CHROM. 3834

THE THIN-LAYER CHROMATOGRAPHY OF METAL IONS ON CELLULOSE IMPREGNATED WITH PRIMENE JM-T HYDROCHLORIDE

R. J. T. GRAHAM, L. S. BARK AND D. A. TINSLEY

Department of Chemistry and Applied Chemistry, University of Salford,
Salford 5, Lancs. (Great Britain)

(Received September 28th, 1968)

SUMMARY

Metal ions have been chromatographed on thin layers of cellulose impregnated with the hydrochloride of the long-chain amine Primene JM-T, using hydrochloric acid (1.0–9.0 M) as the mobile phase. Many separations are possible at a high impregnation coefficient which are not possible at a low one. The influence of the cellulose, of micellar aggregations of the stationary phase and chloro-complex formation are discussed.

INTRODUCTION

The relationship which exists between the concentration of the impregnant solution and the R_M values of species chromatographed by reversed-phase thin-layer chromatography has been substantiated by us for some phenols[1,2], and for some inorganic species[3]. This linear relationship between the logarithm of the concentration of the impregnant solution and the R_M value is to be expected from the underlying theories of partition chromatography which relate the partition coefficient, α, to R_F values[4], and R_F values to R_M values[5], *viz.*

$$\alpha = \frac{A_L}{A_S}\left(\frac{1}{R_F} - 1\right) \tag{1}$$

and

$$R_M = \log_{10}\left(\frac{1}{R_F} - 1\right) \tag{2}$$

with substitution of (2) in (1) to give

$$R_M = \log_{10}\alpha + \log_{10}A_S - \log_{10}A_L \tag{3}$$

The dependence of R_F values on the concentration of the impregnant solutions has been observed for the system Amberlite LA-1 hydrochloride using hydrochloric acid eluents[6] and for the impregnants Amberlite LA-2, triisooctylamine or Aliquat

336 with either aqueous hydrochloric acid or aqueous lithium chloride as the eluents[7]. In the first of these systems[6] optimum R_F values were obtained when a solution (0.1 M) of the amine hydrochloride was used to impregnate the support, silica gel. In the investigations involving other amines as impregnants[6], 0.1 M solutions of these amines were also used to impregnate the support. On this comparative basis, it was concluded that the primary amine hydrochloride, Primene JM-T hydrochloride, had weak adsorbing properties. This was confirmed in a later paper[8] in which the authors systematically investigated the behaviour of 55 ions in hydrochloric acid (1.0 M– 9.0 M)–amine hydrochloride (0.1 M) systems. Reference to these works[6,8] shows that few worthwhile separations of ions were obtained when Primene JM-T hydrochloride (0.1 M) was used as the impregnant. However, it has been shown by us that varying the concentration of this same impregnant over the range 0.1–0.7 M (ref. 3) the R_F values of some of the metal ions were significantly altered. For this reason it was decided to investigate metal ions in the system Primene JM-T hydrochloride using a high impregnation coefficient.

A significant difference between the present work and that of BRINKMAN et al.[6,8] is our use of cellulose as the support for the impregnant. The reasons for this have been discussed[3,7].

EXPERIMENTAL

The standardisation of the amine with respect to the amine functional group, the preparation of the amine solution in chloroform (0.3 M), its conversion to the amine hydrochloride and the checking of the completeness of the conversion of the free amine to the hydrochloride form have been reported earlier[3].

Cellulose (15 g of MN 300 HR) was slurried with either chloroform (70 ml) or with the amine hydrochloride solution in chloroform (70 ml of 0.3 M) and the slurries were used to coat clean glass plates (5 × 20 cm × 20 cm) with an applied layer thickness of 0.3 mm, to give non-impregnated layers and impregnated layers, respectively.

After air drying the layers to allow the chloroform to evaporate, they were spotted with the metal ion solutions (1 μl of 5 mg of metal ion per ml).

The chromatoplates were eluted with aqueous hydrochloric acid of different molarities in a sandwich-type saturation chamber[9]. The solvent front was allowed to rise a standard distance (14.0 ± 0.5 cm) from the point of application of the spots. After elution, the chromatoplates were first viewed under U.V. light whilst wet, then dried in an air oven at 120° for 15 min. After this time they were viewed under both visible and U.V. light. The ions were further identified by spraying with one or more of the following chromogenic reagents:

(i) 2-(pyridylazo)-2-naphthol, PAN (0.1 % w/v in ethanol);
(ii) 8-hydroxyquinoline (0.1 % w/v in ethanol);
(iii) Arsenazo(III) (0.1 % w/v in water);
(iv) 1,2-dihydroxybenzene-3,5-disulphonic acid (Na salt) (0.1 % w/v in water);
(v) p-dimethylamino-benzilidene-rhodanine (0.1 % w/v in ethanol).

