

CHROMATOGRAPHIC TECHNIQUES USING LIQUID ANION-EXCHANGERS*

I. HCl SYSTEMS

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INTRODUCTION

Liquid ion-exchangers have received considerable attention in analytical chemistry since their introduction in 1948¹. These high-molecular-weight acids and bases have been used mainly as extractants and they have met with remarkable success, as is clearly shown in the reviews by COLEMAN², COLEMAN *et al.*³, GREEN⁴ and MOORE⁵.

During recent years, however, an interesting situation has arisen, in which these liquid ion-exchangers are used in chromatographic techniques, similar procedures having been developed at the same time for high-molecular-weight neutral organophosphorus compounds (*cf.* refs. 6 and 7). The early successful work in this branch of chemistry has been reviewed by CERRAI⁶, who mainly describes the results of his own group. After the initial use of TnOA***, this group has shifted its attention mainly towards HDEHP, that has been extensively used for *e.g.* rare earth separations. Other groups of workers (*cf.* literature in ref. 6 and *e.g.* refs. 8-11) have also paid attention to the use of HDEHP in chromatography and a detailed study has been made of the theoretical aspects of the column procedures^{12,13}.

Amines and substituted ammonium salts, however, have been used only infrequently, although far more compounds of this class are commercially available than are the high-molecular-weight acids—of which up to date only HDEHP and DNS^{14,15} appear to have been used to any extent. The summary of the uses of basic liquid ion-exchangers in chromatography given in Table I shows that these compounds have hardly been investigated, though the initial results were very successful. We have therefore turned our attention to a more systematic study in order to investigate both the possibility of qualitative and quantitative separations and the correspondence between data on extraction, ion-exchange and chromatography (*cf. e.g.* ref. 6).

In order to simplify the time-consuming preliminary investigations, a rapid thin-layer technique has been developed²⁸.

* A preliminary communication of our work has been published²⁸.

** This paper forms part of the work done by U.A.Th.B. for his Ph. D. Thesis.

*** Abbreviations: TnOA = tri-*n*-octylamine; TiOA = triisooctylamine; HDEHP = hydrogen di-(2-ethylhexyl) phosphate; DNS = dinonylnaphthalenesulphonic acid.

TABLE I
LITERATURE SURVEY OF LIQUID ION-EXCHANGE CHROMATOGRAPHY USING HIGH-MOLECULAR-WEIGHT AMINES AND SUBSTITUTED AMMONIUM SALTS*

Solution**	Methods	Eluant	Ions separated***	References
TnOA				
0.2 M in kerosene (b.p. 30-50°)	Paper: Whatman No. 1; radial (7 cm in 15 min) and descending	HCl (1-10 N) (+ HNO ₃); H ₂ SO ₄ (0.4-2.0 N)	HCl; U-Zr-Th; Fe-Cr-Al; Fe/Zn-Co-Mn-Ni; Zr-Hf; U-V-Ti; H ₂ SO ₄ ; U/Mo-Fe/Cr-Ni; etc.	16
0.01-0.6 M in benzene eq. with HNO ₃ or acidified nitrate (1:3, v/v) for 5 min; dried	Paper: Whatman No. 1; radial (7 cm in 15 min) and descending; 20°	HNO ₃ (1-10 N); acidified nitrates of Li, Ca, Al (0-6 M), Na (0-8 M) and NH ₄ (0-10 M)	Rare spectra for Th, U and La (Ce)	17
0.1 M in benzene eq. with HCl or NH ₄ NO ₃ (1:2, v/v) for 10 min; dried	Column (approx. 20 × 1 cm ² ; 0.2-0.3 ml/min): Whatman No. 1 cellulose powder, dried 2 h at 85° before and after equilibration; mostly 1-15 mg per element	HCl, HNO ₃ and NH ₄ NO ₃	Ni-Co-Fe; Th-Zr-U; Zr-La; Hf-Zr; etc.	18
0.2-0.25 (paper) and 0.5 (column) M in benzene eq. with 2 N HNO ₃ (1:2, v/v); dried	Paper: Whatman No. 1 (CR1/1); ascending; column (1.40 × 13 mm ² ; 0.5 ml/min): Whatman No. 1 cellulose powder, mixed with TnOA in benzene for 12 h; dried 2 h at 80°; approx. 20 mg per element	LiNO ₃ (1-10 M) acidified with 2 · 10 ⁻³ N HNO ₃	Rare earth elements and Sc, Y, Th and Ba; e.g.: Th-Ce-Nd-Gd and Pr-Sm-Dy on paper (with 3 M LiNO ₃) and Ba-Yb-Nd-La on column (gradient elution)	19
0.1 M in cyclohexane	Paper: Whatman No. 1; ascending	80% (v/v) methanol-HNO ₃ mixtures	Rare earths; no positive results	20
0.2 M in benzene eq. with 2 N HNO ₃ (1:2, v/v)	Paper: Whatman No. 1; ascending (2 h); 15°; 0.3 ml TnOA solution for 1.5 × 21 cm ² paper	NH ₄ NO ₃ (2-10 M) + HNO ₃ (2 · 10 ⁻³ -1 N)	R _F spectra for U, La, Y, Sm, Eu and Gd	21, 22
Undiluted TnOA	Column (30 × 7 mm ² ; 1-2 ml/min): 1.5 g Kef-F (per column) + 1.5 ml TnOA + a few ml 4 N H ₂ SO ₄ slurried into column	H ₂ SO ₄ (0.2 N) and HNO ₃ (1-5 N)	3 μg Pu (HNO ₃) from 5 mg U (H ₂ SO ₄)	23
Undiluted TnOA	Column (80 × 2.8 mm ² ; 0.03	HCl (0.01-6 N) and ammoniacal	Mn/Co/Ni/Cu or Ca/Sr/Y from Fe	24

