

ADSORPTION CHROMATOGRAPHY ON CELLULOSE
VII. THE ADSORPTION ON CELLULOSE OF CHLOROauric AND
BROMOauric ACIDS FROM AQUEOUS SOLUTIONS OF ACIDS

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INTRODUCTION

In two previous papers of this series¹ we have shown that chloroauric and bromoauric acid are adsorbed on cellulose paper and that this kind of adsorption is similar to the adsorption of these compounds on other organic surfaces² or to solvent extraction.

The presence of HCl (or HBr) or of their salts leads to the typical salting-out effects usually encountered in solvent extraction. Recently another effect has been studied extensively in solvent extraction. This effect, usually called the "synergic effect", is the alteration of the partition coefficient of the substance to be extracted, on addition of a second solvent or complexant. IRVING AND EDGINGTON³ have recently discussed such synergism for the extraction of U(VI) with tributyl phosphate and TTA (thenoyltrifluoroacetone) and could show that compound formation with both complexants occurs.

In this paper the effect of the presence of acids other than HCl (or HBr) on the adsorption of chloroauric acid on cellulose will be discussed. We considered it of interest to examine whether synergic effects could be observed in the adsorption of chloroauric acid on cellulose, because the extracted species is a well-known and very stable anion and because, owing to its high solubility in organic solvents, only poor results could be expected from solvent extraction experiments.

EXPERIMENTAL

Chloroauric acid was prepared by dissolving gold(III) chloride in 2 *N* HCl and bromoauric acid by heating a gold(III) chloride solution with conc. HBr on the water bath and subsequently diluting to about *N* HBr.

Whatman No. 3 MM paper was used throughout with ascending development. In our previous work we noted¹ that in high concentrations of acids (HCl or HBr higher than 6 *N* and 3 *N* respectively) there is an increase of adsorption due to the change in the polarity of the solvent. On the other hand there are hydrolysis comets when chloroauric acid is developed in neutral solutions or at acidities below pH 1.

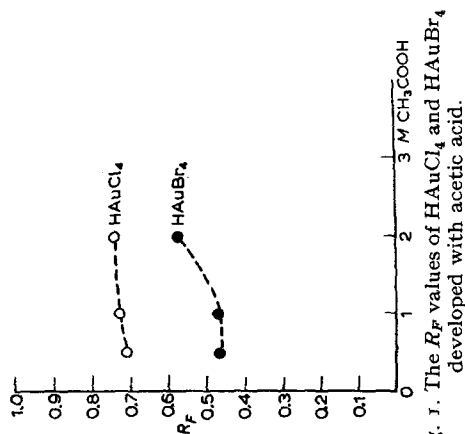


Fig. 1. The R_F values of HAuCl_4 and HAuBr_4 developed with acetic acid.

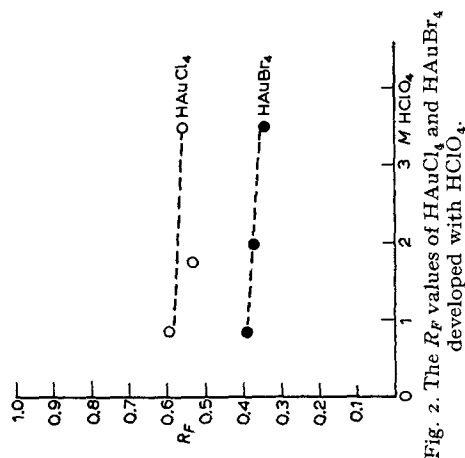


Fig. 2. The R_F values of HAuCl_4 and HAuBr_4 developed with HClO_4 .

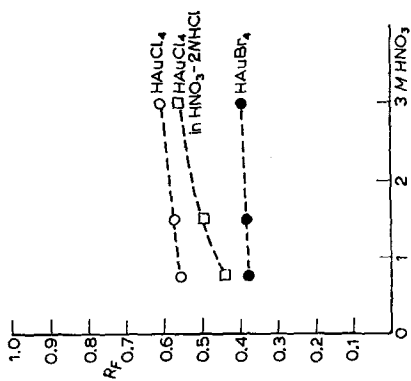


Fig. 3. The R_F values of HAuCl_4 and HAuBr_4 developed with HNO_3 and a mixture of HNO_3 - HCl (2 N HCl throughout).

