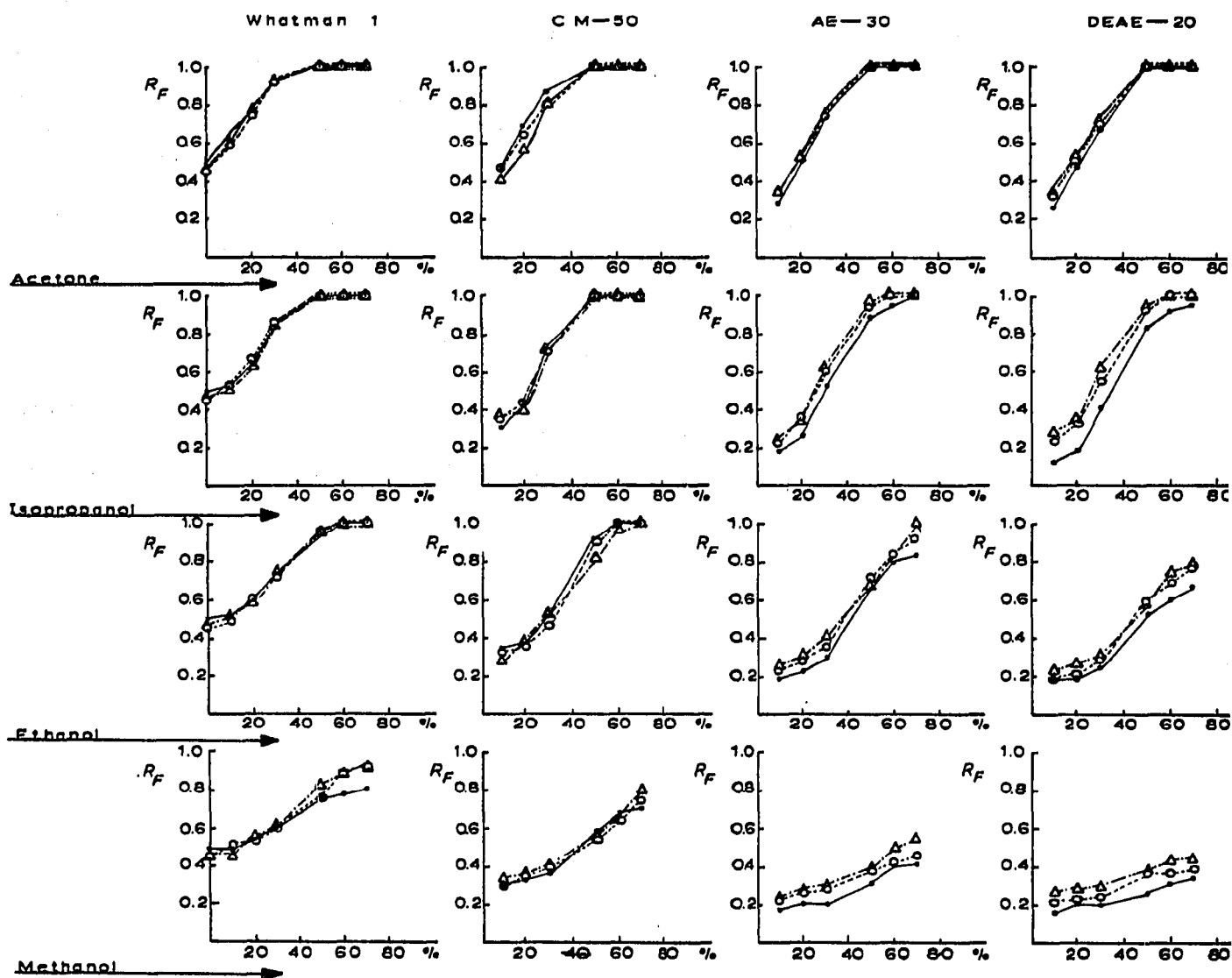
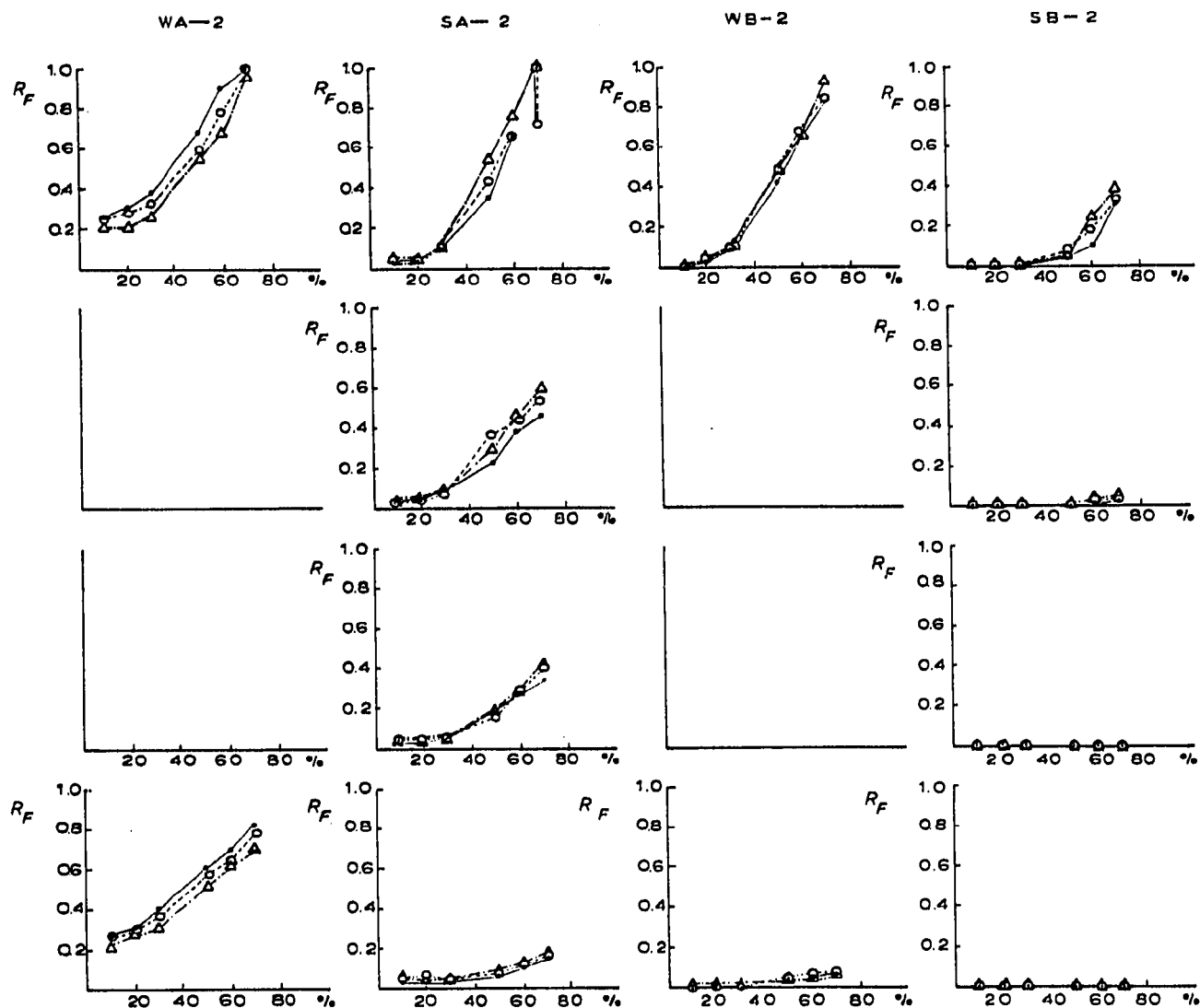


