

## ADSORPTION CHROMATOGRAPHY ON CELLULOSE

## IX. THE ADSORPTION

## CHROMATOGRAPHY ON CELLULOSE OF INORGANIC SUBSTANCES\*

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## INTRODUCTION

Until quite recently the only adsorption effects of inorganic substances that were recorded in the literature dealt with the adsorption of cations. RIPAN *et al.*<sup>1</sup> then separated polyanions on paper with aqueous solvents, and the author studied quite a range of inorganic compounds. This has been reviewed in detail<sup>2</sup>. The possibilities of cellulose as adsorbent for inorganic substances is interesting from several angles: in radiochemistry a knowledge of the adsorption properties of such a commonly used material is quite important, as it is also for many analytical problems; at the moment a search is also being made for adsorbing materials with properties other than those of synthetic ion-exchange resins and here also cellulose can compete as regards cost and properties with such materials as hydrous oxides or insoluble phosphates, etc., and finally we were able to extend the scope of paper chromatographic methods in inorganic chemistry to problems where partition chromatography proved unsuitable.

In this paper several investigations are reported which are all continuations of work previously published. In this manner we hope to be able to review the whole field while presenting new results.

## THE ADSORPTION OF IODIDE COMPLEXES

We had noted an analogy between adsorption on cellulose and ether extraction for chloro- and bromo-complexes when developed with HCl, HBr and their salts<sup>3</sup>. Iodo-complexes present experimental difficulties as development in air with HI rapidly produces free iodine on the paper. However, if chromatograms are run for relatively short times with a mixture of 1.5 N KI-1.5 N H<sub>2</sub>SO<sub>4</sub> only little iodine is formed. This mixture of KI-H<sub>2</sub>SO<sub>4</sub> was used by IRVING AND ROSSOTTI<sup>4</sup> for studies of ether extraction of iodo-complexes and thus a comparison of the two processes is possible.

The  $R_F$  values obtained and the percentage of the metal extracted, as reported by IRVING AND ROSSOTTI<sup>4</sup>, are shown in Table I.

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TABLE I

$R_F$  VALUES OF METAL IONS WHEN DEVELOPED WITH AQUEOUS 1.5 N KI-1.5 N H<sub>2</sub>SO<sub>4</sub> ON WHATMAN 3 MM PAPER COMPARED WITH THE PERCENTAGE EXTRACTED WITH ETHER FROM THE SAME AQUEOUS SOLUTION

Metal ion	$R_F$ value	% extracted with ethyl ether*
Hg (II)	0.57	33
Mo (VI)	0.74	1
Cd (II)	0.65	100
Au (III)	0.29	
Sb (III)	0.64	50
U (VI)	1.0	
Ag (I)	0.77	
Pt (VI)	0.54	
Bi (III)	0.69	10
Fe (III)	1.0	0
Co (II)	1.0	
V (V)	1.0	
Zn (II)	1.0	33

\* Values taken from IRVING AND ROSSOTTI<sup>4</sup>.

Already from the relatively few results shown it is clear that there is no correlation between cellulose adsorption and ether extraction for iodide complexes. Cd (II) and Sb (III) are adsorbed to about the same degree but extracted to quite different degrees (100 % and 50 % resp.). From the results with chloro- and bromo-complexes<sup>3</sup> higher  $R_F$  values would also be expected for Bi (III) and Mo (VI).

It seems thus that the analogy of ether extraction and adsorption on cellulose is not very close and differences in behaviour may be expected.

During this work we observed a rather interesting adsorption of the I<sup>3-</sup> ion. When a solution of iodine in KI is placed on the paper there is an immediate darkening in colour. The  $R_F$  values of this dark spot when developed with KI of different concentrations are shown in Table II.

