

ADSORPTION PAPER CHROMATOGRAPHY OF
INORGANIC SUBSTANCESVI. THE ADSORPTION PAPER CHROMATOGRAPHY
OF THE COMPOUNDS OF BIVALENT TIN WITH PLATINUM METALS

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The coloured compounds obtained when solutions of platinum metals in HCl are mixed with SnCl₂ were first considered to be colloidal forms of the metals¹. A series of papers by AYRES *et al.*² deals with their application in spectrophotometry. The nature of the compounds was also studied and for the platinum compound the formula (Pt^oSn₄Cl₄)⁴⁺ is suggested on the basis of the analysis of its salt with phenylarsonic acid.

Similar compounds were also observed when platinum metals were mixed with Sn(II) in HBr^{3,4}. One of us⁵ recently studied the paper electrophoresis of these compounds and noted that they migrate as anions in HCl (in an electric field) and that they are adsorbed on paper. It was also noted that Rh(III) when mixed with Sn(II) in HCl gives a red compound which may be converted to a yellow form by addition of HCl, by extraction with butanol or by removing the Sn(II) during electromigration. The yellow form is not identical with any of the ionic forms of Rh(III).

In this paper a detailed study of the adsorption of the Sn(II)-platinum metal compounds on cellulose is described.

EXPERIMENTAL

Whatman No. 3MM paper and ascending development on narrow strips of paper (3 cm wide) on which the solution was applied as a thin band, were employed throughout. No reagents are necessary as the colours of the compounds are very intense.

Preliminary experiments showed that it is essential to include Sn(II) in the solvent. The Pt and the Pd compound spots disappear during development with 6 N HCl and the red rhodium compound is separated into a yellow comet (R_F : 0.49 to 0.79) and a Sn(II) spot (R_F : 0.83).

(1) *The compounds with stannous chloride in HCl*

The following compounds of the platinum metals were employed: a solution of H_2PtCl_6 in dilute HCl, commercial $PdCl_2$, commercial $RhCl_3$, OsO_4 , commercial $RuCl_3$ and K_2IrCl_6 . Solutions of about 1 mg of these compounds in about 1 ml of water were mixed with equal volumes of M $SnCl_2$ in HCl. Fig. 1 shows the R_F values

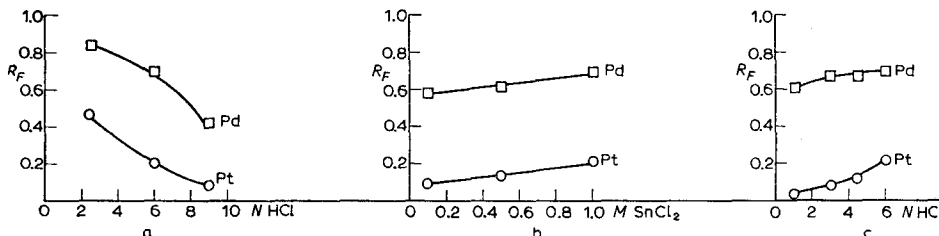


Fig. 1. (a) The variation of the R_F values of Pt and Pd with the concentration of HCl in the solvent. The concentration of $SnCl_2$ is maintained at 1 M . (b) The variation of the R_F values of Pd and Pt with the concentration of $SnCl_2$ in the solvent. The concentration of HCl is maintained at 6 M . (c) The variation of the R_F values of Pd and Pt with the concentration of hydrogen ions. All solutions contain 1 M $SnCl_2$ and the ratio of $LiCl:HCl$ is varied while the total concentration of $LiCl + HCl$ is maintained at 6 M .

of the Pd and the Pt compounds when the concentration of HCl, of $SnCl_2$ or of H^+ (by replacing by Li^+) is varied in the developing solution. Pt and Pd always yield well defined spots and give a better separation than can be obtained by partition chromatography of the chloro-complexes. Rhodium forms an elongated spot with a red coloured front and a yellow rear. Fig. 2 shows the extent of the rhodium zone and its variation with the concentration of $SnCl_2$ and HCl. The movement of all the platinum metals in M $SnCl_2$ -6 N HCl is given in Table I. Solutions that have been heated on the water-bath do in some instances change their colours. Except for Pd, which after heating forms a trail (colloidal Pd?), there is little difference in the chromatographic behaviour.

TABLE I

R_F VALUES OF THE STANNOUS CHLORIDE COMPOUNDS OF PLATINUM METALS IN 6 N HCl
Paper: Whatman No. 3 MM. Solvent: 1 M $SnCl_2$ in 6 N HCl.