Fig. 1. R_F values of gold chloride plotted against the concentration of organic solvent in aqueous HCl (1 N, 2 N and 3 N). Solvents (from top to bottom): acetone, isopropanol, ethanol and methanol. Papers (from left to right): Whatman No. 1, Whatman CM-50 (carboxymethylcellulose), Whatman AE-30 (aminoethylcellulose), Whatman DEAE-20 (diethylaminoethylcellulose), Amberlite WA-2 (carboxylic resin paper), Amberlite SA-2 (sulphonic acid resin paper), Amberlite WB-2 (weak base anion-exchange resin paper) and Amberlite SB-2 (strong base anion-exchange resin paper). (●—●) 1 N HCl; (○---○) 2 N HCl; (△-·-·-△) 3 N HCl.

discuss the mechanism of the adsorption process and suggest adsorption of undissociated HAuBr_4 with the formation of a molecular (charge transfer) complex between the aromatic rings of the resin network and the complex acid.

The paper prompted us to go over our previous results² and we noted that the behaviour of Au(III) is still more interesting as it can be eluted from both cation and anion exchangers by organic solvents. Similar results have also been obtained in column and equilibrium experiments³. MARCUS⁴ in a discussion of the ion-exchange behaviour of metal complexes concludes that gold chloride should exist mainly as an ion pair $\text{H}^+\text{AuCl}_4^-$ in more than 2 N HCl but that the species on the anion exchanger should be AuCl_4^- . However he states that spectra of HAuCl_4 in HCl contradict



this and tend to indicate that AuCl_4^- exists even at high concentrations of HCl.