Undiluted TnOA	Column (80 × 2.8 mm ² ; 0.03 ml/mm): powdered Teflon (150-250 mesh) + 375 mg TnOA; washed with H ₂ O and 1 N HCl; 20°; 2 mg-60 µg per element	HCl (0.01-6 N) and ammoniacal NH ₄ acetate (0.2 M)	Mn/Co/Ni/Cu or Ca/Sr/Y from Fe and Zn or Cd; Th/Pa-U	24
0.1 M in benzene	Paper: Whatman No. 1 (CRL/1); ascending (approx. 15 cm). One end of paper dipped in TnOA solution; after drying rest of paper treated with 0.1 M HDEHP in cyclohexane	HCl (1-4 N) and HNO ₃ (6 N)	Fe-Zr-Gd-Pr; U-Se-Yb-Y-La; Zr-Th-Al, etc.	25
<i>Aliquat (and TnOA)</i> 0.25 M in benzene eq. with 0.1 N HCl (1:1, v/v) to remove Fe(III); after dilution to 0.1 M, eq. with 6 N HCl (1:2, v/v)	Paper: Whatman No. 1 (CRL/1)	HCl (0-11.5 N)	R _F spectra for Fe, Co, Ni, U, Zr and Hf, compared with those found using TnOA	26
<i>TiOA</i> 0.185 M in ether eq. with acid (1:2, v/v) for 2 min	Thin layer (2-7 cm in 5-30 min): kieselgel G (16.8 g) + TiOA in ether 2 h at 100°; then plus CaSO ₄ ·2 H ₂ O (2.4 g) + 36 ml H ₂ O; dried 2 h in the air and 2 h at 100°	HCl (3 and 8 N); HNO ₃ (5 N) and H ₂ SO ₄ (2 N)	2- and 3-component separations from the series Mo, V, Cu, Fe, Co, Ni, Zn, U, Ti, Th, Zr, Mn, Cr(VI)	27
<i>Tri-n-alkylamines</i> 0.1 M (n-C ₄ H ₉) ₃ N to (n-C ₈ H ₁₇) ₃ N in benzene; saturated with 1 N HNO ₃	Paper: Whatman No. 1; ascending (2 h); 15°	NH ₄ NO ₃ (4 M) + HNO ₃ (2·10 ⁻³ N)	U-La-Sm/Eu/Gd/Y	21
<i>Ambertite LA-1</i> 0.1 M in CHCl ₃ or benzene eq. with 2 N HCl (1:3, v/v) for 10 min; dried over Na ₂ SO ₄	Paper: Whatman No. 1 (or S and S 2043a); ascending (15 cm in 3 h); room temp. Thin layer (approx. 3 cm in 10 min); silica gel (Fluka DO); room temp.	HCl (0.5-11.5 N)	R _F spectra for Ni, Co, Zn, Mn, Al, Fe, Sb(III), Cu, Cd, Hg(II), Pb and Bi	28

* A review of early chromatographic work with TnOA is included in ref. 6.

