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## THIN-LAYER CHROMATOGRAPHY OF METAL IONS ON CELLULOSE IMPREGNATED WITH THIOCYANATE SALTS OF LIQUID ANION EXCHANGERS

## II. THE SYSTEMATIC INVESTIGATION OF METAL IONS IN THE SYSTEM AMBERLITE LA-2-THIOCYANATE/AQUEOUS AMMONIUM THIOCYANATE

R. J. T. GRAHAM AND A. CARR

*Department of Chemistry and Applied Chemistry, The University of Salford, Salford, M5 4WT, Lancs. (Great Britain)*

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## SUMMARY

Sixty-eight metal ions have been chromatographed on thin layers of cellulose impregnated with Amberlite LA-2-thiocyanate using aqueous ammonium thiocyanate (0.1–7.0 *M*) as mobile phases. Most of the ions chromatographed exhibited the extremes of chromatographic behaviour in that they either remained at the point of application or they migrated with the solvent front. Chromatographic distribution was observed for VO<sup>2+</sup>, Mn(II), Ni(II), Cu(II), Ag(I), Cd(II), Tl(I), Pb(II) and Bi(III). Where distribution of the metal ions occurred the results are explained in terms of an anion-exchange mechanism.

## INTRODUCTION

Using thiocyanate media as mobile phases, metal ions have been chromatographed on substrates (paper or thin layer) impregnated with organophosphorous compounds, both neutral (*i.e.* tri-*n*-butyl phosphate<sup>1,2</sup> and tri-isooctyl phosphate<sup>3</sup>) and cationic (*i.e.* bis(diethylhexyl)orthophosphoric acid<sup>3</sup>), long chain tertiary amines<sup>4,5</sup> and the thiocyanate salts of long chain amines<sup>6,7</sup>.

In a previous paper<sup>7</sup> we considered the effects of a number of experimental parameters which were likely to affect the behaviour of metal ions when these are chromatographed on the thiocyanate form of the secondary amine—Amberlite LA-2 using ammonium thiocyanate solutions (0.1–7.0 *M*) as eluents. From these studies it was concluded that:

(a) Cellulose is to be preferred to silica gel as the support medium for the liquid ion exchanger.

(b) The  $R_F$  values obtained are independent of whether the amine is converted

to the salt form directly or indirectly, *i.e.* by forming the amine hydrochloride initially and using this to form the thiocyanate salt.

(c) The  $R_F$  values depend upon the degree of impregnation of the support with the amine salt.

By controlling the experimental conditions it was shown that a high degree of reproducibility of  $R_F$  values of the metal ions was obtained. Using the strictly standardised conditions discussed in the previous paper, we have extended our investigation to a systematic study of the behaviour of 68 metal ions on thin layers of cellulose impregnated with the thiocyanate form of the secondary amine—Amberlite LA-2 with aqueous ammonium thiocyanate of appropriate molarities as eluent system. The results of these studies are reported in this paper.

#### EXPERIMENTAL

Solutions of the metal ions (1 mg/ml) were prepared as previously described<sup>8</sup>. The standardisation of the amine, the preparation of the amine solution (0.1 *M* in chloroform), the preparation of the salt form of the amine by the indirect method and the preparation of the aqueous ammonium thiocyanate solutions, (0.1–7.0 *M*) have also been described<sup>7,9</sup>.

We used the method discussed in an earlier paper<sup>7</sup> for the preparation of the impregnated layers (Cellulose MN 300 HR + Amberlite LA-2-thiocyanate (0.1 *M*), the application of metal ions to the layer and the subsequent elution of the chromatolayers in our double saturation chamber—the polythene bag technique<sup>10,11</sup>.

The eluted plates were either viewed under ultraviolet light whilst still wet, inspected under visible light or sprayed with one of the following chromogenic reagents in order to identify the position of the metal ions on the chromatolayers:

- (1) 1-(2-pyridyl-azo)-2-naphthol(PAN) (0.1% w/v in ethyl alcohol);
- (2) 8-hydroxyquinoline (0.1% w/v in ethyl alcohol);
- (3) diphenyldithiocarbazon (dithizone) (0.1% w/v in chloroform);
- (4) (2,7-bis-(O-arsono-phenyl-azo)-;1,8-dihydroxy-naphthalene-;3,6-disulphonic acid (sodium salt) (Arsenazo III) (0.1% in water);
- (5) Potassium iodide solution (0.5 *M*);
- (6) Acidic stannous chloride solution.