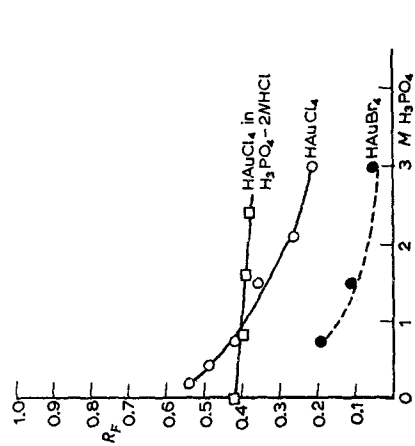


Fig. 4. The R_F values of HAuCl_4 and HAuBr_4 developed with H_3PO_4 and with a mixture of H_3PO_4 - HCl (2 N HCl throughout).

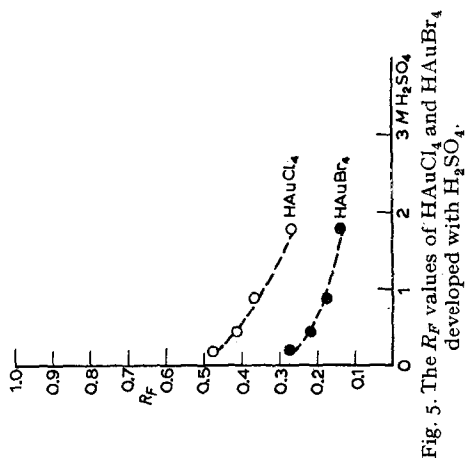


Fig. 5. The R_F values of HAuCl_4 and HAuBr_4 developed with H_2SO_4 .

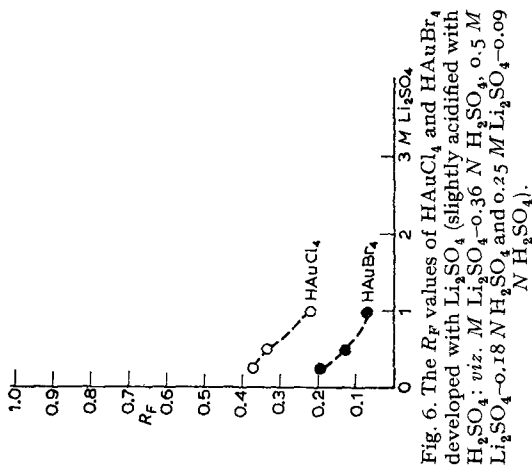


Fig. 6. The R_F values of HAuCl_4 and HAuBr_4 developed with Li_2SO_4 (slightly acidified with H_2SO_4): viz. $M \text{Li}_2\text{SO}_4$ - $0.36 N \text{H}_2\text{SO}_4$, $0.5 M \text{Li}_2\text{SO}_4$ - $0.18 N \text{H}_2\text{SO}_4$ and $0.25 M \text{Li}_2\text{SO}_4$ - $0.09 N \text{H}_2\text{SO}_4$.

Hence we limited our investigations to the range of about 0.3 *N* to 3 *N* acid solutions in most cases.

(i) *The effect of organic acids*

The presence of acetic acid increases the R_F values of (*i.e.* desorbs) both chloroauric and bromoauric acid as shown in Fig. 1. This effect is similar to that of small amounts of butanol (see ref.¹) and is probably due to the non-polar nature of acetic acid. Oxalic acid in presence of HCl (2 *N* HCl saturated with oxalic acid) increases the R_F value only slightly (from 0.42 to 0.46).

(ii) *The effect of HClO₄ and HNO₃*

Both perchloric and nitric acid desorb HAuCl₄ and HAuBr₄ slightly as shown in Figs. 2 and 3. There is no definite increase in the desorption with an increase of the concentration of HNO₃ or HClO₄. In both solvents the colour of the two gold compounds remains unchanged.