** Under this heading is given the organic solution equilibrated (eq.) with the inorganic solution under the specified conditions.

*** From articles giving merely a large number of two- to four-component separations, only a few representative ones are tabulated; this is indicated by "etc." A/B-C means that either A or B can be separated from C.

Unless otherwise indicated, the ions mentioned were in their normal oxidation state, e.g., Fe(III), U(VI), Cu(II), Ce(III), V(V) and Mo(VI).

MATERIALS AND METHODS

Chemicals

Amberlite LA-1, a fairly viscous yellow liquid (viscosity at 25° 72 c.p. (ref. 4)) is a N-dodecenylntrialkylmethyl-amine. The unsaturated amine contains 24-27 carbon atoms and has an average mol. wt. of 372.

Amberlite LA-2, also yellow coloured, but with a much lower viscosity (18 c.p. at 25° (ref. 4)) is a saturated secondary amine, N-laurylntrialkylmethyl-amine, with an average mol. wt. of 374.

Hyamine 2389, a slightly yellow coloured, very viscous "wetting agent", is a mixture of methyl-dodecylbenzyltrimethyl-ammonium chloride and methyl-dodecylxylylene-bis-(trimethylammonium chloride). The average mol. wt. was calculated to be 420, based on the assumption that the mole ratio of the chlorides was 1:1.

Hyamine 10X, a white crystalline powder used as a germicide or as a deodorant, is diisobutylcresoxyethoxyethyl-dimethylbenzyl-ammonium chloride (Lot No. 2762, with 1.2% inert ingredient); the mol. wt. of the pure monohydrate is 480.

Hyamine 1622, also a white crystalline substituted ammonium chloride used as a germicide or deodorant, is diisobutylphenoxyethoxyethyl-dimethylbenzyl-ammonium chloride and the pure monohydrate has a mol. wt. of 466.

Primene JM-T is a yellow coloured primary trialkylmethylamine with 18-24 carbon atoms and an average mol. wt. of 311.

The six chemicals mentioned above are all manufactured by Rohm and Haas Co., Philadelphia, Pa. (U.S.A.).

Tetrahexylammonium iodide, a white crystalline product from Eastman Kodak, Rochester, N.Y. (U.S.A.) has a mol. wt. of 481. It is converted into the chloride by shaking the solution of the iodide in CHCl_3 for some minutes with a 5-fold excess of freshly precipitated Ag_2O , decanting off the supernatant solution and treating the hydroxide with HCl.

Triisooctylamine, a nearly colourless technical grade product (Lot No. 55055X) from K and K Laboratories, Plainview, N.Y. (U.S.A.) has a mol. wt. of 353. TiOA contains a mixture of dimethylhexyl, methylheptyl, etc. chains, principally 3,5-, 4,5- and 3,4-dimethylhexyl.

Tri-n-octylamine is a colourless practical quality product (mol. wt. 353) purchased both from K and K Laboratories (Lot No. 48485) and from Fluka, Buchs, S.G. (Switzerland).

Tribenzylamine, a white crystalline solid (mol. wt. 287) of purissimum (> 99%) quality was also purchased from Fluka.

Aliquat 336, obtainable as the chloride, is a methyltri-n-alkyl-ammonium salt ("methyltricaprylyl-ammonium chloride") with 27-33 carbon atoms on an average. The alkyl groups mainly consist of octyl and decyl chains, and the average mol. wt. of this yellow viscous liquid was assumed to be 475.

Alamine 336, a pale yellow liquid (Lot No. 4L108), also called "tricaprylyl-amine", is a tertiary amine with three straight-chain alkyls, mainly octyls and decyls. The number of carbon atoms totals 26-32 and the average mol. wt. of the tertiary amine content (min. 90%; typical 95%) is 392. Both Alamine and Aliquat were gifts from General Mills Inc., Kankakee, Ill. (U.S.A.).

Adogen 364, a tri-*n*-alkylamine with 27 carbon atoms on an average, principally consists of octyl (60%) and decyl (33%) chains. It contains minimally 95% tertiary amine. In the yellow turbid liquid a waxy deposit is formed on standing. For our work, 380 was used as average mol. wt.