Platinum metal	Solution of the metal ion mixed with $SnCl_2$ in 6 N HCl		Solution of the metal ion mixed with $SnCl_2$ in 6 N HCl and heated a few minutes on the water-bath	
	R_F value	Spot colour	R_F value	Spot colour
Pt (H_2PtCl_6)	0.21	orange	0.21	orange
Pd ($PdCl_2$ commercial)	0.70	blue	0-0.70	dark
Rh ($RhCl_3$ commercial)	0.13-0.56	yellow to red	0.13-0.56	yellow to red
Os (OsO_4)	0.69	pale brown	0.51	yellow
Ru ($RuCl_3$ commercial)	0.77	pink	0.46 (elongated)	yellow
Ir (K_2IrCl_6), two spots	0.18	yellow-brown	0.13 comet to 0.87	yellow
	0.78	yellow-brown		yellow

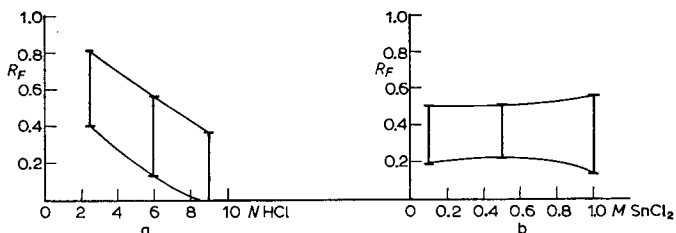


Fig. 2. (a) The variation of the height of the rhodium comet with the concentration of HCl. The SnCl_2 concentration is always 1 M . (b) The variation of the height of the rhodium comet with the concentration of SnCl_2 . The concentration of HCl is always 6 M .

(2) *The compounds with stannous bromide in HBr*

We prepared a solution of SnBr_2 in HBr by dissolving 30 g of Sn in 250 ml conc. HBr and diluting this to 500 ml. An $M/2$ Sn(II) solution in 3 N HBr is so obtained, which is identical to the solvent used by PANTANI AND PICCARDI⁴ for spectrophotometric studies. The R_F values and the colours of the compounds are shown in Table II. Separations of mixtures of Ru-Pd, Os-Ru, Pt-Pd, Pt-Rh-Pd were carried out successfully.

TABLE II

R_F VALUES OF THE STANNOUS BROMIDE COMPOUNDS OF PLATINUM METALS IN 3 N HBr
Paper: Whatman No. 3 MM. Solvent: $M/2$ Sn(II) in 3 N HBr (30 g of Sn dissolved in 250 ml conc. HBr and diluted to 500 ml).

Platinum metal	R_F value of the solution of the metal ion mixed with an equal volume of the solvent	
	R_F value	Spot colour
Pt (H_2PtCl_6)	0.24	red
Pd (PdCl_2 commercial)	0.6	dark
Rh (RhCl_3 commercial)	0.37	yellow
Os (OsO_4)	0.76	yellow
Ru (RuCl_3 commercial)	0.81	green
Ir (K_2IrCl_6 either dissolved in water or boiled with HBr)	three spots	{ 0.19 red 0.32 yellow 0.87 yellow
Ir, after heating the mixture of the Ir(IV) salt with SnBr_2 -HBr for 2 or more minutes on the water-bath	four spots	{ 0.23 red 0.37 yellow 0.65 yellow 0.88 yellow

The multi-spots obtained with iridium require further study. The same chromatogram was obtained irrespective of whether the chloroiridate was directly mixed with the Sn(II)-HBr solution or was first boiled with HBr. Heating was carried out for exactly two minutes, as recommended for colorimetry³, and for longer periods. Invariably four spots were separated from heated solutions. The intensity of the spots, however, varies somewhat with the time of heating.

DISCUSSION

In this and in previous work⁵ we were also concerned with the nature of the compounds formed between Sn(II) and platinum metals. The assumption that the platinum metal is zerovalent seems to be doubtful, at least for ruthenium. Partition chromatography of Ru(II), Ru(III)Cl₆³⁻ and the Sn(II)-Ru compound with butanol-3 *N* HCl showed clearly that a Ru-Sn(II) compound is formed which differs in behaviour from either Ru(II) or Ru(III). Since the potential of Ru(II)/Ru(III) is 0.08 V it seems unlikely that the Ru(III) was reduced by SnCl₂ (E_0 : 0.14 V) and rather suggests that the Ru-Sn(II) compound would have Ru(III) as the central atom. The findings that the Pt, Pd and Rh compounds are anions would also suggest a structure similar to heteropolyacids, in which the platinum metal is the central atom and is surrounded by four (or perhaps more) SnCl₃⁻ (or HSnCl₄) groups. The similarity with other heteropolyacids is again shown in their stability in acid solutions and the ready dissociation of the Sn(II) from the Rh in the case of the red rhodium compound.

SUMMARY

Some of the compounds of Sn(II) with platinum metals may be separated by adsorption chromatography on paper. Their behaviour in SnCl₂-HCl and SnBr₂-HBr was noted.

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