TABLE II

$R_F$  VALUES OF KI<sub>3</sub> ON WHATMAN NO. 3 MM PAPER

Solvent	$R_F$ value
0.5 M KI	0.22
1.0 M KI	0.16
2 M KI	0.14
2 M KI-0.1 M HCl	0.15
0.01 M KI	spot disappears

There is only a small change in the  $R_F$  value with variations of the pH and the iodide concentration. In  $M/100$  KI the I<sup>3-</sup> seems to dissociate and the spot disappears. The darkening in colour on placing on the paper suggests the formation of an iodine-cellulose complex similar to the well-known starch and glycogen complexes.

## THE ADSORPTION OF ORGANIC COMPLEXES

Only relatively few chloro- or bromo-complexes and other anions adsorb strongly on cellulose. It was thus obvious to investigate metal complexes with organic ligands which, owing to their organic groups, should show a greater tendency to adsorb. Again we found that only relatively few metal complexes adsorb on cellulose, the best results being obtained with thiourea complexes<sup>5</sup>. We shall report here further experiments with ligands similar to thiourea, which, however, do not show much promise for analytical applications.

Table III shows the  $R_F$  values of osmium complexes with a series of compounds similar to thiourea, with both aqueous HCl and butanol-2 *N* HCl as solvent. All

TABLE III  
 $R_F$  VALUES OF SOME OSMIUM COMPLEXES

Complexing agent	$R_F$ values	
	2 <i>N</i> HCl	Butanol-2 <i>N</i> HCl
Diphenylthiourea	0	1.0
Phenylthiourea	0.15	0.73
Thiourea	0.18	0.05
Thiosemicarbazide	0.55 (double spot)	decomposition comet
Thioglycollic acid	0	decomposition comet
Thioacetamide	0.79	decomposition (3 spots formed)

complexes were prepared by heating an aqueous solution of the ligand with a few drops of a solution of  $\text{OsO}_4$  in 2 *N* HCl. The diphenylthiourea complex is insoluble in water, but readily extracted with butanol and was placed on the paper in a butanol solution.

TABLE IV  
 $R_F$  VALUES OF SUBSTITUTED THIOUREA COMPLEXES OF OSMIUM,  
WITH MIXTURES OF ETHANOL-WATER-HCl

Solvent composition:					
	10	10	10	10	10
Conc. HCl					
Water	80	70	60	50	40
Ethanol	10	20	30	40	50
$R_F$ values of Os complexes of:					
Thiourea	0.21	0.22	0.24	0.24	0.23
Phenylthiourea	0.34	0.57	0.73	0.85	0.85
Diphenylthiourea	0	0	0	comet to 1.0	

It seems that the type of complex which adsorbs well on cellulose also has a tendency to be only little soluble in water. The presence of phenyl-groups in the thiourea molecule renders most complexes insoluble. As a matter of fact chromatography with other platinum metals as their phenylthiourea complexes proved impossible owing to insufficient solubility in water or HCl.

The osmium-phenylthiourea complex may be desorbed with water-ethanol mixtures but not the osmium-thiourea complex (Table IV). The diphenylthiourea complex of Os, however, is already too insoluble in aqueous phases; it either remains on the origin or is carried toward the liquid front in the form of a comet.

In aqueous HCl on the other hand the thiourea complex is desorbed with an increase in the HCl concentration and the substituted thiourea complexes are more strongly held (Table V).

TABLE V  
R<sub>F</sub> VALUES OF SUBSTITUTED THIOUREA COMPLEXES IN AQUEOUS HCl AND LiCl

Os complexes of:	R <sub>F</sub>			
	2 N HCl	6 N HCl	8.4 N HCl	7 N LiCl
Thiourea	0.18	0.35	0.50	0.11
Phenylthiourea	0.15	0.02	0.02	0
		(comet)	(comet)	
Diphenylthiourea	0	0	0	0

A possible application of the results of Table IV is the concentration of osmium from dilute aqueous solution and the subsequent elution with a mixture of ethanol-water-HCl.