RESULTS

The R_F values quoted are the mean values for at least five determinations of a given ion on different plates. The individual R_F values are reproducible to ± 0.02 R_F

units of that mean. Each plate carried a spot of Zn(II) as an internal standard[3].

The R_F values obtained from the non-impregnated chromatoplates are given in Table I whilst those obtained from the impregnated layers are given in Table II. The R_F spectra of the metal ions are given in Fig. 1.

DISCUSSION

The role of the cellulose

The behaviour of the metal ions on non-impregnated cellulose (Table I and Fig. 1) indicates that the alkaline earths, Fe(III), Ga(III), Se(IV), Pd(II), Th(IV) and UO_2^{2+} show no adsorption at low acid concentrations but that they have a significantly increasing adsorption at high acid concentrations. Pb(II) and Tl(I) are significantly adsorbed at low acid concentrations whilst the adsorption of Mo(VI) and Au(III) is independent of acid concentration. By contrast, it was found that on non-impregnated silica gel, using the same eluent systems[8], most metals travelled with the solvent front; exceptions were: Ti(IV), Zr(IV), Ag(I), Hg(I) and Sb(V), where significant adsorption occurred, and Sn(II), Sn(IV) and Sb(III), where some adsorption occurred at low acid concentrations. The differences between the two support media are therefore significant and the part played by them must be borne in mind when interpreting the results obtained from impregnated layers, particularly when low impregnation coefficients are used so that incomplete coverage of the substrate may be apparent[3]. However, for reasons given earlier[3], we considered cellulose to be preferable to silica gel.

The exact nature of the role of the cellulose is difficult to interpret. The alkaline earth elements, at high acid concentrations, show a decreasing adsorption with in-

TABLE I

R_F VALUES OF METAL IONS ON CELLULOSE LAYERS ELUTED WITH HYDROCHLORIC ACID

The followings metals were at the solvent front at all eluent concentrations: the alkali metals, Cu(II), Co(II), Ni(II), Mn(II), Cd(II), Y(III), In(III), and Bi(III).

Metal	Molarity of acid				
	1	3	5	7	9
Mg(II)	1.00	1.00	1.00	1.00	0.80
Ca(II)	1.00	1.00	1.00	0.88	0.80
Sr(II)	1.00	1.00	0.88	0.80	0.72
Ba(II)	1.00	0.86	0.78	0.67	0.54
Fe(III)	1.00	1.00	1.00	0.86	0.62
Zn(II)	1.00	1.00	1.00	1.00	0.90
Mo(VI)	0.72	0.66	0.67	0.70	0.70
Pd(II)	1.00	0.86	0.88	0.78	0.69
Ag(I)	Streaks	—	—	0.87	0.83
{ Re(VII)	1.00	1.00	1.00	1.00	0.91
{ Re(VII)	0.82	0.76	0.80	0.81	0.80
Au(III)	0.48	0.47	0.50	0.49	0.53
Ga(III)	1.00	1.00	1.00	0.74	0.65
Tl(I)	0.71	0.73	0.76	0.83	0.83
Sn(II)	0.89	0.74	0.68	0.61	0.63
Sn(IV)	0.88	0.83	0.69	0.67	0.61
Pb(II)	0.79	0.88	1.00	1.00	1.00
Se(IV)	0.90	0.92	0.89	0.88	0.79
Th(IV)	1.00	1.00	1.00	0.85	0.75
UO_2^{2+}	0.94	0.86	0.94	0.77	0.72

creasing atomic number. However, this cannot be simple cation exchange with the cellulose because, at the high acid concentrations used, the dissociation of the carboxylic acid groups on the cellulose is probably suppressed and no exchange is possible. As the general behaviour of these ions seems to be independent of the presence or absence of the impregnant from the cellulose, a possible explanation of this behaviour is precipitation chromatography. This is in agreement with the theory reported[8].