(iii) *The effect of H₂SO₄ and H₃PO₄ and sulphates*

There is a marked increase in adsorption when HAuCl₄ and HAuBr₄ are developed with H₂SO₄, H₃PO₄ or with lithium sulphate as shown in Figs. 4, 5 and 6. As in the interpretation of synergic effects in solvent extraction we can plot the logarithm of the equilibrium constant against the logarithm of the concentration, since R_M ($= \log (\frac{1}{R_F - 1})$) is directly proportional to the logarithm of the equilibrium constant.

Figs. 7 and 8 show that there is a straight line relationship for the adsorption from H₂SO₄ solutions with a slope of approximately 1/2, a slope of 1 for higher concentrations of H₃PO₄ and a slope of 1/2 for lower concentrations of H₃PO₄ for HAuCl₄.

(iv) *Adsorption from salt solutions*

Only sulphates were examined as the buffer action of phosphates would complicate the question unduly.

Fig. 9 shows the R_M -log concentration relationship for the adsorption from lithium sulphate solutions that were acidified slightly with H₂SO₄ to prevent hydrolysis of the gold compounds. The slope is 1. There is also an influence due to the cation of the salt: molar Li, NH₄ and Mg sulphates (containing 0.36 *N* H₂SO₄) gave the following R_F values for HAuCl₄ (respectively): 0.22, 0.29 and 0.30.

(v) *The influence of HCl on the adsorption of HAuCl₄ from solutions of other acids*

There is a definite competition between HCl and other acids. H₃PO₄ exerts practically no influence on the R_F value of HAuCl₄ in presence of 2 *N* HCl (Fig. 4). In the case of H₂SO₄ there remains an influence on the R_F value which decreases with the increasing concentration of HCl as shown in Figs. 10 and 11.

Fig. 7 also shows the R_M -log concentration relationship for the adsorption of HAuCl₄ from sulphuric acid containing *N* HCl. There is no change in the adsorption

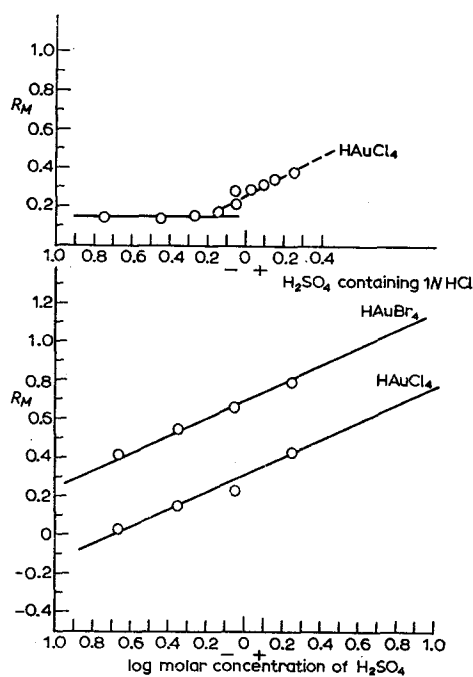


Fig. 7. The R_M -log concentration $[H_2SO_4]$ relationship for chromatograms developed with H_2SO_4 or HCl- H_2SO_4 (above).

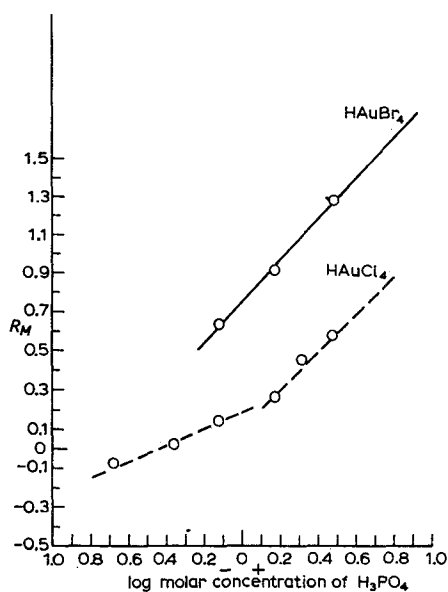


Fig. 8. The R_M -log concentration $[H_3PO_4]$ relationship for chromatograms developed with H_3PO_4 .

