THE CHROMATOGRAPHY OF METAL IONS ON POLYAMIDE THIN LAYERS

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SUMMARY

The retention of a range of heavy metal ions on Polyamide 11 thin layers was examined. Aqueous HCl, ethanol–HCl, butanol–HCl and acetone–HCl mixtures were used as solvents.

INTRODUCTION

Polyamides are being used extensively as adsorbents in the chromatography of organic substances. Their adsorption mechanism has been investigated[1] and it is believed to involve mainly a hydrogen-bonding mechanism when phenols are adsorbed. Another important property of polyamides as adsorbents is the extensive swelling, which led GRASSMAN *et al.*[2] to consider them as "solid solvents".

The review by HÖRHAMMER *et al.*[1] lists numerous separations on polyamide thin layers, but so far nothing has been reported concerning the behaviour of inorganic ions. We believe that this is due to the fact that Polyamide 6 does not yield satisfactory chromatograms in solvents containing HCl and shows signs of decomposition. However, we showed recently[3] that Polyamide 11 is resistent to butanol–HCl mixtures and produces good chromatograms with metal ions.

The purpose of this paper is to report more fully on the chromatography of metal ions on Polyamide 11.

EXPERIMENTAL AND RESULTS

Pre-coated Polygram Polyamid 11 thin layers on plastic sheets (from Macherey-Nagel and Co.) were used in this work and developed in rectangular glass tanks with ground-glass lids for 13–15 cm.

The metal ions were dissolved in aqueous $3N$ HCl. We examined a range of 18 heavy metals that could all be detected with hydrogen sulphide, ammonium sulphide or ammoniacal ethanolic 8-hydroxyquinoline.

Aqueous solvents

Aqueous $1N$ HCl yields rather poor chromatograms. Many metal ions leave an intense spot on the point of application from which a long trail moves forward and is clearly less concentrated. It seems that from aqueous solutions, penetration into the polymer and desorption from it take considerably longer than would be required for the formation of compact spots.

TABLE I

R_F VALUES OF METAL IONS ON POLYAMIDE 11 AND ON CELLULOSE CELL 400 MN THIN LAYERS WITH ETHANOL–HCl MIXTURES

Solvents: S_1 = ethanol–aqueous $4N$ HCl; S_2 = ethanol–aqueous $6N$ HCl; S_3 = ethanol–aqueous $8N$ HCl (all 1:1 mixtures).