Chromatography on impregnated layers
 Nature of the amine hydrochloride impregnant
  In an earlier paper[3] we indicated that plots of R_M values *vs.* the logarithm of the amine hydrochloride in the slurrying solvent were linear up to 0.5 M loading. Above this concentration, the slopes of the plots altered. By a consideration of our results and the work of other authors[10,11] this may be explained in the following way. At low concentrations the amine hydrochloride molecules in the slurrying solvent, and hence on the layers are essentially monomeric, thus all the functional groups are available for the ion exchange process. This results in the rapid attainment of equilibrium and the establishment of sharp zones on the chromatogram[12]. At higher concentrations, intermolecular hydrogen bonding occurs resulting in the formation of micellar aggregates—caused by some polymerisation of the amine. We suggest that these micellar aggregates are transferred from the slurrying solvent to the layers. In the separation of ions on ion exchange resins there are probably two diffusion factors which are rate controlling, *viz.*

  (i) film diffusion;
  (ii) diffusion within the particle.
  The second of these becomes significant in liquid ion exchange systems only where micellar aggregates are present. This results in lower R_F values than could be expected where the system consists of monomers. Furthermore, this particle diffusion will slow down the rate of attainment of equilibrium and hence will contribute to the phenomenon of zone-spreading. This has been observed by us[3] for the species Zn(II), Pd(II) and Re(VII) at high amine hydrochloride loadings.

  A decrease in the ΔR_F values with a change in the loading of the impregnant on the cellulose has been observed by other workers[7]. They attributed this to changes in the A_L/A_S ratio consequent upon the increased amine hydrochloride loading reducing the availability (and effectiveness) of the capillaries of the cellulose so that smaller volumes of the mobile phase are drawn into the layer.

  Variations in the $\Delta R_F/R_M$ values caused by this effect alone would be gradual and would not result in the sharp change in the slope of the plots which we have observed. The sudden change in the slope of the plots becomes tenable only if we postulate a change in the nature of the impregnant on the layer from a monomeric species to a polymeric species which probably also drastically reduces the effective capillary volume of the cellulose. The combined effect would thus be exponential and would result in the phenomenon observed.

Separation in the Primene JM-T hydrochloride–hydrochloric acid systems
 The alkali metals (Table IIa). These are not separable.
  Beryllium, magnesium and the alkaline earths (Table IIb). Separation of the members of this group is possible in 8 M or in 9 M hydrochloric acid. Using the sub-

strate of amine hydrochloride with 9 M hydrochloric acid as the eluent a good separation of all five ions is obtained (Ba(II) tails at this high acid concentration).

The first-row transition metals (Table IIc). Except for Zn(II) and Fe(III) these metals have similar R_F values. It is possible to obtain separations of these two from each other and from the other elements of this third period in the acid range 7–9 M. The importance of the separation of iron from the other elements of this period is of interest in the investigation of the corrosion products of alloy steels. The conditions under which partial or complete separation of these components can be effected can be seen from Table II. The quantitative determination of the ions separated by this system will be reported soon.

TABLE II

R_F VALUES OF METAL IONS IN THE PRIMENE JM-T HYDROCHLORIDE/CELLULOSE–HYDROCHLORIC ACID SYSTEM

Location methods: (1) PAN/ammonia; (2) baking; (3) U.V. before drying; (4) visible; (5) Oxine/ U.V.; (6) Arsenazo(III)/U.V.; (7) 1,2-dihydroxybenzene-3,5-disulphonic acid (Na salt)/U.V.; (8) *p*-dimethylamine-benzilidene-rhodamine/U.V.