Adogen 368, a pale yellow coloured tri-*n*-alkylamine, of which the alkyl groups principally consist of octyl (40%), decyl (25%) and dodecyl (30%) chains, has a minimal percentage tertiary amine of 95%. We used 430 as average mol. wt.

Adogen 464, a methyltri-*n*-alkyl-ammonium chloride with a yellow-brown colour, has a minimal percentage of quaternary ammonium salt of 92%; its average mol. wt. is 431.

All Adogens mentioned above were received as gifts from Archer-Daniels-Midland Co., Minneapolis, Minn. (U.S.A.); the Lot numbers were 296-442-910, 281-22-306 and SR No. 27822, respectively.

All amines and substituted ammonium salts were used without further purification. They must be handled with care, as, *e.g.*, in the case of aliphatic amines the manufacturers point out that although the volatility is low, it is very important, particularly before dilution, to provide adequate ventilation to prevent inhalation of the vapours. Every precaution should be taken to avoid contact with the eyes or prolonged contact with the skin⁴. With some of the quaternary Hyamines the same rules are prescribed.

The ions tested included: Ag(I), Ni(II), Mn(II), Co(II), Zn(II), Cu(II), Pb(II), Fe(III), Sb(III) and Bi(III). The solutions of their chlorides—lead and silver were present as the nitrates—contained 2–8 μg cation per μl and were acidified as far as necessary in order to prevent hydrolysis. Hydrochloric acid solutions, made from HCl, analytical purity, were standardized to within $\pm 0.03 N$ of the desired normality.

Preparation of thin-layer plates and papers

The amine is converted into its HCl salt by equilibrating a 0.10 (thin layer) or 0.15 (paper) molar solution in chloroform or benzene for 10 min in a separatory funnel with 3 vol. of 2 *N* HCl (*cf.* RESULTS). The organic solution is separated, filtered and dried for some hours over sodium sulphate. Quaternary ammonium chlorides are equilibrated with HCl in the same way.

Thin layer. The amine·HCl or quaternary ammonium chloride solution, freed from sodium sulphate by filtration, is mixed thoroughly with silica gel (silica gel- CHCl_3 (1:2, v/v)); the resulting suspension is stored overnight and agitated again before use.

Thin-layer plates are prepared by dipping ordinary microscope slides ($2.5 \times 7.5 \text{ cm}^2$) into the silica gel- CHCl_3 mixture for approx. 5 sec. On leaving the glass plates for some minutes in the air, in order to evaporate off the chloroform, a thin film of amine-impregnated silica gel adheres to the slides. Using cotton wool a margin of 4 mm is made along the edges of the slides in order to avoid undesirable contact with the eluting agent.

The thin-layer plates so prepared are spotted (7 mm from the end; 2 spots per plate) with the solution to be investigated using a 1-mm wide strip of filter paper; the resulting spot ought to have a diameter of 1–2 mm. When the spots have been air-dried, the thin-layer plates are put into small vessels (Hellendahl staining jars) containing the eluting agent (approx. 3.5 ml; 6 slides per vessel) and the chromato-

gram is developed for approx. 10 min using the ascending technique. Subsequently, the plates are dried in air and the spots are visualized using conventional techniques.

Sometimes rather thin silica gel layers are obtained, when using the technique described above. This causes an uneven and slow flow of the eluants. In these cases a thicker layer may be obtained by dipping once more after the CHCl_3 has evaporated. This technique was used with *e.g.* Hyamine 1622 and Aliquat 336.

Paper. Air-dried Whatman paper No. 1, used without further purification, is treated with the amine·HCl or quaternary ammonium chloride solution for some seconds. This is conveniently done by continuously pulling the paper at a rate of 2–3 cm/sec through a Hellendahl staining jar, partly filled with the solution of exchanger. It is then dried in an air stream or by hanging it in the air for some minutes and cut into strips of the desired length; both 2- and 3-cm wide papers were used.

The papers are spotted (2.5 cm from the end) by using a micropipette or analogous device, so that spots with a diameter of 3–5 mm are formed. When the spots are air-dry the papers are hung in a suitable rack in glass jars ($30 \times 9 \text{ cm}^2$) containing the eluting agent (50 ml; 6 strips per jar). The chromatograms are developed for 2–3 h using an ascending technique; after air-drying, the spots are visualized using conventional techniques.