| Metal ion	S_1		S_2		S_3	
	Polyamide 11	Cell 400	Polyamide 11	Cell 400	Polyamide 11	Cell 400
Pb(II)	0.45	0.56	0.31	0.60	0.44	0.55
Hg(II)	0.08	1.00	0.05	1.00	0.06	1.00
Bi(III)	0.08	1.00	0.05	1.00	0.06	1.00
Cu(II)	0.83	0.64	0.47	0.62	0.32	0.62
Cd(II)	0.24	1.00	0.19	1.00	0.16	1.00
Au(III)	0.0	1.00	0.0	1.00	0.0	1.00
Sb(III)	0.13	1.00	0.09	1.00	0.10	1.00
Fe(III)	0.16	0.68	0.02	0.66	0.0	0.71
Tl(III)	0.0	1.00	0.0	1.00	0.0	1.00
Co(II)	0.95	0.64	0.89	0.52	0.76	0.50
Mn(II)	1.00	0.67	1.00	0.58	1.00	0.54
Ni(II)	1.00	0.61	1.00	0.51	1.00	0.45
UO₂(II)	0.30	0.70	0.09	0.63	0.05	0.59
Zn(II)	0.27	1.00	0.16	1.00	0.15	1.00
Sn(IV)	0.33	1.00	0.16	1.00	0.16	1.00
Pt(IV)	0.02	1.00	0.02	1.00	0.03	1.00
Pd(II)	0.12	1.00	0.10	1.00	0.13	1.00
As(III)	0.80	1.00	0.70	0.74		
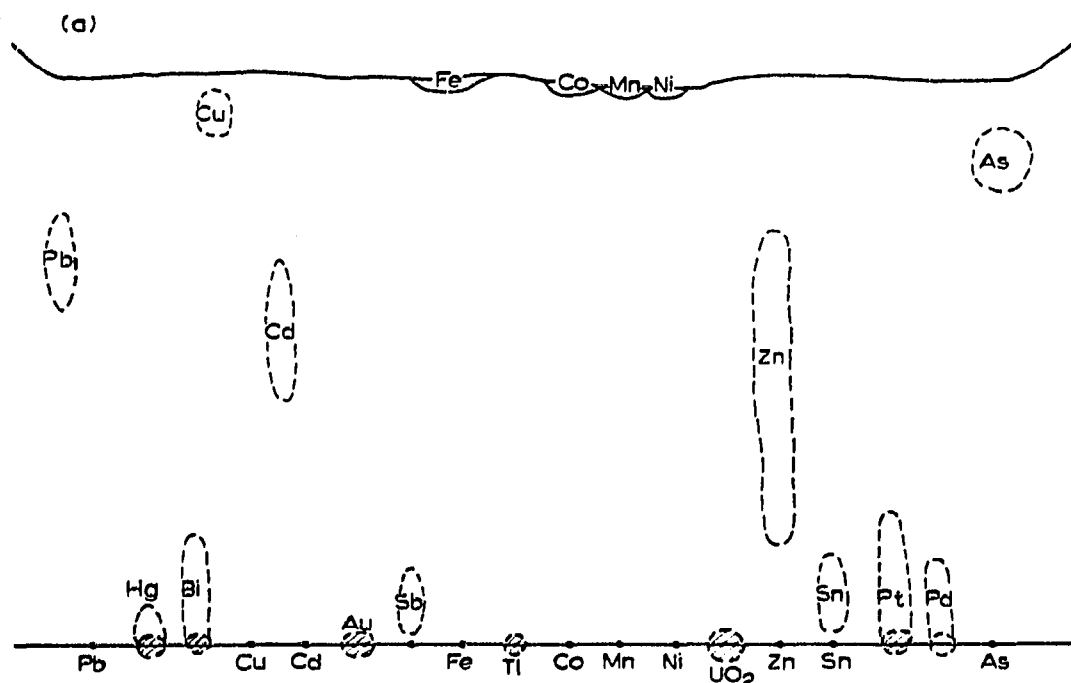
Fig. 1a.
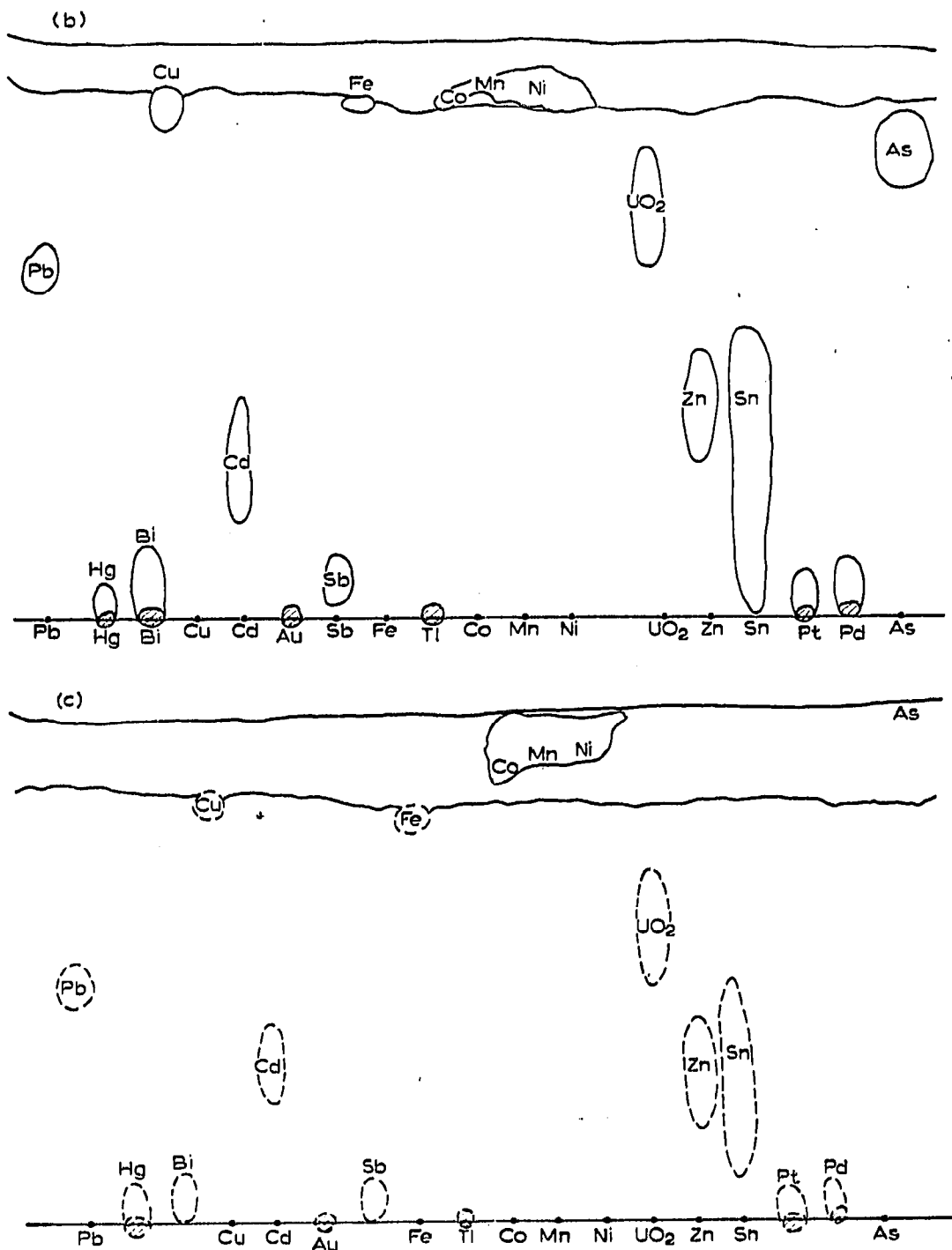
Fig. 1. Chromatograms on Polyamide 11 with aqueous solvents. (a) Developed with aqueous $1N$ HCl; (b) developed with $1N$ HCl in an ethanol–water (1:9) mixture; (c) developed with $1N$ HCl in an ethanol–water (3:7) mixture.