| Metal | Molarity of acid | | | | | | | | | Location method |
	1	2	3	4	5	6	7	8	9	
(a) The alkali metals										
Li(I)	1.00	1.00	1.00	1.00	1.00	1.00	0.90	0.85	0.81	2
Na(I)	1.00	1.00	1.00	1.00	1.00	0.90	0.89	0.86	0.82	2
K(I)	1.00	1.00	1.00	1.00	1.00	0.90	0.87	0.86	0.80	2
Rb(I)	1.00	1.00	1.00	1.00	0.90	0.87	0.85	0.81	0.77	2
Cs(I)	0.90	0.90	0.90	0.90	0.90	0.86	0.87	0.86	0.83	2
(b) Beryllium, magnesium and the alkaline earth metals										
Be(II)	Solvent front at all acid concentrations									5
Mg(II)	1.00	1.00	1.00	1.00	1.00	1.00	0.86	0.84	0.83	5
Ca(II)	1.00	1.00	1.00	1.00	1.00	1.00	0.86	0.71	0.66	5
Sr(II)	1.00	1.00	1.00	1.00	1.00	0.80	0.76	0.66	0.58	2,5
Ba(II)	1.00	1.00	0.83	0.79	0.78	0.65	0.55	0.50	0.33	5
(c) The first-row transition metals										
Sc(III)	1.00	1.00	1.00	1.00	0.92	0.87	0.81	0.77	0.72	5
TiO^{2+}	0.92	0.90	0.91	0.93	0.90	0.83	0.73	0.69	0.59	7
VO$_2$$^+$	1.00	1.00	1.00	1.00	0.92	0.91	0.91	0.85	0.84	1
Cr(III)	1.00	1.00	1.00	1.00	0.91	0.87	0.81	0.77	0.74	5
Mn(II)	1.00	1.00	1.00	1.00	0.92	0.87	0.85	0.81	0.76	1
Fe(III)	1.00	1.00	0.90	0.85	0.49	0.26	0.07	0.03	0.00	1
Co(II)	1.00	1.00	1.00	1.00	0.91	0.85	0.80	0.72	0.55	1
Ni(II)	1.00	1.00	1.00	1.00	0.91	0.86	0.82	0.80	0.74	1
Cu(II)	1.00	1.00	1.00	0.93	0.87	0.81	0.73	0.68	0.60	1
Zn(II)	0.56	0.43	0.47	0.54	0.57	0.59	0.59	0.58	0.54	1
(d) The second-row transition metals										
Y(III)	1.00	1.00	1.00	1.00	0.91	0.84	0.82	0.79	0.72	2,5
ZrO^{2+}	Streaks at all acid concentrations									
Nb(V)	a	a	0.69	0.74	0.83	a	a	a	a	2
Mo(VI)	0.55	0.55	0.56	0.54	0.53	0.53	0.49	0.42	0.44	3
Ru(IV)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4
Rh(III)	0.91	0.81	0.82	0.80	0.83	0.84	0.86	0.84	0.81	3
Pd(II)	0.02	0.09	0.17	0.25	0.28	0.29	0.31	0.29	0.28	1
Ag(I)	0.00	0.08	0.27	0.58	0.62	0.65	0.70	0.71	0.67	8
Cd(II)	0.32	0.35	0.43	0.55	0.57	0.60	0.61	0.61	0.59	1

TABLE II (continued)

Metal	Molarity of acid									Location method
	1	2	3	4	5	6	7	8	9	
(e) The third-row transition metals										
La(III)	0.82	0.87	0.89	0.85	0.82	0.79	0.75	0.74	0.71	2,5
Hf(IV)	Streaks at all acid concentrations									
Re(VII)	0.35	0.51	0.64	0.69	0.72	0.68	0.68	0.66	0.65	2
	0.05	0.13	0.23	0.32	0.40	0.43	0.46	0.49	0.49	2
Os(VIII)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3
Pt(II)	0.32	0.40	0.43	0.45	a	a	a	a	a	3
	0.00	0.02	0.03	0.04	0.05	0.04	0.04	0.04	0.04	3
Au(III)	0.00	0.00	0.00	0.00	0.02	0.02	0.03	0.03	0.03	3
Hg(II)	0.84	0.89	0.94	0.96	0.94	0.90	0.85	0.79	0.76	2
(f) Some p-block elements										
Al(III)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	5
Ga(III)	1.00	1.00	1.00	0.94	Str.	0.11	0.00	0.00	0.00	5
In(III)	0.86	0.85	0.83	0.80	0.74	0.66	0.66	0.54	0.47	1
Tl(I)	0.64	0.68	0.67	0.78	0.81	0.81	0.85	0.72	0.70	3
Sn(II)	0.63	0.46	0.31	0.23	0.18	0.12	0.10	0.08	0.08	3,5
Sn(IV)	0.12	0.04	0.01	0.01	0.00	0.00	0.00	0.00	0.00	3,5
Pb(II)	0.27	0.26	0.42	0.57	0.67	0.73	0.72	0.73	0.74	1
Sb(III)	0.78	0.79	0.82	0.85	0.84	0.78	0.76	0.73	0.72	2
Bi(III)	0.00	0.02	0.06	0.13	0.21	0.25	0.26	0.27	0.29	1
Se(IV)	0.90	0.89	0.90	0.88	0.90	0.32	0.25	0.20	0.16	2
(g) Some lanthanides										
Ce(IV)	1.00	1.00	1.00	1.00	1.00	1.00	0.91	0.86	0.80	5
Pr(III)	1.00	1.00	1.00	1.00	0.93	0.86	0.78	0.76	0.76	5
Nd(III)	0.79	0.86	0.89	0.89	0.91	0.90	0.86	0.82	0.77	2
Eu(II)	1.00	1.00	1.00	1.00	0.93	0.89	0.79	0.76	0.75	5
Dy(III)	1.00	1.00	1.00	1.00	1.00	0.85	0.77	0.78	0.78	5
Ho(III)	1.00	1.00	1.00	1.00	0.87	0.84	0.83	0.76	0.68	2
Er(III)	1.00	1.00	1.00	1.00	1.00	0.87	0.80	0.80	0.78	5
Tm(III)	1.00	1.00	1.00	1.00	1.00	0.92	0.90	a	a	5
Yb(III)	1.00	1.00	1.00	1.00	1.00	0.90	0.84	0.82	0.79	5
Lu(III)	1.00	1.00	1.00	1.00	0.91	0.87	0.84	0.81	0.78	5
(h) Some actinides										
Th(IV)	0.43	1.00	1.00	1.00	0.93	0.80	0.82	0.78	0.71	6
UO_2^{2+}	0.91	0.87	0.84	0.82	0.76	0.63	0.54	0.29	0.20	1