Detection

The ions were identified using conventional reagents. In some instances serious difficulties were encountered, *e.g.* with Mn and Pb. The same phenomena were occasionally found with ions not mentioned in this paper and in experiments with HDEHP-treated supports. Apparently, the liquid ion-exchangers sometimes decrease the sensitivity of normally well established spot tests. In these cases, Mn was detected by spraying with the KIO_4 -tetrabase reagent²⁰ and Pb was identified by dipping into a sodium rhodizonate solution²⁰, after carefully driving off the amine by heating over a small bunsen flame.

General remarks

All experiments were done at ambient temperature (20°) and were carried out at least in duplicate; with regard to the composition of the eluting agents, acclimatization was not deemed necessary.

In thin-layer work some suspensions altered their behaviour somewhat on standing, older suspensions giving thicker silica gel layers and sometimes also altered R_F values. Therefore care was taken to obtain roughly comparable conditions by leaving all suspensions standing for one night. Even then the first 5–10 thin layers prepared were sometimes quite unsatisfactory, but no difficulties were ever encountered after the suspension had been duly agitated again. This point needs further attention when investigating *e.g.* quantitative correlations between chromatography and extraction. In this respect paper chromatography may be advantageous, because a more even layer is obtained here.

In paper chromatography, the travelling distance of the solvent front was always taken as approx. 15 cm; development took about 3 h, with notable exceptions only in the presence of sirupy substances such as decanol (see *Paper chromatography*). In thin-layer work, 30 mm was taken as the average travelling distance; travelling time was approx. 10 min for 0.5–7 N HCl and 12.5–15 min for higher concentrations.

RESULTS

Development of the procedure

Preliminary investigations were carried out in order to find methods suitable for rapid and reliable thin-layer and paper chromatography.

Equilibration. Using Amberlite LA-1, equilibration was initially carried out with HCl of the same normality as that used as eluting agent. However, it was soon found that equilibration with 2 N HCl in all cases—irrespective of the normality of the eluting agent—gave insignificant differences only. Therefore, this technique was used in all further work.

Supports. Thin-layer plates were made using either silica gel, cellulose powder, kieselguhr or polyethylene and polyglycol powder. Layers made with silica gel were far better than all others and therefore all further research was done using this support.

The silica gel was used without further purification or drying. It contained some iron, which could be detected as a zone when Fe(III) had an R_F value of 0.6–1.0.

Paper chromatograms made using Whatman paper No. 1 and S and S paper 2043a give quite analogous results; S and S 2040a and 2045a proved somewhat less satisfactory, though still useful. Whatman paper No. 1 was used for all systematic work.

The necessity of rigorously drying both the organic solution and the paper strips was investigated using the following modifications: (a) air-dried paper is impregnated with the organic solution obtained after equilibration with 2 N HCl; (b) air-dried paper is impregnated with the same solution, dried for some hours over sodium sulphate; (c) paper dried for 2 h at 80° is impregnated with the sodium sulphate-dried solution.