The appearance of the metal ions on the layers after the appropriate treatment are listed in Table I.

#### RESULTS AND DISCUSSION

The  $R_F$  values, being the mean values of at least 6 determinations are given in Table II. A spot of Mn(II) was applied to each plate as an internal standard. The  $R_F$  value of this standard has been shown to be highly reproducible<sup>7</sup> (*i.e.* to  $\pm 0.02 R_F$  units). The data given in Table II were obtained from plates on which the  $R_F$  values of the standard were reproducible to within its predetermined mean value.

Using these highly reproducible  $R_F$  values we have investigated the system in light of the possible mechanisms *viz.*:

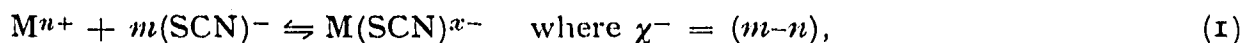


TABLE I

METHODS USED FOR THE IDENTIFICATION OF METAL IONS ON CHROMATOLAYERS

<i>Treatment of plates</i>	<i>Metals</i>	<i>Colour</i>
Coloured complexes without any treatment	TiO <sub>2</sub>	pale yellow
	Fe(III)	blood red
	Co(II)	turquoise
	Ru(III)	black
	Pd(II)	yellow
	UO <sub>2</sub> <sup>2+</sup>	pale yellow
	Bi(III)	pale yellow
UV wet plate	VO <sup>2+</sup>	dark spot
	ZrO <sup>2+</sup>	dark spot
	Nb(V)	dark spot
	Hg(II)	dark spot
	Ta(V)	dark spot
	Pt(II)	dark spot
	Pt(IV)	dark spot
Rh(III)	dark spot	
Spray plates with PAN and expose to ammonia vapour	Mn(II)	red spot
	Ni(II)	red spot
	Zn(II)	red spot
	Ga(III)	red spot
	Mo(VI)	purple spot
	In(III)	red spot
Spray with Oxine and expose to UV	Alkaline earths	fluorescent spot under UV
	Al(III)	
	Cr(III)	
Dithizone	Cu(II)	pink-red spot
	As(III)	orange spot
	As(V)	orange-yellow spot
	Ag(I)	pink spot
	Cd(II)	pink spot
	Sn(II)	orange spot
	Sb(III)	orange spot
	Bi(III)	orange spot
	Au(III)	orange spot
	Hg(II)	orange spot
	Se(IV)	orange spot
	Te(IV)	orange spot
Arsenazo(III)	Sc(III), Y(III)	green spot on blue background
	Lanthanides, UO <sub>2</sub> <sup>2+</sup> ,	green spot on blue background
	Th(IV)	
Potassium iodide	Tl(I)	faint yellow spot in visible light, dark spot under UV
Stannous chloride	W(VI)	dark spot under UV, pale yellow spot in visible light

TABLE II

$R_F$  VALUES OF METAL IONS CHROMATOGRAPHED ON CELLULOSE IMPREGNATED WITH AMBERLITE LA-2-THIOCYANATE/AQUEOUS AMMONIUM THIOCYANATE

Ion	Molarity of ammonium thiocyanate solution								
	0.1	0.5	1.0	2.0	3.0	4.0	5.0	6.0	7.0
<i>Block elements</i>									
<i>Alkali metals</i>									
Li	a								
Na	a								
K	a								
Rb	a								
Cs	a								
<i>Alkaline earths</i>									
Be	1.00	1.00	1.00	1.00	1.00	1.00	streaked		0.00
Mg	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Ca	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Sr	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Ba	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
<i>First row transition elements</i>									
Sc(III)	1.00	1.00	1.00	streaked		0.00	0.00	0.00	0.00
TiO <sup>2+</sup>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
VO <sup>2+</sup>	0.00	0.02	0.05	0.06	0.07	0.10	0.12	0.15	0.17
Cr(III)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Mn(II)	0.81	0.70	0.58	0.48	0.44	0.41	0.42	0.44	0.46
Fe(III)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Co(II)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni(II)	0.69	0.76	0.85	1.00	1.00	1.00	1.00	1.00	1.00
Cu(II)	0.00	0.03	0.07	0.17	0.34	0.52	0.74	0.79	0.81
Zn(II)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<i>Second row transition elements</i>									
Y(III)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
ZrO <sup>2+</sup>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nb(V)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mo(VI)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ru(IV)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Rh(III)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pd(II)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ag(I)	0.00	0.02	0.08	0.31	0.58	0.74	0.85	1.00	1.00
Cd(II)	0.00	0.00	0.00	0.04	0.08	0.18	0.30	0.44	0.58
<i>Third row transition elements</i>									
Hf(IV)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ta(V)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
W(VI)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Re(VI)	a								
Os(VII)	a								
Ir(III)	a								
Pt(II)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Au(III)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hg(II)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