a Ion could not be detected.

The second-row transition metals (Table IId). If ZrO^{2+}, which streaks at all acid concentrations, is excluded, it is possible to separate the remaining elements.

Nb(V) was chromatographed at all acid concentrations but could not be detected except under the conditions shown (the sensitivities of many of the blanket reagents used for the visualisation of metal ions are very dependent not only upon the nature of the mobile phase but also upon the nature of the substrate).

The third-row transition elements (Table IIe). Some of the elements were difficult to detect in the systems used. For those which could be positively identified the following separations could be effected at all acid concentrations, *viz.* (a) Hg(II)–Au(III) and (b) Re(VII)–Os(VIII).

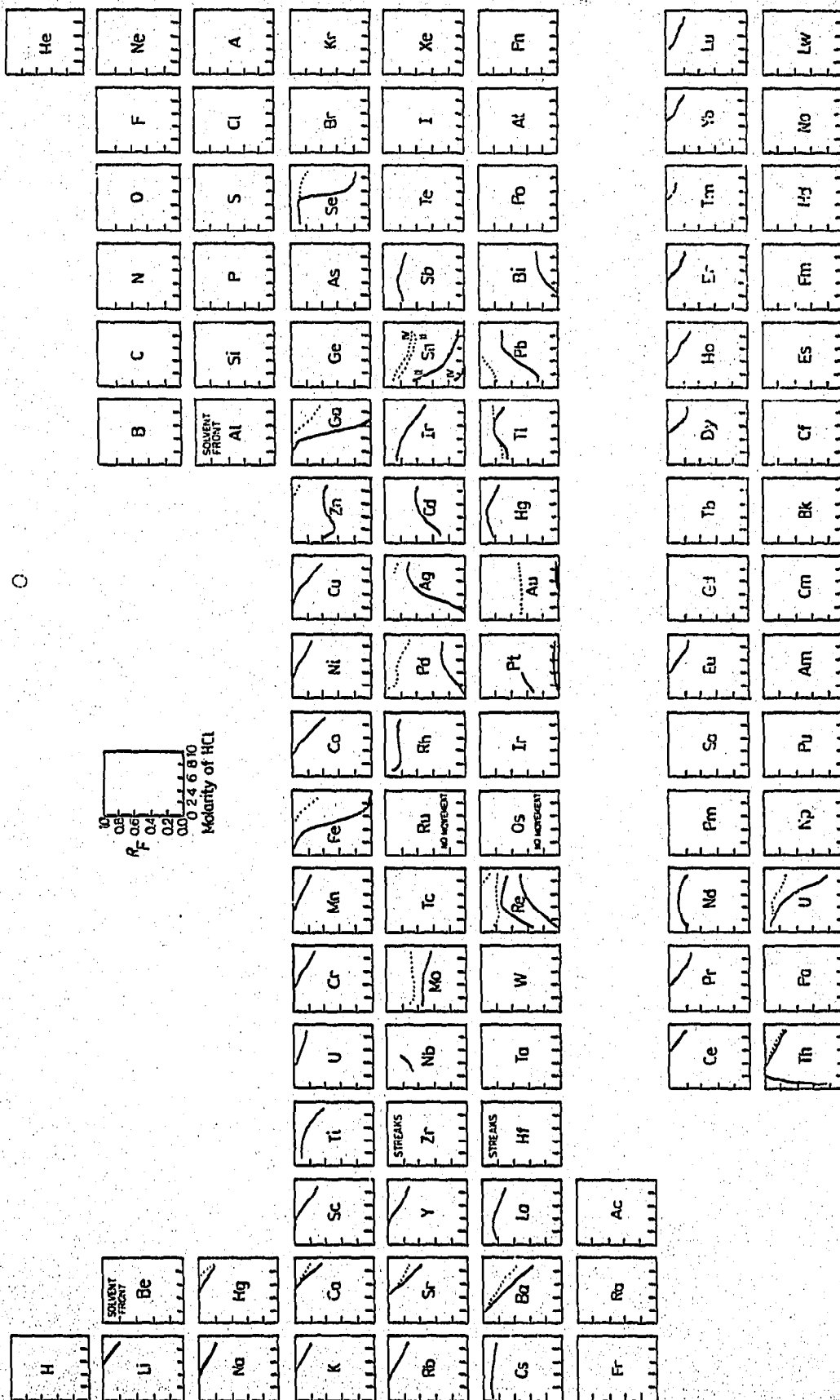At all acid concentrations except 1 *M*, Re(VII) could be separated from Pt(II)