A chromatogram is shown in Fig. 1a. It can be seen that Polyamide 11 adsorbs very strongly complexes of the type of $HgCl_4^{2-}$, $BiCl_4^-$, $AuCl_4^-$, $SbCl_4^-$ and $TlCl_4^-$; cations such as Pb(II), Cu(II), Fe(III), Co(II), Mn(II) and Ni(II) have high R_F values while less complexed metal ions such as Cd(II) and Zn(II) move with intermediate R_F values and have rather elongated spots.

The tendency to form intense spots at $R_F = 0$ with forward comets can be eliminated by adding ethanol to the aqueous HCl, as shown in Figs. 1b and c.

The separation sequence remains the same in the presence of 30 % ethanol and the elongated spots of Cd(II) and Zn(II) are more compact. We think that this is due to a faster establishment of equilibrium between the polyamide phase and the mobile phase when ethanol is present.

To summarize, Polyamide 11 seems to be unsuitable for chromatography with purely aqueous solvents, but relatively small amounts of other solvents added to the aqueous solvent can produce satisfactory separations.

Ethanol–HCl mixtures

Table I shows the R_F values of metal ions on Polyamide 11 and on cellulose thin layers in ethanol–aqueous HCl (1:1) mixtures. There is generally an inversion of R_F values when one compares polyamide with cellulose. On cellulose, variation of the HCl concentration gives a less pronounced variation of R_F values than can be observed on polyamide. This is best seen with some examples in Fig. 2.

Butanol–HCl mixtures

Table II shows the R_F values on Polyamide 11 with butanol–aqueous HCl (1:1) mixtures as solvents. Analogous results on cellulose have been obtained by CARVALHO[4]. The spots in all the solvents are generally good and rather good separations are possible, *e.g.*, Fig. 3.

In these solvents, the more weakly complexed metals such as Ni(II), Mn(II) and Co(II) have low R_F values in butanol–1N HCl and increase gradually to $R_F = 1.0$ with increasing HCl concentration.