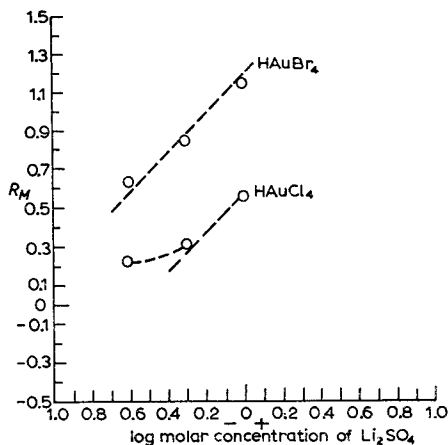


Fig. 9. The R_M -log concentration $[\text{Li}_2\text{SO}_4]$ relationship for chromatograms developed with acidified Li_2SO_4 (see Fig. 6).

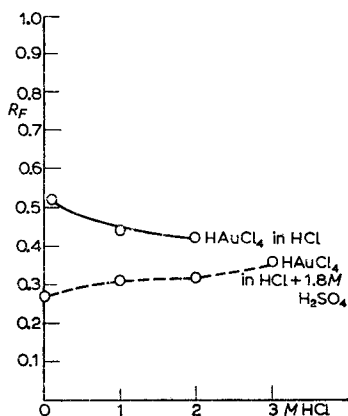


Fig. 10. The R_F values of HAuCl_4 in HCl and a mixture of HCl- H_2SO_4 (the latter being 1.8 M throughout).

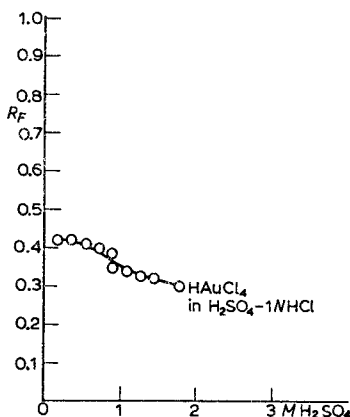


Fig. 11. The R_F values of HAuCl_4 in mixtures of H_2SO_4 -HCl (the latter being 1 N throughout).

until the sulphuric acid concentration reaches about 1.5 N and then the slope is 1/2. HNO_3 in presence of 2 N HCl still lowers the adsorption of HAuCl_4 (Fig. 3).

DISCUSSION

By analogy with the arguments used in interpreting solvent extraction data, it can be inferred that compound formation takes place between HAuCl_4 or HAuBr_4 and mineral acids such as H_3PO_4 or H_2SO_4 and their salts. This effect seems to be quite general; preliminary results with H_3AsO_4 and metaphosphoric acid also showed a lowering of the R_F values.

So far we can not offer any evidence for the structure of these compounds. However, the well-known tendency of HAuCl_4 to hydrolyse to HAuCl_3OH and to

form complexes of the type HAuCl_3X would suggest that phosphoric acid or sulphuric acid replaces one of the four coordinated chloro-groups. The competitive action of HCl would also speak in favour of this. On the other hand neither HAuBr_4 nor HAuCl_4 change their characteristic colours during development with the various acids. We hope that further work with other methods will elucidate these questions.

It was, however, possible to demonstrate synergic effects or negative synergic effects between several purely anionic species in aqueous solution.

SUMMARY

The adsorption of HAuCl_4 and HAuBr_4 on cellulose was found to be influenced by H_2SO_4 , H_3PO_4 and other compounds.

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- ² K. A. KRAUS, D. C. MICHELSON AND F. NELSON, *J. Am. Chem. Soc.*, 81 (1959) 3204.
- ³ H. IRVING AND D. N. EDGINGTON, *J. Inorg. & Nuclear Chem.*, 15 (1960) 158.

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