Fig. 1. R_F Spectra of metal ions chromatographed on (a) ······ cellulose; (b) —— cellulose impregnated with Primene JM-T hydrochloride (0.3 M) using hydrochloric acid (0.0 to 9.0 M) as the mobile phase.

in spite of two spots appearing for Re(VII) over the whole acid range studied and for Pt(II) in the range 1–4 M.

Some p-block elements (Table IIf). One of the most interesting separations here is that of the aluminium group, Al(III), Ga(III), In(III) and Tl(I), all the members of which can be separated from each other in the acid range 6–9 M.

The two oxidation states of tin are separable from each other and from Pb(II) over the whole range of acid concentrations studied.

It was not possible to locate arsenic with any of the above reagents, nor with those reagents often used for the detection of this element, *e.g.* hydrogen sulphide, dithizone, so that a complete separation of the elements of this group cannot be claimed. Separation of the remaining two elements of the group Sb(III) and Bi(III) was possible at all acid concentrations.

The separation of Pb(II), Sn(II and IV) and Sb(III) in hydrochloric acid (1–5 M) is of potential importance since these metals are often used in industrial alloys.

Some lanthanides and some actinides (Table II, g and h). The separation of the lanthanides is generally not possible with the exception of the separation of Nd(III) from the others at low acid concentrations.

The separation of nuclear fission products is of importance, thus Th(IV) is separable from the rare earths and from the uranyl ion at 1 M acid concentration. The uranyl ion is separable from the bulk of the lanthanides at all acid concentrations though there is overlap with Nd(III) at low concentrations.

Other separations

Other separations of importance include: (a) Cr(III)–Mo(VI) at all acid concentrations. (b) Cu(II)–Ag(I)–Au(III) at 3 M acid. (c) Zn(II)–Hg(II)–Cd(II) at 1 M acid. (d) The platinum group metals are amenable to certain separations although it is not possible to separate all members of the group from each other, *e.g.* at 4 M acid, Pd(II) can be separated from Os(VIII), at 6 M acid, Ru(IV)–Rh(III)–Pd(II) are separable. The separation of Rh(III) from Os(VIII) occurs at all acid concentrations.

Some of the separations obtained are illustrated in Fig. 2.

A comparison of R_F values obtained from different systems

The R_F values obtained for a number of metal ions from different amine hydrochloride impregnated layers using aqueous hydrochloric acid as the eluent[8,13] are given in Table III.