The strongly complexed metals such as Hg(II), Au(III), Pt(IV) and Pd(II) have low R_F values in butanol–1N HCl that generally decrease with an increase in the HCl concentration.
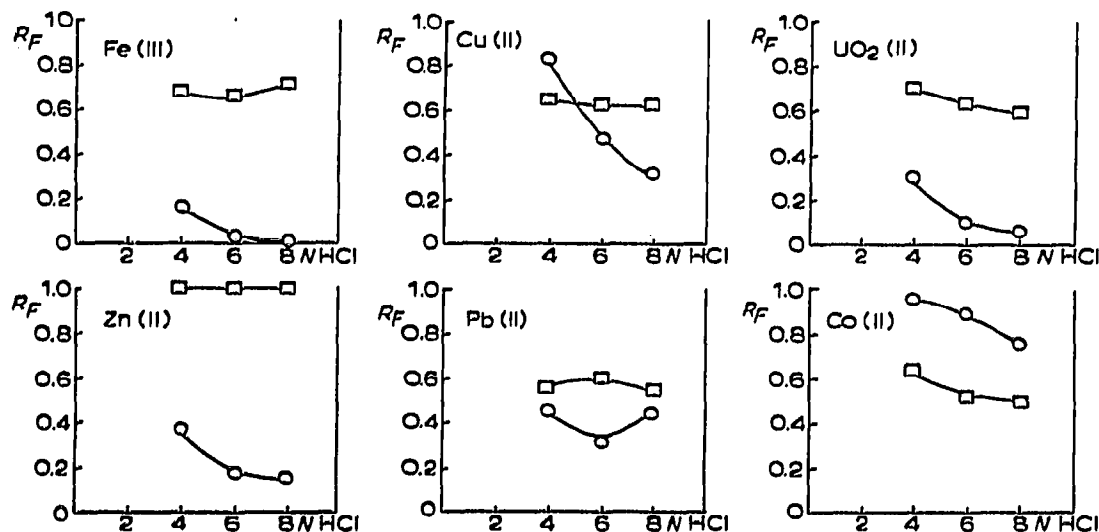

Fig. 2. Some R_F *versus* HCl concentration plots for ethanol–HCl (1:1) mixtures on Polyamide 11 (○) and Cell 400 layers (□).

TABLE II

R_F VALUES OF METAL IONS ON POLYAMIDE 11 THIN LAYERS WITH BUTANOL–HCl MIXTURES

Solvents: S_1 = butanol–aqueous $1N$ HCl; S_2 = butanol–aqueous $4N$ HCl; S_3 = butanol–aqueous $6N$ HCl; S_4 = butanol–aqueous $8N$ HCl (all 1:1 mixtures).

| Metal ion	S_1	S_2	S_3	S_4
Pb(II)	0.15	0.50	0.62	0.59
Hg(II)	0.06	0.09	0.08	0.07
Bi(III)	0.06	0.13	0.15	0.17
Cu(II)	0.22	0.57	0.60	0.40
Cd(II)	0.14	0.20	0.17	0.19
Au(III)	0.06	0.05	0.02	0.03
Sb(III)	0.14	0.19	0.14	0.15
Fe(III)	0.17	0.07	0.02	0.0
Tl(III)	0.0	0.0	0.0	0.0
Co(II)	0.16	0.55	0.90	1.0
Mn(II)	0.14	0.11–0.51	~0.9	1.0
Ni(II)	0.14	0.16–0.51	~0.9	1.0
UO_2(II)	0.18	0.26	0.14	0.07
Zn(II)	0.28	0.23	0.18	0.18
Sn(IV)	0.37	0.33	0.02–0.30	0.08
Pt(IV)	0.0	0.0	0.03	0.05
Pd(II)	0.03	0.16	0.15	0.19
As(III)	0.55	0.72	0.66	0.76
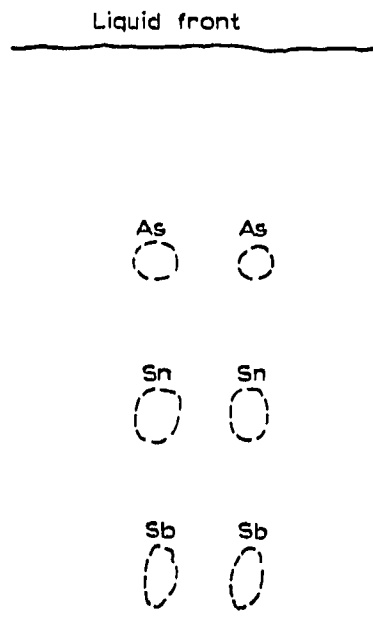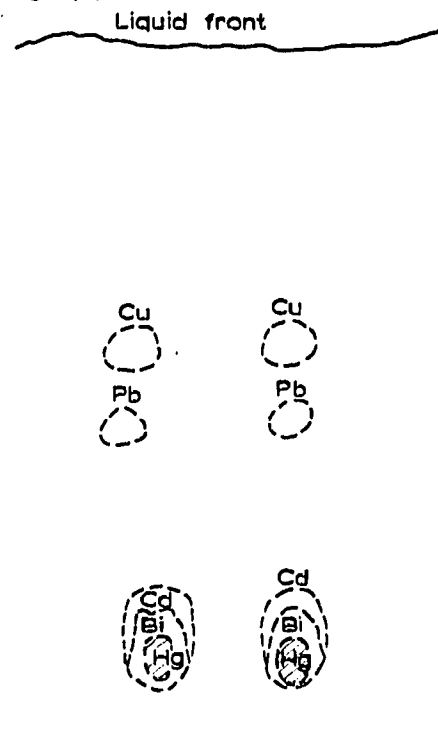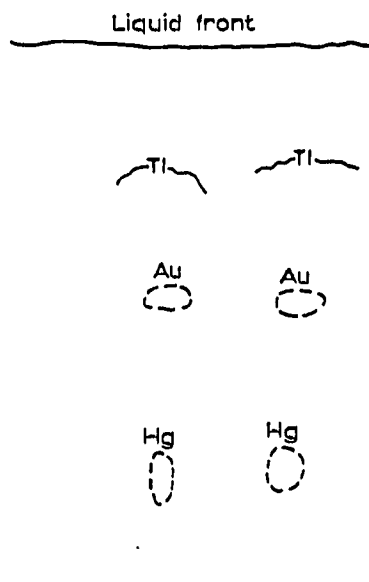
Fig. 3. Some separations of metal mixtures in butanol–HCl mixtures on Polyamide 11 layers. (a) Separation of As(III), Sn(IV) and Sb(III) with butanol–1N HCl; (b) separation of Cu and of Pb from Cd, Bi and Hg with butanol–4N HCl.

