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SOME ASPECTS OF THE USE OF A LIQUID ANION EXCHANGER IN INORGANIC THIN LAYER CHROMATOGRAPHY

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SUMMARY

The metal ions zinc(II), palladium(II) and rhenium(VII) have been chromatographed in hydrochloric acid (3 M) on layers of cellulose impregnated with different amounts of the liquid anion exchanger Primene JM-T-HCl (0.0 M–0.7 M) and on layers of cellulose of fixed exchanger loading (0.3 M) at various concentrations of aqueous hydrochloric acid (1 M–9 M). The optimum loading of amine hydrochloride is discussed. The mechanism of the chromatographic process is discussed in terms of the formation of the complex anion and the suppression of the ionisation of these complex species.

Various liquid anion exchangers have been used as substrates in the thin-layer chromatographic separation of metal ions[1–6]. The materials used as the support for the exchangers include silica gel[1–5], kieselguhr[3], polyethylene[3], polyglycol[3] and cellulose[6].

This paper reports the results of investigations of the behaviour of metal ions in a chromatographic system of thin layers of the liquid anion exchanger Primene JM-T-hydrochloride, supported on cellulose and using various concentrations of aqueous hydrochloric acid as the eluent. The effects on the R_F values of the metal ions, of varying the loading of the amine hydrochloride, and the eluent composition have been investigated. The metals zinc, palladium and rhenium were chosen as typical members of the 1st, 2nd and 3rd long periods of the Periodic Table. Each of these compounds is known to form anionic chloro complexes.

The mechanism of the behaviour of such complexes on chromatographic systems is of potential importance in compiling chromatographic systems for the rapid qualitative and quantitative analysis of metal solutions. The importance of combining a separation technique with a concentration technique has been previously discussed[1].

EXPERIMENTAL

Preparation of standard solutions of the exchanger

Primene JM-T is a mixture of C_{18} to C_{24} trialkyl methylamines. In order to prepare solutions of known amounts of amine, it was standardised by titration with

perchloric acid in a glacial acetic acid medium. Crystal violet was used as the visual indicator. The molarity is stated with respect to the amine functional grouping.

The amine, in chloroform, was converted to the hydrochloride by shaking with a known and excess amount of $2M$ hydrochloric acid. The degree of conversion of the amine group to the hydrochloride was ascertained by a Volhard determination of the chloride in the organic layer, and by titrating the excess acid with standard alkali. Each batch of amine used was quantitatively converted to the hydrochloride.

Preparation of chromatoplates

Cellulose (15 g MN 300HR) or silica gel (30 g) (MN-N-HR) was slurried with various concentrations of solutions of the amine hydrochloride in chloroform and the resultant slurry was used to coat glass plates (5 × 20 cm × 20 cm). The plates were air dried for 30 min after which they were ready for use.

Solutions (1 μl) of each of the three metal ions Zn(II), Pd(II) and Re(VII) containing 1 mg/ml of metal ion were simultaneously spotted on to the chromatoplates[7]. The spots were air dried.

The chromatoplates were then placed in a double saturation chamber[7] and eluted by an ascending technique with aqueous hydrochloric acid solutions of various molarities (1.0–9.0 M). The solvent front was allowed to travel a standard distance (14 ± 0.5 cm) in each of the systems studied.

The plates were then dried in an air oven at 120° for 15 min. When dry, they were examined under visible light. Rhenium appeared as two spots, the upper spot being light coloured and the lower one dark. The zinc and palladium were visualised by spraying the plates with PAN (1-(2-pyridyl-azo)-2-naphthol) and then exposing them to ammonia vapour. The zinc appeared as a red spot and the palladium as a green one.

RESULTS

Table I shows the variation of the R_F/R_M values with the loading of the plates at a fixed eluent composition.

Table II shows the variation in the R_F values of the metal ions caused by variation of the composition of the eluent, with a fixed loading of stationary phase.

The average time of elution for a standard distance from the point of application is given in both tables.