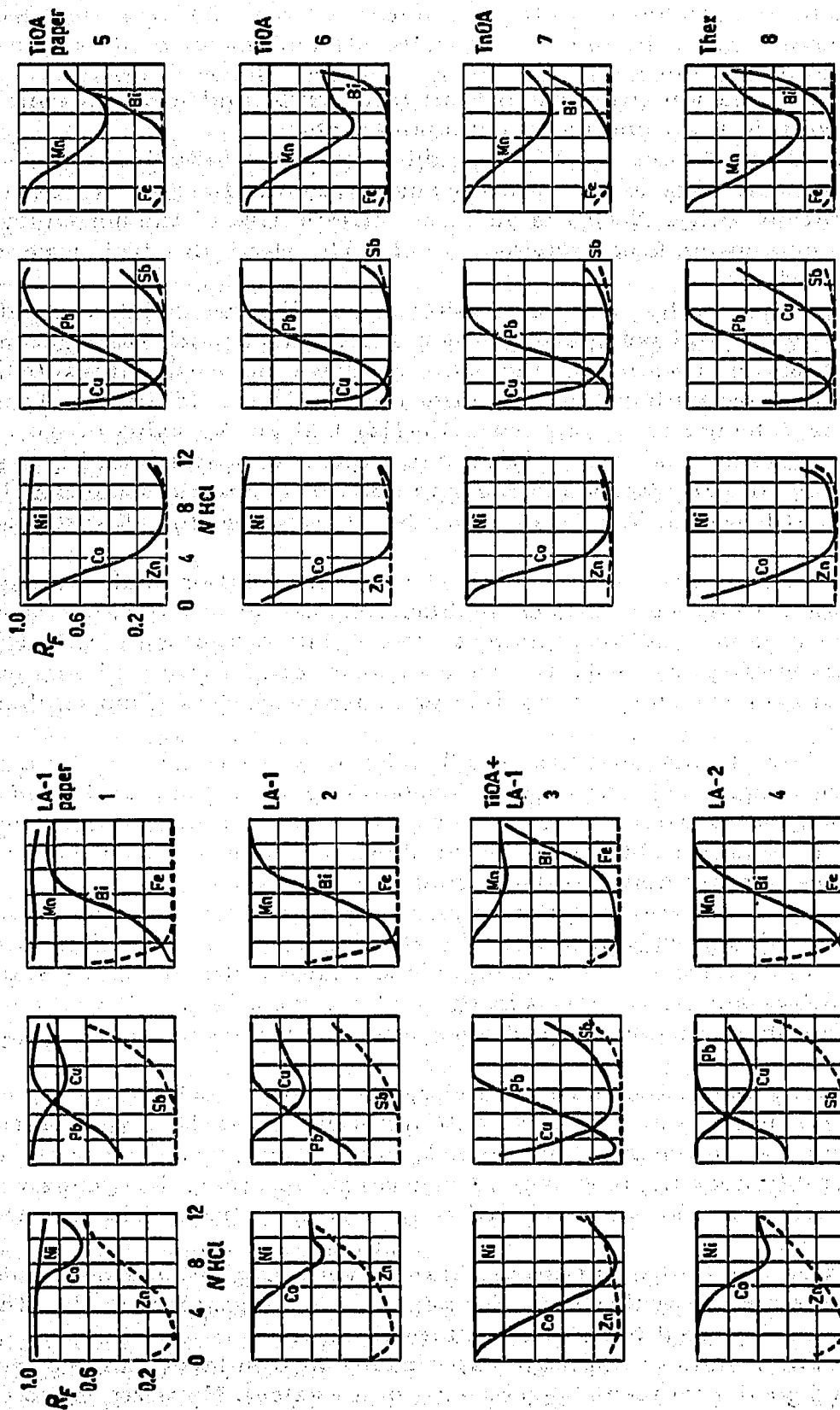
Experiments showed only relatively small differences, especially at the 0.10–0.15 M concentration range mostly used by us. Therefore, both techniques (b) and (c) may be recommended, but it would be better to reject (a) because the variable water content of the organic solution obtained after equilibration is an unknown factor in the subsequent processing and may adversely influence the results.

Paper strips—either air-dried or after having been heated for 2 h at 80°—were impregnated with liquid ion-exchanger both by dipping them in or pulling them through the organic solution for 2–5 sec. The organic solvent was driven off afterwards either using a fan or by hanging the strips in the air for some minutes. It was found that these and similar slight modifications did not alter the results to any significant extent.

Concentration dependence. Using the thin-layer technique, preliminary experiments were carried out using from 0.05 to 0.25 M Amberlite LA-1·HCl equilibration solutions. Some results are summarized in Table II, where it may be seen that the R_F values vary considerably over the 0.05–0.25 M concentration range, decreasing with increasing concentration, as does the migration rate of the eluant (also see DISCUSSION).

It was found that the best results were obtained with 0.10 M solutions, which were used for all systematic investigations. For paper chromatography, on the other hand, 0.15 M solutions appeared to be more suitable.

Reproducibility. The results of duplicate experiments in thin-layer chromatography generally showed good agreement (± 0.02 – 0.03 in R_F value). However, when ex-



Figs. 1-4. R_F spectra for 9 ions using various amine-HCl systems. (1) 0.15 *M* Amberlite LA-1; paper. Bi forms elongated spots from 0.5 to 6 *N* HCl. (2) 0.10 *M* Amberlite LA-1-0.10 *M* TiOA (1:1, v/v); thin layer. (3) 0.10 *M* Amberlite LA-1-0.10 *M* TiOA (1:1, v/v); thin layer. (4) 0.10 *M* Amberlite LA-2; thin layer.