Whilst these values generally support the view[6] that the adsorptive strength of the amines is: tertiary amine > secondary amine > primary amine, the table equally shows that the apparent adsorptive strength of a particular amine may be increased by an increase in the amount of amine hydrochloride on the layers. This is probably due to the increase in the number of active sites over the same area of plate. Irrespective of the reason for it, incontrovertable evidence is presented here for the advantage to be gained by using the higher loading of the weakly active impregnant. This is further emphasised by the following (selected) separations which were not possible in System 1 (Ref. 8) but have been found to occur in System 2: (a) Sb–Bi, (b) Zn–Cd–Hg, (c) Al–Ga–In–Tl, (d) Th–U, and (e) Fe–Co–Ni.

Not only has the higher loading of the weakly active impregnant advantages over lower loadings of the same material, but it has in many cases advantages over

TABLE III

A COMPARISON OF R_F VALUES OBTAINED FROM DIFFERENT AMINE HYDROCHLORIDE–HYDROCHLORIC ACID SYSTEMS

Systems: (1) Primene JM-T hydrochloride (0.1 M); (2) Primene JM-T hydrochloride (0.3 M); (3) Amberlite LA-1 hydrochloride (0.1 M); (4) Alamine 336 hydrochloride (0.1 M); (5) tri-n-octylamine hydrochloride (0.1 M).

Metal	Eluent (HCl) molar concentration	System 1[n8]	System 2	System 3[n8]	System 4[n8]	System 5[13]
Zn(II)	2	0.70	0.43	0.00	0.00	0.04
Cd(II)	2	0.70	0.35	0.00	0.00	—
Ag(I)	2	0.20	0.08	0.00	0.00	—
Pd(II)	3	0.50	0.17	0.00	0.00	—
Bi(III)	5	0.70	0.21	0.66	0.00	—
Mo(VI)	6	0.60	0.53	—	0.00	—
Re(VII)	6	0.80	0.68	0.02	0.00	—
Pb(II)	6	1.00	0.73	0.93	0.60	—
Fe(III)	7	0.50	0.07	0.00	0.00	0.00
In(III)	7	1.00	0.66	0.02	0.00	—
Co(II)	8	1.00	0.72	0.53	0.50	0.05
Cu(II)	8	0.90	0.68	0.73	0.00	0.04
UO_2^{2+}	8	0.80	0.29	0.00	0.00	—
Mn(II)	9	1.00	0.72	0.53	0.05	0.05

ᵃ Approximate R_F values obtained from R_F spectra[8].

low loadings of more strongly active impregnants where the increased binding of the metals to the substrates in many cases results in very low R_F values or even no migration at all. In a number of cases this has meant that in order to effect separations high acid molarities are required, e.g. Cu–Cd–Pb–Bi–Hg(II), and Zn–Cd–Hg(II). These elements were separable at 9 M acid in System 3 but the separation can be brought about in 1 M or 2 M acid in System 2.
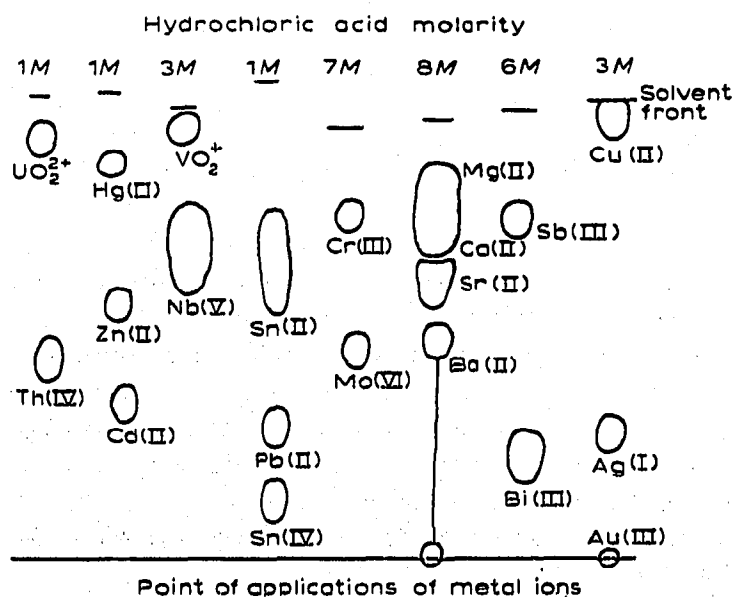

Fig. 2. Chromatomaps of some metal ions chromatographed on cellulose impregnated with Primene JM-T hydrochloride (0.3 M) using hydrochloric acid as the mobile phase.