DISCUSSION

Choice of support material

In preliminary investigations we considered both cellulose and silica gel as supports for the amine hydrochloride. The silica gel supported layers gave slightly more discrete spots than did the corresponding cellulose layers but this advantage over the cellulose layers was completely nullified by the tendency of the silica gel to flake off the plates when the eluents were placed in the saturation chamber. The result of this was either to prevent the eluent from flowing through the layers or to cause such irregular solvent fronts, as to make many of the chromatograms run on silica gel impregnated layers, of insufficient reproducibility to be used for comparative or

TABLE I

R_F AND R_M VALUES OF SOME METAL IONS ON CELLULOSE LAYERS IMPREGNATED WITH VARYING CONCENTRATIONS OF PRIMENE JM-T HYDROCHLORIDE WITH 3 M HYDROCHLORIC ACID AS THE ELUENT

		Loading of Primene JM-T-HCl (molarity with respect to $-NH_2$)							
		0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7
Zn	R_F	0.945	0.700	0.560	0.470	0.380	0.35(5)	0.26(5)	0.190
	R_M	−1.222	−0.368	−0.105	0.052	0.194	0.260	0.443	0.630
Pd	R_F	0.860	0.400	0.240	0.170	0.120	0.090	0.060	0.04(5)
	R_M	−0.788	0.176	0.501	0.689	0.865	1.005	1.195	1.326
Re	R_F	0.75(5)	0.460	0.310	0.230	0.170	0.135	0.09(5)	0.08(5)
	R_M	−0.488	0.070	0.348	0.525	0.689	0.806	0.978	1.032
Re	R_F	0.92(5)	0.800	0.720	0.635	0.570	0.520	0.420	0.34(5)
	R_M	−1.097	−0.602	−0.410	−0.240	−0.122	−0.035	0.140	0.279
Average time of run (min)		38	55	80	97	122	147	200	233

Each R_F value is the average of at least four values, differing by not more than 0.02 units from the stated mean. Values such as 0.35(5) indicate the value as being very much nearer 0.355 than 0.350 or 0.360.

TABLE II

R_F VALUES OF SOME METAL IONS ON CELLULOSE LAYERS IMPREGNATED WITH 0.3 "MOLAR" PRIMENE JM-T HYDROCHLORIDE WITH VARYING CONCENTRATIONS OF HCl AS THE ELUENT

		Concentration of HCl (molar)								
		1	2	3	4	5	6	7	8	9
Zn	R_F	0.560	0.430	0.470	0.53(5)	0.570	0.590	0.58(5)	0.57(5)	0.540
Pd	R_F	0.020	0.090	0.170	0.250	0.280	0.290	0.310	0.290	0.280
Re	R_F	0.350	0.510	0.63(5)	0.690	0.720	0.680	0.680	0.660	0.650
Re	R_F	0.050	0.130	0.230	0.320	0.400	0.430	0.460	0.490	0.490
Time of run (min)		54	73	97	110	125	146	184	220	303

quantitative studies. The elution rate on silica gel layers was slower than on the comparable cellulose layer. This may be caused by the tendency of the layers to flake off the plate at or below the level of the eluent reservoir surface and hence to give a small "wick". For these and other reasons[8] we have thus preferred to use cellulose as the support.

Where it was possible to obtain acceptable R_F values from the impregnated silica gel layers, they were invariably higher than those obtained from the corresponding cellulose system (Fig. 1). The order of these values is similar to that reported for the separation of some metal ions using TBP impregnated cellulose and silica layers[8].
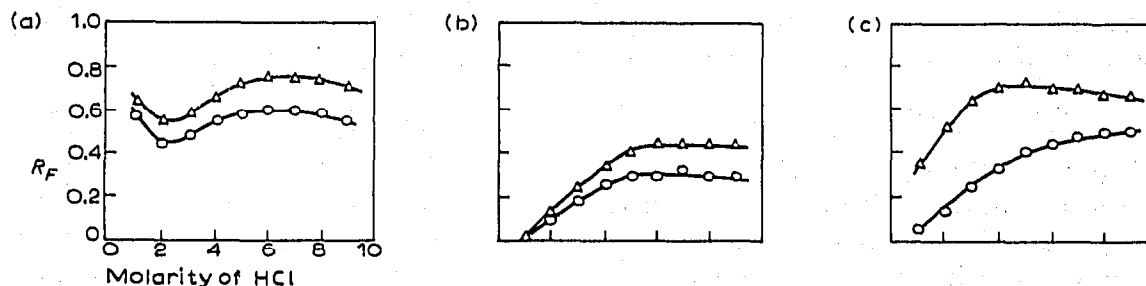
Fig. 1. R_F values *versus* molarity of hydrochloric acid. (a) (— △— △—) Zn on silica gel impregnated with 0.3 M Primene JM-T-HCl. (—O—O—) Zn on cellulose imperganted with 0.3 M Primene JM-T-HCl. (b) (— △— △—) Pd on silica gel impregnated with 0.3 M Primene JM-T-HCl. (—O—O—) Pd on cellulose impregnated with 0.3 M Primene JM-T-HCl. (c) (— △— △—) Re on silica gel impregnated with 0.3 M Primene JM-T-HCl. (—O—O—) Re on cellulose impregnated with 0.3 M Primene JM-T-HCl.