Figs. 5-8. R_F spectra for 9 ions using various amine-HCl and quaternary ammonium salt systems. (5) 0.15 *M* TiOA; paper. Fe forms comets at all HCl concentrations. (6) 0.10 *M* TiOA; thin layer. (7) 0.10 *M* TiOA; thin layer. Small Fe-comets at 10 *N* and conc. HCl. (8) 0.10 *M* tetrahexylammonium chloride; thin layer. Elongated spots found for Mn over the whole range, and for Co and Cu at low HCl concentrations.

periments were repeated after the silica gel suspension had been left standing for some time, somewhat altered R_F values were occasionally obtained (also see above). In view of the qualitative character of the work this aspect of our analyses has not been deeply investigated until now. In paper chromatography the results showed good reproducibility.

Amines*

Amberlite LA-1. This secondary unsaturated amine is very suitable for chromatographic work. Figs. 1 and 2 summarize results of both thin-layer and paper chromatography, which show close correspondence, with some divergence only in the case of Co. These results indicate that many interesting qualitative separations may be realised in approx. 10 min, using the thin-layer technique developed by us, which has already been used²⁸ for a few cases.

TABLE II

DEPENDENCY OF R_F VALUES AND MIGRATION RATE OF ELUANT ON MOLARITY OF AMINE · HCl SOLUTION
Amberlite LA-1 was used as liquid ion-exchanger and approx. 7 N HCl as the eluting agent.

Ion	R_F value at amine molarity			
	0.05	0.10	0.15	0.25
Cu	0.79	0.64	0.45	0.30
Co	0.76	0.62	0.46	0.23
Bi	0.89	0.72	0.58	0.38
Zn	0.32	0.17	0.11	0.02

Length of run				
(mm)	35	32	26	20
Time (min)	10	10	10	20

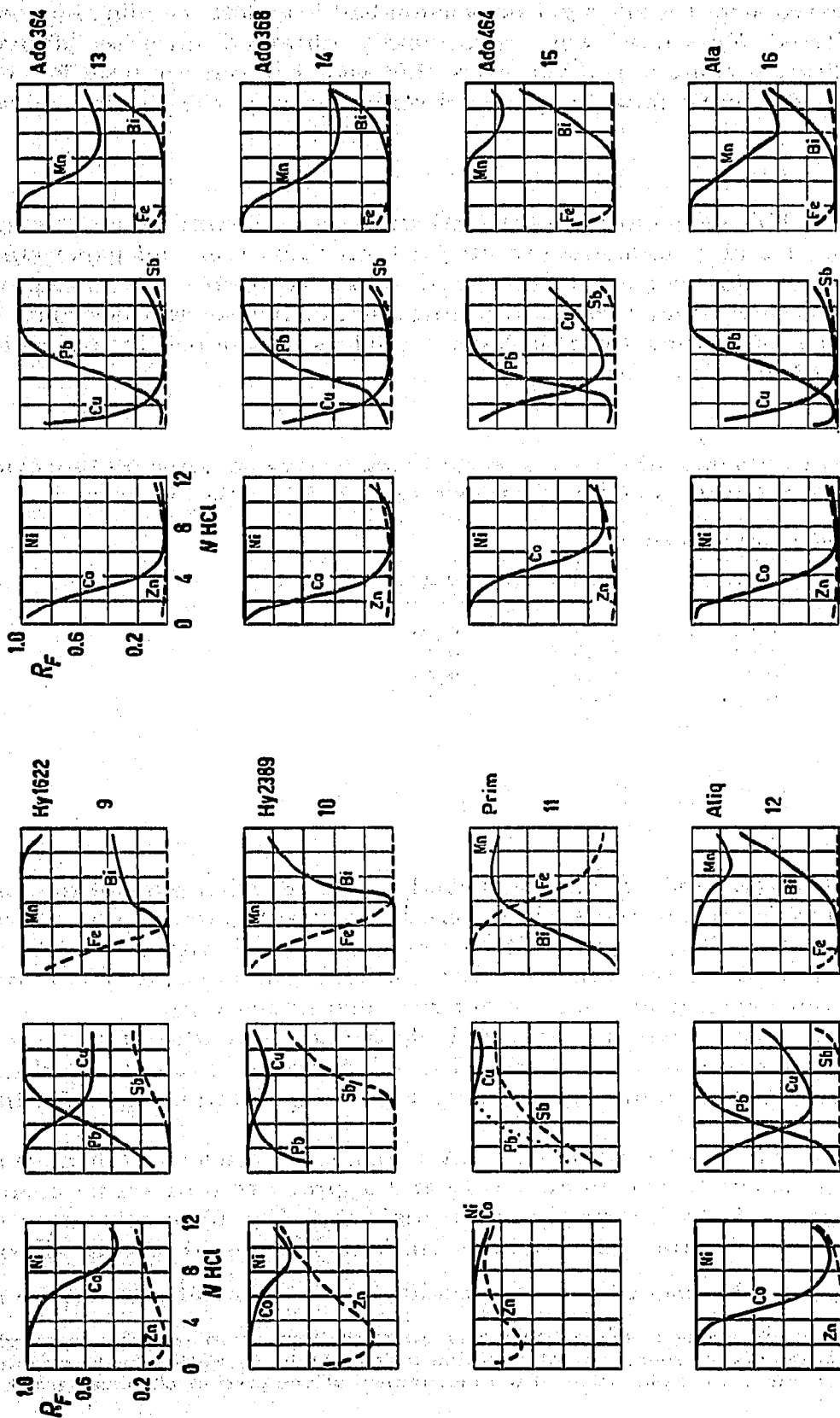
For data on Al, Hg(II) and Cd, one is referred to ref. 28; with some of the ion-exchangers discussed in this paper, these 3 ions were again investigated. It was shown, however, that Al always had $R_F = 1.0$, with a tendency to tail with conc. HCl as eluant, while Hg(II) and Cd behaved analogously to Sb(III). Therefore, they were not included in most of our experiments and are not recorded in the Figs.