Fig 4. Separation of Tl(III), Au(III) and Hg(II) on Polyamide 11 with acetone–HCl–water (90:5:5).

We shall attempt to explain this as follows: in butanol–$1N$ HCl, the polyamide is strongly hydrated (owing to hydrogen-bond formation) and thus a water-rich stationary phase is formed. Metals such as Ni(II), Mn(II) and Co(II) are held in this phase while the chloro-complexes of Hg(II), Au(III), etc., are also retained but by adsorption on the polyamide (even when hydrated). At high HCl concentrations, the stationary water-rich phase is not formed and the non-complexed metals tend to go with the mobile phase (which is now more polar than the polyamide). The chloro-complexes of Hg(II), Au(III), etc., are slightly desorbed at higher HCl concentrations because the mobile phase becomes progressively less polar and hence more able to desorb them (even if the effect is small). Fe(III), which increases its complexation with the HCl concentration, is first retarded as cationic $FeCl^{2+}$ in the aqueous stationary phase and then as $HFeCl_4$ at high HCl concentrations by adsorption on the polyamide.

Acetone–HCl mixtures

The R_F values of the metals in acetone–HCl–water mixtures are given in Tables III and IV.

On cellulose, acetone–HCl mixtures give excellent separations of Fe, Cu, Co, Mn and Ni, while many other ions move with the solvent or the acid front.

On polyamide, a number of interesting separations can be obtained: in 9:1

TABLE III

R_F VALUES OF METAL IONS ON POLYAMIDE 11 THIN LAYERS WITH ACETONE–HCl MIXTURES

Solvents: acetone–conc. HCl–water, in the following proportions by volume: S_1, 90:5:5; S_2, 90:1:9; S_3, 90:3:7; S_4, 90:7:3; S_5, 90:9:1. Supports: Polyamide 11 = Polygram Polyamid 11 MN layers; SA-2 = Sulphonic resin ion-exchange paper Amberlite SA-2; Cell 400 = Polygram Cell 400 MN layers.