The reproducibility of R_F values

In order to ascertain whether values obtained from different plates coated with the same batch of impregnant slurry, or from plates obtained from different batches, were reproducible enough to be used in comparative studies, a series of values were obtained for Zn(II) in each acid system, at a loading of 0.3 M amine hydrochloride.

Over 500 values were obtained at each acid concentration (a total of approximately 4,700 values). The results show that in all acid systems the R_F values for zinc (II) are reproducible to ± 0.02 of an R_F unit. The average deviation at each eluent concentration used is given in Table III. It is to be noted that the lowest reproducibility is associated with those systems in which the largest spots are obtained. Such reproducibility is in our opinion necessary for studies of the mechanism of chromatography, and for any quantitative work. It is also necessary to have a length of run, such that clean separations are obtained for R_F differences of 0.10 units so that closely related metal species may be studied.

The effect of variation of the amine loading

Assuming that the support is either completely covered with impregnant or that it is inert, it is to be expected that to a first approximation the effective thickness of the stationary phase, *viz.* the impregnant will be directly proportional to the loading. The system, may then be considered as a true partition system and hence a relationship can be established between loading and R_F or R_M values.

For partition systems MARTIN and co-workers[9] have stated that:

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

where α = partition coefficient of the substance between the stationary phase (S) and the liquid mobile phase (L) and A_L and A_S are the areas of cross section of the mobile and stationary phases, respectively.

Since

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

substituting eqn. 2 into eqn. 1 and rearrangement we have:

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

Since by definition α is constant and in the system considered A_L may be assumed to be constant, then

$$R_M = \log_{10} A_S + \text{constant} \tag{4}$$

This relationship is valid only if all the assumptions are valid. A plot of the R_M values for the metal species against the logarithm of the loading (Fig. 2) shows that a break in each of the parallel curves occurs at the same loading for each species, *i.e.* it is a result of the amine loading and not of the metal species. Above this loading of impregnant all the spots became noticeably more diffuse, and the time taken for the
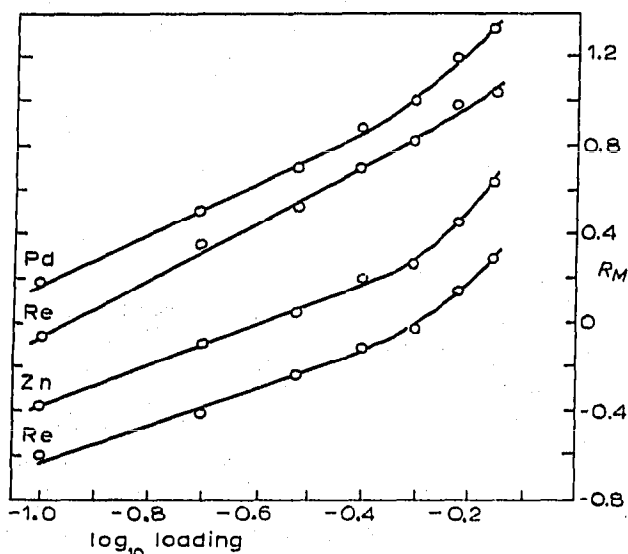

Fig. 2. R_M values *versus* $\log_{10}$ loading of Primene JM-T.

eluent to traverse the standard distance, also altered radically at this loading. These phenomena have been previously reported[10] in the systems of phenols chromatographed on layers of cellulose impregnated with formamide. It is considered that in both types of systems, the chromatographic process at loadings below the "break point" are not simply partition between two liquid phases but also involve the support. The support is thus not inert but is involved in the chromatographic system, which must involve both partition and adsorption. The mechanisms involved are thus similar to those previously reported for cellulose layers impregnated with an ion-association solvent extraction system[8,11,12] and probably involve both adsorption, ion exchange and simple partition.

Although at loadings corresponding to greater than 0.5 M of amine hydrochloride it is probable that the mechanism of chromatography does not involve adsorption on to the cellulose, the spreading of the spots at these loadings indicates that lateral diffusion is significant and must be considered. The decrease in the rate of elution with increased loading indicates that this diffusion may increase in importance as the loading is increased. Since one of the main advantages of TLC is the rapid and "clean" separation of species, it was thought of greater importance to consider the mechanisms involved for separations at acceptable rates of elution, and consequently at loadings below 0.5 M "amine hydrochloride".

The mechanism of the chromatographic system at low loadings of amine hydrochloride

Plots of the R_F values of the metals against the molarity of the eluent are shown in Fig. 1.