TABLE II (continued)

Ion	Molarity of ammonium thiocyanate solution								
	0.1	0.5	1.0	2.0	3.0	4.0	5.0	6.0	7.0
<i>Some p-block elements</i>									
Al(III)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Ga(III)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
In(III)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Tl(I)	0.74	0.71	0.69	0.76	0.87	1.00	1.00	1.00	1.00
Sn(II)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sn(IV)	"								
Pb(II)	0.32	0.30	0.32	0.52	0.69	0.83	0.95	1.00	1.00
As(III)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
As(V)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Sb(III)	"								
Bi(III)	0.00	0.00	0.00	0.03	0.04	0.05	0.18	0.32	0.58
Se(IV)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Te(IV)	Streaked at all concentrations								
<i>The lanthanides</i> Excluding Pm(III) which was not chromatographed, all had $R_F$ values of 1.00.									
<i>Some actinides</i>									
Th(IV)	Streaked at all concentrations								
U(VI)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

" These elements were chromatographed but could not be detected on the eluted chromatogram by the spray reagents normally used for their detection<sup>8,10</sup>.

*i.e.* one involving the anionic thiocyanate complexes of the metals, and



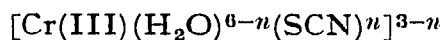
*i.e.* one involving the uptake of a neutral thiocyanate complex of the metal ion<sup>5</sup>.

From Table II, it can be seen that the ions can be classified into three groups according to their chromatographic behaviour, *viz.*, (a) ions which travel with the solvent front; (b) ions which remain at the point of application at all concentrations of ammonium thiocyanate investigated; (c) ions which lie between the extremes of (a) and (b).

#### (a) Ions which travel with the solvent front

Ions which fall into this category include the alkaline earths, some p-block elements and the lanthanides. Apart from the first member of the second row transition metals (*i.e.* Y (III)), the only transition element which falls into this group is Cr(III). The behaviour of this last ion is of interest in the interpretation of the possible mechanisms involved in the system. Thus these elements either (a) form complexes (neutral or anionic) which are not retarded by the anion exchanger of intermediate strength used in this investigations or, (b) do not form such complexes under the conditions of the chromatographic experiments conducted by us.

Cr(III) is known to form a series of well-defined thiocyanato complexes of general formula



where  $n = 1-6$  (refs. 12 and 13).

The anionic complexes of Cr(III) (*i.e.* these compounds in which  $n = 4-6$ ) have been successfully chromatographed on anion exchangers<sup>14,15</sup>. The neutral complex (*i.e.*  $n = 3$ ), however, was hardly retarded at all. This overall behaviour is in contrast with our failure to retard the Cr(III) ion at any ammonium thiocyanate molarities. A similar failure to retard this ion on the stronger tertiary amine exchangers has been reported<sup>5</sup>. BAGLIANO *et al.*<sup>16</sup> using either thiocyanic acid or mixtures of thiocyanic acid and aqueous potassium thiocyanate as eluent have chromatographed Cr(III) on filter paper, anionic cellulose exchange paper and anionic resin impregnated paper. For the most part they found little differences in  $R_F$  values, which with one exception were greater than 0.8  $R_F$  units.

These results strongly suggest that the  $[\text{Cr(H}_2\text{O)}_6]^{3+}$  is, under the conditions of the systems studied, kinetically inert so that replacement of the water ligand with the thiocyanate ligand does not take place and consequently the ion travels close behind the solvent front.

BAGLIANO *et al.* did not comment on the comparability of the behaviour of the  $[\text{Cr(H}_2\text{O)}_2]^{3+}$  on the normal cellulose and on the modified (*i.e.* chemically or impregnated) celluloses. We suggest that some form of interaction with the common factor, *i.e.* the cellulose matrix, is responsible for the behaviour observed by them—possibly with residual carboxylic acid groups in the cellulose functioning as weak cation exchangers for the cation. That such a behaviour is not observed either by us or by others using reversed-phase systems is taken as evidence for the complete coverage of the cellulose by the liquid anion exchanger<sup>7,9</sup>.