From aqueous solutions of HCl, gold chloride adsorbs very strongly not only on anion exchangers but also on cation exchangers and neutral surfaces. If it were present as AuCl_4^- it should not really be desorbed from an anion exchanger by organic solvents, as a lowering of the dipole moment of the solvent should decrease the hydration of AuCl_4^- and of the quaternary ammonium groups and thus produce rather the contrary effect.

We therefore felt that it would be interesting to study the behaviour of AuCl_4^- further and adopted an approach used previously², namely to obtain data for various exchangers and adsorbants, which then give a clearer picture of the factors involved.

Experimental

The hydrogen or chloride form of the various ion-exchange papers were prepared by equilibrating twice with 2 *N* HCl (30 min) and then washing exhaustively with distilled water.

Chromatograms of chlorauric acid dissolved in 1 *N* HCl were developed by the ascending method in small jars at $20 \pm 1^\circ$. The spots were usually visible as yellow spots and when sprayed with stannous chloride in HCl yielded purple spots.

The results are given in Fig. 1.

Discussion

Fig. 1 shows that the differences between cellulose, cellulose exchangers and resins (cationic and anionic) is rather one of degree and not of different types of mechanism, also that there is a regular decrease in effect with the decrease in the polarity of the solvent.

Spectrochemical evidence (see ref. 4) seems to indicate that AuCl_4^- is the predominant species in aqueous HCl solution. Supporting evidence is also obtained by the R_F -HCl curve of HAuCl_4 on cellulose paper, which is practically linear from 1 *N* to about 10 *N* HCl ($R_F \sim 0.45$), together with the fact that HAuCl_4 is strongly anionic in paper electrophoresis in 0.5–2 *N* HCl (the practical upper limit); thus there is evidence of little change in the type of species present from 1 *N* to 10 *N* HCl as well as evidence that this species moves anionically.

We thus have to account for the adsorption of an anion (presumably AuCl_4^-) on surfaces less polar than aqueous HCl and its desorption by organic solvents. This can probably be done by numerous hypotheses, one that seems plausible to us is that AuCl_4^- favours ion pair formation on non-polar solids and in non-polar solutions. When there are anion-exchanging groups on the solid, obviously three mechanisms are possible: electrostatic attraction towards the groups; adsorption of $\text{H}^+\text{AuCl}_4^-$; and ion pair formation between AuCl_4^- and the exchanging groups (unless this is identical with the first).

Elution with a non-polar solvent then either helps the ion-pair $[\text{H}^+\text{AuCl}_4^-]$ to re-enter the solution or destroys the electrostatic bond $-\text{NR}_3^+ \text{AuCl}_4^-$ to form preferentially $[\text{H}^+\text{AuCl}_4^-]$. Incidentally the latter does not seem to occur to a large extent with methanol.

On the anion-exchange celluloses a high HCl concentration gives a high R_F -solvent concentration curve while the contrary is observed on carboxylic cellulose, carboxylic resin and acetylated cellulose (Fig. 2). In the first case there seems to be

an anion-exchange (law of mass action) effect operating, while in the second the somewhat higher polarity of the mobile phase (in higher HCl concentration) will favour adsorption.

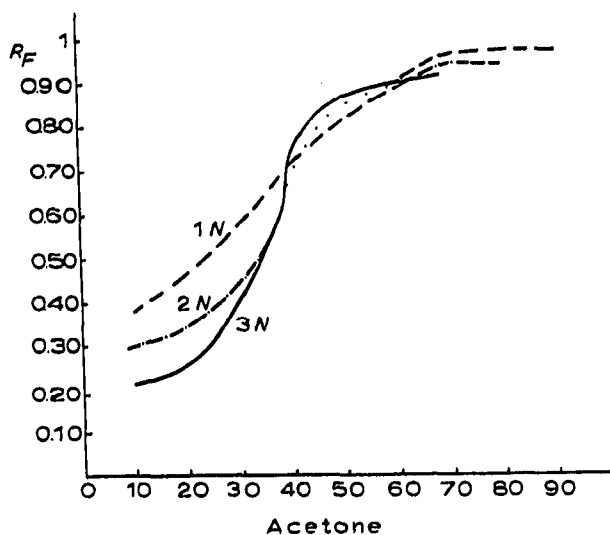


Fig. 2. R_F values of gold chloride plotted against the concentration of acetone in 1 N, 2 N and 3 N HCl on Polygram CEL 300 AC-10 (a ready-made thin layer consisting of acetylated cellulose).

To sum up, comparing the adsorption of HAuCl_4 on various types of cellulose and resin papers all effects can be explained by assuming AuCl_4^- to be the preferred species in aqueous solution and an ion pair $[\text{H}^+\text{AuCl}_4^-]$ the preferred species in organic solids and solutions. There is no need to assume the formation of a charge transfer complex on the resin network.

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