The pattern for zinc is similar to that obtained by BRINKMAN and co-workers using a similar system of Primene JM-T[2,5] and also by BARK and co-workers using the system TBP/HCl[8,11,12].

In the extraction of zinc from aqueous hydrochloric acid into TBP, MORRIS AND SHORT[13] have shown that three charged species are of importance, Zn^{2+}, $ZnCl_3^-$ and $ZnCl_4^{2-}$. These workers stated that the second of these species exists at $\sim$ 0.82 M HCl and that the last species predominates at 2.7 M HCl. Thus the descending portion of the R_F value/HCl curve corresponds to the formation of the divalent anion, *via* the monovalent anion, from the divalent cation. Thus the minimum of our curve corresponds to the point at which the divalent anion is known to predominate.

The ascending portion of the curve in the range 3.0 M to 6.0 M may be interpreted by SCHINDEWOLF's[14] explanation of the decreased extraction of zinc by TBP at high acid concentrations. This was stated to be the result of the suppression of the ionisation of the chloroacid H_2ZnCl_4 by the excess hydrogen ions in the solution. Thus the ascending portion of the curve may be considered to be a consequence of the change in the point of equilibrium in the system

$$H_2ZnCl_4 \rightleftharpoons 2H^+ + ZnCl_4^{2-}$$
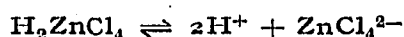
That an equilibrium process is involved, and that this is not a rapid equilibrium is evidenced by the increase in spot size (with the associated reduction in reproducibility) of the R_F values) in the range 3.0 M–6.0 M (Table III).

TABLE III

VARIATION OF SIZE OF SPOT OF ZINC WITH VARIATION IN ACID CONDITIONS

	Concentration of HCl (molar)								
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
Max. difference in R_F values	0.012	0.013	0.012	0.018	0.018	0.020	0.020	0.013	0.014
Spot length	0.8	1.3	1.4	2.2	2.1	2.4	1.5	1.7	1.4

The levelling off of the curve above 6.0 M acid probably represents the chromatography of the undissociated molecule which dissolves in the stationary phase by the normal forces of dissolution.

In the case of palladium (II) (Fig. 1) applied to the layers as $PdCl_2$ in dilute HCl, it is probably initially adsorbed as the $PdCl_4^{2-}$ ion at very dilute acid concentrations. Suppression of the ionisation of this acid begins at $\sim$ 1 M hydrochloric acid and the chloropalladous acid is completely undissociated at $\sim$ 5 M hydrochloric acid.

Rhenium (Fig. 1) applied to the layers as potassium perrhenate, will probably be present as the perrhenate anion in the early stages. Two spots were obtained from this compound. The upper spot was the larger of the two. It was assumed that this

was, in fact, the perrhenate ion. This ion is completely dissociated and hence has low R_F values at an acid molarity of less than 1 but is completely undissociated at $5\ M$ acid.

It was thought that the second spot obtained for rhenium could possibly be a species of a different oxidation state. This species does not appear to be completely undissociated until the acidity is $8\ M$. In an attempt to elucidate the oxidation state, a sample of ammonium chloro-rhenate $(NH_4)_2ReCl_6$ (provided by Dr. M. LEDERER) was chromatographed under the same conditions, *i.e.* on the same plate as the rhenium previously used. The Re(IV) (from the $(NH_4)ReCl_6$) appeared as an elongated streak from near the starting line to near to the solvent front in all acid systems. Attempts to obtain a discreet spot, by decreasing the amount of spot applied, were unsuccessful. Two different sources of Re(VII) were investigated, *viz.* (a) potassium perrhenate $KReO_4$ was used as purchased, (b) rhenium metal was oxidised and dissolved by aqua regia. In both cases, identical spots were obtained; both samples gave, at the appropriate acidity conditions, two spots with practically identical R_F values for each type of spot. Samples of spots with the lower R_F value were collected from the plate, and attempts were made to identify the material by its absorption spectrum in the acidic conditions obtaining on the plate. No definite evidence was obtained to indicate the oxidation state of the material, or to allow for elucidation of its structure.

CONCLUSIONS

In attempting to use any liquid anion exchanger as a substrate for the reversed-phase thin-layer chromatographic separation of metal ions, attention must be given to the nature of the supposedly inert support and also to the loading of the exchanger on that support in order to devise a chromatographically effective system both in relation to the efficiency of the separation and to the speed of running. Bearing in mind these considerations, it is possible not only to utilise the technique for the separation of the metal ions, but also to consider the mechanisms by which such separations occur. Some insight into the natures of the species involved may also be obtained from such experiments.

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