Overall, we here present evidence for the failure of the Cr(III) ion to form anionic thiocyanate complexes in the chromatographic systems studied. Whilst, by implication, it is possible that a similar behaviour is responsible for the failure of the remaining ions in this group to be retarded by the ion-exchange mechanism, we have no evidence here to discount the second possibility outlined above, namely the part played by the strength of liquid anion exchanger in governing retardation of the ions. (This effect will be considered in a subsequent paper.)

#### (b) Ions which remain at the point of application

The metals which remained at the point of application in all ammonium thiocyanate solvent systems are for the most part transition elements. It is particularly noticeable that the whole of the second row transition elements, with the exception of Ag(I) and Cd(II) are completely retarded, as are all those elements of the third transition series which could be positively identified on the chromatogram.

The strong absorption of these ions could be due either to the formation of strongly absorbed complexes or the formation of insoluble thiocyanates. The former appears to be the more likely explanation because a number of crystalline salts of the second and third transition series have been prepared containing the metal and the thiocyanate ion as the complex anions<sup>17,18</sup>.

The low instability constants of  $[\text{Au(SCN)}_4]^-$ ,  $[\text{Hg(SCN)}_4]^{2-}$ ,  $[\text{Co(SCN)}_4]^{2-}$  and

$[\text{Zn}(\text{SCN})_4]^{2-}$  (ref. 19), also suggest that these metals remain at the point of application because of the formation of strongly absorbed anionic complexes.

(c) *Ions which show chromatographic distribution*

Eqns. 2 and 4 suggest that the interaction between the metal ions and the stationary phase involves either ion exchange (eqn. 2) or an association which results in the neutral complex being converted to an anionic form on the exchanger (eqn. 4). Thus the latter mechanism appears to differ from the former in degree only, *i.e.* in the manner of uptake for, after the initial uptake, the metal species is held in its anionic form. Consequently its subsequent displacement from the layers is likely to be in the same form. This is a reasonable supposition for if the anionic form is kinetically stable on the liquid ion exchanger in the presence of a relatively small number of  $(\text{SCN})^-$ , it will also be stable in a solution rich in such ions, *i.e.* we are of the opinion that it is not possible to distinguish kinetically between the labile  $(\text{SCN})^-$  on the liquid ion exchanger and those present in the mobile phase. Therefore the system can be treated simply as one in which, whilst accepting the possibility of the original uptake of the species as a neutral complex, its subsequent removal will be one of ion exchange and as such will therefore depend to a large extent on the concentration of the displacing anion, the  $[\text{SCN}]^-$  in the mobile phase.

Fig. 1 shows the  $R_F$  spectra of those metal ions, all of which are known to form

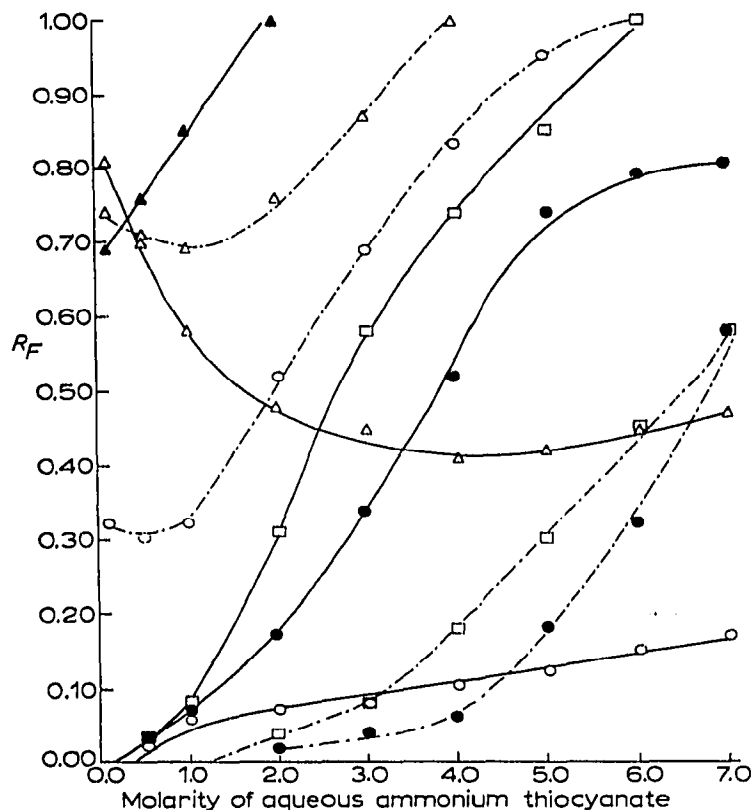
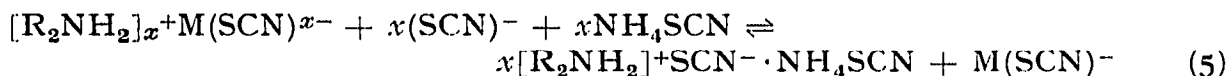