Metal ion	Layer						
	Polyamide 11	SA-2	Cell 400	Polyamide 11			
	S_1	S_1	S_1	S_2	S_3	S_4	S_5
Pb(II)	0.37	0.73	1.0	0.32	0.29	0.25	0.33
Hg(II)	0.31	0.51	0.93	0.24	0.23	0.25	0.37
Bi(III)	0.05	0–0.25	1.0	0.10	0.05	0.03	0.06
Cu(II)	0.33	0.48	0.71	0.34	0.32	0.24	0.32
Cd(II)	0.42	0.70	0.80	0.31	0.34	0.37	0.54
Au(III)	0.62	0.70	1.0	0.56	0.50	0.62	0.92
Sb(III)	0.58	0.70	1.0	0.44	0.49	0.52	0.65
Fe(III)	0.72	0.70	1.0	0.56	0.50	0.81	0.98
Tl(III)	0.72	0.93	1.0	0.56	0.57	0.64	0.87
Co(II)	0.38	0.28	0.50	0.13	0.22	0.23	0.30
Mn(II)	0.39	0.11	0.23	0.14	0.20	0.31	0.43
Ni(II)	0.10	0.0	0.0	0.07	0.08	0.07	0.09
UO_2(II)	0.23	0.39	0.69	0.10	0.16	0.27	0.37
Zn(II)	0.34	0.62	0.89	0.37	0.30	0.26	0.32
Sn(IV)	0.61	0.84	0.97	0.64	0.50	0.59	0.80
Pt(IV)	0.06	0–0.39	1.0	0.05	0.04	0.04	0.07
Pd(II)	0.05	0.11	1.0	0.04	0.03	0.04	0.06
As(III)	0.61	0.66	0.8	0.56	0.49	0.60	0.89
HCl front				0.56	0.50	0.60	0.81

'ABLE IV

R_F VALUES OF METAL IONS ON POLYAMIDE II THIN LAYERS WITH ACETONE–HCl MIXTURES

olvents: acetone–5 N aqueous HCl in the following proportions by volume: S_1, 90:10; S_2, 80:20; 3, 60:40.

Metal ion	S_1	S_2	S_3
Pb(II)	0.37	0.31	0.38
Hg(II)	0.31	0.27	0.13
Bi(III)	0.05	0.08	0.06
Cu(II)	0.33	0.35	0.41
Cd(II)	0.42	0.43	0.34
Au(III)	0.62	0.64	0.08
Sb(III)	0.58	0.42	0.17
Fe(III)	0.72	0.64	0.09
Tl(III)	0.72	0.70	0.0–0.09
Co(II)	0.38	0.28	0.60
Mn(II)	0.39	0.30	0.84
Ni(II)	0.10	0.22	0.78
UO$_2$(II)	0.23	0.17	0.07
Zn(II)	0.34	0.35	0.25
Sn(IV)	0.61	0.65	0.42
Pt(IV)	0.06	0.04	0.03
Pd(II)	0.05	0.06	0.10
As(III)	0.61	0.64	0.73
HCl front	0.62	0.64	1.0

mixtures of acetone–aqueous HCl, only a few ions change their R_F values with the concentration of the HCl, viz., Mn(II), Co(II) and UO$_2$(II). Au(III) travels on the HCl front and is not adsorbed as from butanol–HCl mixtures. Similarly, Hg(II), Sb(III), Tl(III) and Fe(III) are not adsorbed and move with rather high R_F values. On the other hand, Bi(III), Pt(IV) and Pd(II) are strongly retained. Separation of Tl(III), Au(III) and Hg(II) is readily obtained, as shown in Fig. 4.

When the amount of water in this solvent system is increased (Table IV), the R_F values of Hg(II), Au(III), Sb(III), Fe(III), Tl(III) and UO$_2$(II) decrease considerably, while those of Ni(II), Co(II) and Mn(II) increase. The others remain essentially unchanged.

Thus, as the polarity (= water content) of the solvent increases, the chloro-complexes of the type HAuCl$_4$ are more strongly attracted to the polyamide phase.

The fact that Ni(II) is desorbed cannot be explained by a dissociation of the chloro-complex in the presence of more water because it does not form a chloro-complex. Therefore there seems to be a change from a stationary polar phase at low water concentrations to a one-phase system at higher water concentrations. While this would explain the considerable differences in R_F values for Ni(II), Mn(II) and Co(II), it does not explain why many metal ions, such as Zn(II), Cu(II), do not change their R_F values to any extent.

There is also a remarkably strong adsorption of the chloro-complexes of Bi(III) Pt(IV) and Pd(II) on the polyamide, irrespective of the solvent system, and this cannot be explained by arguments of the type used above.

The same ions are also retained very strongly on the sulphonic resin paper SA-2 (see Table III), and thus the phenomenon does not seem to be one tied to specific properties of polyamide.

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