The elements Pb–Bi–Sn(IV)–Cd, the components of Wood's metal, could not be completely separated in System 3, but in System 2 they can be separated in acid concentrations of $1\ M$ or 5–$8\ M$.

The R_F spectra and chloro-complex formation

Some of the variations of the R_F values of the metal ions have been shown to be due to the effect of the cellulose, but other variations are undoubtedly caused by the exchange of anionic chloro-complexes of the metals and the chloride ions of the amine hydrochloride. Metals which do not form chloro-complexes, such as the alkali metals, alkaline earths and the lanthanides, have high R_F values, whilst those metals which form chloro-complexes have values which depend upon the concentration of the acidic eluent.

The R_F spectra reported here show a close similarity with those obtained for the same metal ions chromatographed on layers of cellulose impregnated with a neutral organo-phosphorus compound, tri-*n*-butyl phosphate[14], when the results were explained on the basis of an anion exchange system involving chloro-complexes of the metal ions.

The possible natures of the chloro-complexes present in the organic phase in reversed-phase chromatography involving liquid anion exchangers have been discussed[15].

Comparison of R_F spectra with the corresponding liquid–liquid extraction behaviour

A comparison of our R_F spectra with extraction data obtained from similar systems[16] shows that those ions which have high extractability have low R_F values and *vice versa*. Where maxima occurred in the extraction curves minima appeared in the R_F spectra (*e.g.* Zn(II) and Cd(II)).

Comparisons of R_F spectra with extraction data can sometimes be misleading because of the effects of the substrate (*e.g.* the effect of the cellulose on the behaviour of the alkaline earths) in chromatography and the possibly synergistic or antagonistic effects of the supposedly inert organic diluent in extraction studies.

CONCLUSIONS

In reversed-phase chromatographic systems involving weakly active substrates an increase in the concentration of the impregnant on the support results in an increase in the retardation of the solutes and can lead to improved separations.

ACKNOWLEDGEMENTS

REFERENCES

1 L. S. BARK, J. DALY AND R. J. T. GRAHAM, *Intern. Symp. IV, Chromatog. Electrophorèse, 1966*, Presses Académiques Européennes, Brussels, 1968, p. 128.
2 R. J. T. GRAHAM, L. S. BARK AND J. DALY, *J. Chromatog.*, 33 (1968) 107.
3 R. J. T. GRAHAM, L. S. BARK AND D. A. TINSLEY, *J. Chromatog.*, 35 (1968) 416.
4 R. CONSDEN, A. H. GORDON AND A. J. P. MARTIN, *Biochem. J.*, 38 (1944) 224.

5　E. C. BATE-SMITH AND R. G. WESTALL, *Biochim. Biophys. Acta*, 4 (1950) 427.
6　U. A. TH. BRINKMAN, G. DE VRIES AND E. VAN DALEN, *J. Chromatog.*, 22 (1966) 407.
7　R. W. MURRAY AND R. J. PASSARELLI, *Anal. Chem.*, 39 (1967) 282.
8　U. A. TH. BRINKMAN, G. DE VRIES AND E. VAN DALEN, *J. Chromatog.*, 25 (1966) 447.
9　L. S. BARK, R. J. T. GRAHAM AND D. McCORMICK, *Talanta*, 12 (1965) 112.
10　Y. MARCUS, *Chem. Rev.*, 63 (1963) 139.
11　D. DRYSSEN AND M. DE J. TAVARES, *Acta Chem. Scand.*, 20 (1966) 2050.
12　E. CERRAI AND C. TESTA, *J. Chromatog.*, 6 (1961) 443.
13　D. McCORMICK, R. J. T. GRAHAM AND L. S. BARK, *Intern. Symp. IV, Chromatog. Electrophorese, 1966*, Presses Académiques Européennes, Brussels, 1968, p. 199.
14　L. S. BARK, G. DUNCAN AND R. J. T. GRAHAM, *Analyst*, 92 (1967) 347.
15　U. A. TH. BRINKMAN, G. DE VRIES AND E. VAN DALEN, *J. Chromatog.*, 31 (1967) 182.
16　T. ISHIMORI, K. KIMURA, E. NAKAMURA, W. P. CHENG AND R. ONO, *Nippon Genshiryoru Gakkaishi*, 5 (1963) 566.