Fig. 1.  $R_F$  values of metal ions vs. concentration of aqueous ammonium thiocyanate mobile phase (moles ( $\blacktriangle$ — $\blacktriangle$ ), Ni(II); ( $\triangle$ — $\triangle$ ), Mn(II); ( $\triangle$ — $\cdot$ — $\triangle$ ), Tl(I); ( $\circ$ — $\circ$ ),  $\text{VO}^{2+}$ ; ( $\circ$ — $\cdot$ — $\circ$ ), Pb(II); ( $\square$ — $\square$ ), Ag(I); ( $\square$ — $\cdot$ — $\square$ ), Cd(II); ( $\bullet$ — $\bullet$ ), Cu(II); ( $\bullet$ — $\cdot$ — $\bullet$ ), Bi(III).

anionic thiocyanate complexes<sup>20</sup>, which migrate in the systems studied. For the greatest number of ions, it is seen that the  $R_F$  values increase with an increase in the  $(\text{SCN})^-$  concentration of the mobile phase thus giving credence to the above supposition. In the case of Pb(II), Tl(I) and Mn(II), however, the  $R_F$  values initially fall with increasing  $(\text{SCN})^-$  concentration, then they go through a minimum before showing a rise at the highest  $(\text{SCN})^-$  concentration studied. This behaviour for Mn(II) is interpreted as being indicative of the change in the nature of the Mn(II) ion in the system from the cationic  $\text{Mn}^{2+}$  through the neutral species to the anionic thiocyanate form. Evidence for the probable presence of mixed species is based on the nature of the spot which was somewhat diffuse at low  $(\text{SCN})^-$  concentrations becoming more compact at higher concentrations<sup>7</sup> suggesting the presence of more than one species in the system and that during the chromatographic process a slow equilibrium occurred between the species.

The behaviour of Be(II) and Sc(III) is of interest in the above context. These ions, at low  $(\text{SCN})^-$  concentration move with the solvent front but at certain concentrations (5.0–6.0 M for Be(II) and 2.0–3.0 M for Sc(III)) they formed streaks from the point of application in the direction of the travel of the mobile phase. Above these concentrations they remained at the point of application. Both these ions are known to form neutral complexes<sup>20</sup> so that it may be that at the intermediate concentration an equilibrium exists between the simple Be(II) and Sc(III) ions and the neutral complexes but that at high concentrations they exist entirely as the neutral form which, having associated with the liquid anion exchanger, becomes retarded. A similar equilibrium between species probably accounts for the streaking of Te(IV) and Th(VI).

In the foregoing discussion, it is presumed that the displacement of the anionic metal complex from the ion exchanger is a result of a mass action effect in which the equilibrium illustrated by eqn. 2 is driven to the left by an excess of the simple  $(\text{SCN})^-$ . However, alternative mechanisms can be postulated in which the displacer is a combination of the simple  $(\text{SCN})^-$  with the undissociated ammonium thiocyanate, *viz.*:



or



Evidence for the probable existence of these mechanisms (eqns. 5 and 6) has been put forward by Goro<sup>21</sup>, who has made the following observations concerning the extraction of ammonium thiocyanate from water into a solution of a quaternary ammonium thiocyanate salt, Quatamin T-08 in toluene:

(a) ammonium thiocyanate in excess of the stoichiometric amount is absorbed from the aqueous phase by the organic phase and the amount so absorbed increases with the increase in the concentration of the thiocyanate in the aqueous phase.

(b) log–log plots of the distribution coefficients of the ammonium thiocyanate *vs.* the concentration of the extractant in the organic phase indicated the formation of a 1:1 complex between the extractant and the ammonium thiocyanate.



(c) The infrared spectrum of the organic solution of the extractant, after its equilibration with the aqueous phase containing varying concentrations of the ammonium thiocyanate, showed absorption bands which clearly indicated the presence of the ammonium radical in the organic phase. The intensities of these bands increased with an increase in the concentration of the ammonium thiocyanate in the aqueous phase.