THE ADSORPTION OF HALOGENO-COMPLEXES FROM SOLUTIONS OF OTHER MINERAL ACIDS

Only Au(III), Po(IV), Sb(V) and Ga(III) chlorides are appreciably adsorbed on cellulose from HCl solutions<sup>3</sup>. These metal ions are salted out by LiCl and other chlorides. In addition to salting-out effects we found that their adsorption may also be increased by the presence of such acids as H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub> in the developing solution<sup>6</sup>. This effect was observed with most polyvalent mineral acids, but not with monovalent acids. It occurs in presence of HCl as well as in solutions containing only the mineral acid. Work with Sb(V) indicated that loss of chloro-groups from the complex is unlikely during development<sup>7</sup>. On the other hand it seems that some interaction between an acid such as H<sub>2</sub>SO<sub>4</sub> and covalent chloride complexes such as H<sub>2</sub>AuCl<sub>4</sub> occurs in solution.

We shall describe here work carried out on these phenomena, which throws further light on this question.

(a) The adsorption of  $HgCl_2$  and  $TlCl_3$  from sulphuric acid or phosphoric acid

Figs. 1 and 2 show the change of  $R_F$  values for  $HgCl_2$  and  $TlCl_3$  respectively. The  $TlCl_3$  solution was made in HCl because hydrolysis comets were otherwise observed. As can be seen in Fig. 1 perchloric acid does not change the  $R_F$  value of  $HgCl_2$ , HCl desorbs this compound (forming  $H_2HgCl_4$ ) while both sulphuric and phosphoric acid

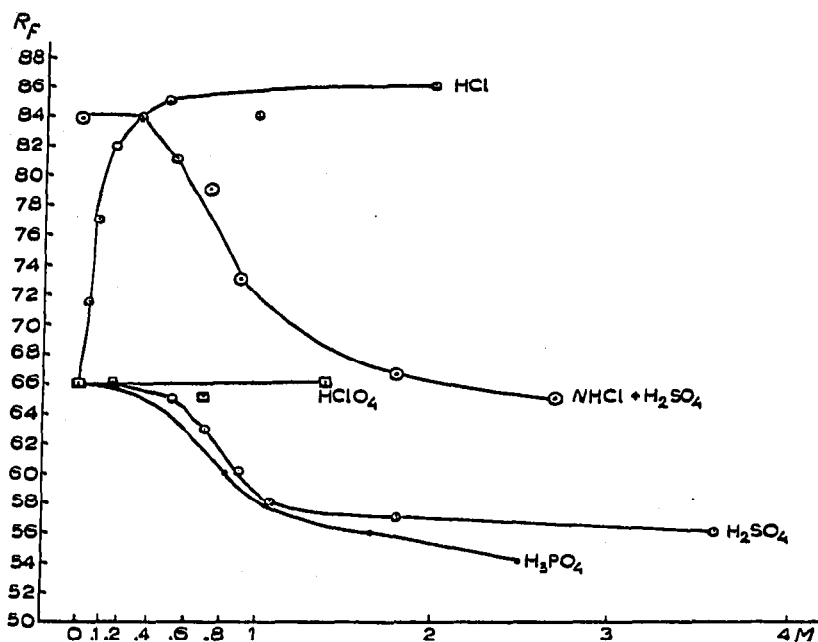


Fig. 1. Graphical representation of the variation of  $R_F$  values of  $HgCl_2$  when developed with HCl,  $HClO_4$ ,  $H_2SO_4$ ,  $H_3PO_4$  and a mixture of N HCl- $H_2SO_4$ .