It is difficult to decide from chromatographic evidence alone if the simple  $(\text{SCN})^-$  is responsible for the displacement of the anionic metal complexes from the liquid anion exchanger or if it is displaced by a combination of the simple  $(\text{SCN})^-$  and the undissociated ammonium thiocyanate. However, it is felt by the present authors that the work of GOTO<sup>21</sup>, coupled with the proposal of the formation of a similar complex during the extraction of  $\text{Co}(\text{SCN})^{2-}$  into tri-*n*-octylamine from acidic thiocyanate media<sup>22</sup> presents strong evidence for the probability of the mechanisms exemplified by eqns. 5 and 6 occurring in our chromatographic system.

*(d) A comparison with other ion-exchange systems*

In general, the behaviour observed by us for those metals which showed chromatographic distribution in our system is comparable with that observed by other workers<sup>4-6</sup>.

An advantage of our system over that proposed by WAKSMUNDSKI AND PRZESZLAKOWSKI<sup>4</sup> and PRZESZLAKOWSKI<sup>5</sup> lies in our use of much smaller impregnation coefficients to achieve comparable results; thus it appears that the  $R_F$  spectra shown by these workers were obtained on layers impregnated with 100% of the impregnant, tri-*n*-butylamine, compared with our use of a low impregnation coefficient (0.1 *M*) of our secondary amine.

The  $R_F$  values obtained by BRINKMAN *et al.*<sup>6</sup> are higher than those obtained by us for the same impregnation coefficient. This, as already discussed by us<sup>4</sup>, is almost certainly because of the use of silica gel as the impregnant support by these workers, though it is accepted that some differences between our respective systems may be a direct result of their use of acidified thiocyanate media.

It is difficult to make a direct comparison of the results obtained by us with results obtained for the elution of metal ions from anion-exchange resins by other workers for frequently these workers have eluted their columns with mixed eluent systems<sup>23-25</sup>. However, TURNER *et al.*<sup>26</sup> and MAJUMDRA AND MITRA<sup>27</sup> both used simple thiocyanate media. Significantly both sets of workers report the precipitation of Cu(II) as a black precipitate on the resin. A similar behaviour was reported for Hg(II) (ref. 26) and for  $\text{VO}^{2+}$  (refs. 26 and 27) though TURNER *et al.*<sup>26</sup> reported that the latter could be eluted with thiocyanate (8.0 *M*). This behaviour is in marked contrast with our observations on the chromatographic distribution of Cu(II) and  $\text{VO}^{2+}$  in our systems. Thus the use of liquid ion exchangers would appear to have certain advantages over the use of resins for these two elements. Surprisingly both groups of workers<sup>26,27</sup> claim that Ni(II) was not absorbed in their system whilst MAJUMDRA AND MITRA<sup>27</sup> stated that Tl(I) and Th(IV) were not absorbed. This again contrasts with our observed retention of Ni(II) and Tl(I) and streaking of Th(VI).

It is not possible at this juncture to compare the results obtained by us on thin layers of liquid anion exchangers with the results obtained by other workers using, in the main, modified cellulose anion exchangers<sup>16,28,29</sup> because they used

acidified thiocyanate media. Such a consideration will therefore be deferred until a subsequent paper. However, we do observe that for many of the metal ions which we report as having migrated with the solvent front, BAGLIANO *et al.*<sup>16</sup> report some retardation. The reason for this is probably, as given for Cr(III) above, the presence of residual carboxylic acid groups on the cellulose matrix retarding the ions by a cation exchange mechanism. This is another reason for favouring the use of liquid anion exchangers as impregnants rather than the use of modified celluloses.

(e) *The separation of metal ions*

From the results obtained, it is obvious that the separation of metal ions in the system Amberlite LA-2 thiocyanate/aqueous ammonium thiocyanate will have little application in the characterisation of metal ions on the basis of their  $R_F$  values. Notwithstanding this, however, a practical potential exists for the technique in the purification of any of the ions which show chromatographic distribution from those which illustrate the extremes of chromatographic behaviour, *i.e.* those which have  $R_F$  values of either 1.00 or 0.00. Such a technique has been used by HAMAGUCHI *et al.*<sup>23-25</sup>.

#### CONCLUSIONS

The chromatographic behaviour of metal ions on thin layers of cellulose impregnated with the liquid anion exchanger Amberlite LA-2-thiocyanate using aqueous ammonium thiocyanate (0.1-7.0 *M*) as stationary phases can be explained in terms of an anion exchange mechanism. The system, however, appears to have little value as a means of characterising the metal ions on the basis of their  $R_F$  values.

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