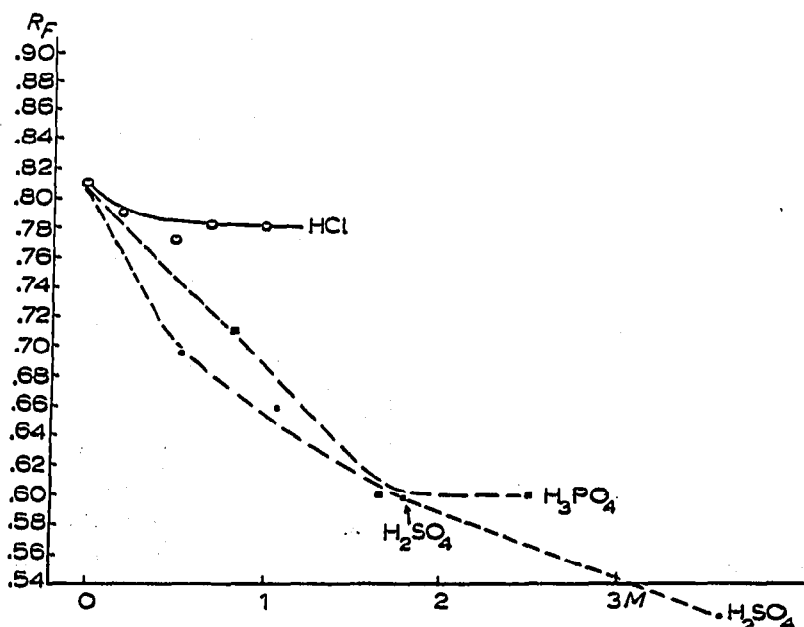


Fig. 2. Graphical representation of the variation of  $R_F$  values of  $TlCl_3$  (in dilute HCl) when developed with HCl,  $H_2SO_4$  and  $H_3PO_4$ .

adsorb it more strongly. In HCl-H<sub>2</sub>SO<sub>4</sub> mixtures the  $R_F$  values are lower than in HCl alone. When chromatograms developed with H<sub>2</sub>SO<sub>4</sub> are sprayed with AgNO<sub>3</sub> it can readily be seen that the Cl<sup>-</sup> spot and the Hg(II) coincide completely and that no Cl<sup>-</sup> dissociates from the HgCl<sub>2</sub> during development.

Although Hg(II) and Tl(III) are only little adsorbed from HCl solutions, the same effects as with Au(III) and Sb(V) can be observed when developing with H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub>.

#### (b) Diffusion measurements

Using a simple method for measuring the increase in spot size on paper<sup>8</sup> it could be shown that HAuCl<sub>4</sub> either increases its molecular size only to a small extent or not at all. Aggregates of the type HAuCl<sub>4</sub>(H<sub>2</sub>SO<sub>4</sub>)<sub>4</sub> or <sub>6</sub>, seem to be ruled out but aggregates such as HAuCl<sub>4</sub>·H<sub>2</sub>SO<sub>4</sub> are possible.

#### (c) Electrophoretic studies

A solution of HgCl<sub>2</sub> in sulphuric or phosphoric acid behaves as a neutral substance when electrophorised on paper (150 V for 35 min) and HAuCl<sub>4</sub> is anionic. Since there is considerable decomposition during electrophoresis, exact comparisons of mobilities are impossible for Au(III). From electrophoretic studies there is thus no indication for a change of charge on the halogeno-complexes.

#### (d) Discussion

The rather remarkable increase of adsorption of halogeno-complexes in sulphuric and phosphoric acids would of course suggest some kind of compound formation. Both diffusion experiments and paper electrophoresis do not support the formation of polyacids. However, interactions between different kinds of similarly charged anions has already been observed by DAVIDSON *et al.*<sup>9</sup> for mixtures of Sb(V) and Sb(III) and other ions, so that such a suggestion cannot be ruled out as unlikely. We hope to be able to find further evidence to explain the phenomena observed.

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#### SUMMARY

In this paper we have discussed the adsorption of iodo-complexes on cellulose, the adsorption of some metal complexes with organic ligands and the adsorption behaviour of halogeno-complexes in solutions of sulphuric or phosphoric acids.

Although much work has still to be done on the adsorption of inorganic substances on cellulose we were able to show that the field has many interesting possibilities.

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