Amberlite LA-2. Apart from its saturated character, Amberlite LA-2 has a structure fairly analogous to that of Amberlite LA-1. Therefore, it is not surprising that the results found with this amine agree closely with those found using Amberlite LA-1 (see Fig. 4).

Triisooctylamine. TiOA, like Amberlites LA-1 and LA-2, yields excellent thin layers, but the eluting agent travels more slowly and approx. 15 min are necessary for development. Because TiOA is strongly adsorbing** (see Fig. 6), combination of TiOA with another less powerful amine such as an Amberlite could lead to an ex-

* The term amines has sometimes been used to indicate both amines and substituted ammonium salts.

** High (low) adsorption strength means that the anion-exchanger in question strongly (weakly) retards the movements of anions, thereby leading to low (high) R_F values for those ions. Use of this term does not imply an explanation of the mechanism of the present chromatographic processes.



Figs. 9-12. R_F spectra in thin-layer chromatography for 9 ions using various amine-HCl and quaternary ammonium salt systems. (9) 0.10 *M* Hyamine 1622; Pb forms elongated spots for 0.5-4 *N* HCl. (10) 0.10 *M* Hyamine 2389. Pb and Zn form elongated spots below 4 *N* HCl; R_F spectra for Sb and Bi are irreproducible (\pm 0.10 R_F value) above 6 *N* HCl. (11) 0.10 *M* Primene JM-T. For 2-6 *N* HCl part of Pb is found back at the origin. (12) 0.10 *M* Aliquat 336.

Figs. 13-16. R_F spectra in thin-layer chromatography for 9 ions using various amine-HCl and quaternary ammonium salt systems. (13) 0.10 *M* Adogen 364. Fe forms comets at all HCl concentrations. (14) 0.10 *M* Adogen 368. Fe-comets more pronounced than with Adogen 364. (15) 0.10 *M* Adogen 464. Small comets for Fe at high normalities of HCl, and for Pb at 0.5-4 *N* HCl. (16) 0.10 *M* Alamine 336.

cellent mixture. Therefore, thin layers were prepared using 0.10 *M* TiOA-0.10 *M* Amberlite LA-1 (1:1, v/v) as amine mixture. Comparison of the data so obtained (Fig. 3) with those summarized in Figs. 2 and 6 shows a close agreement between that predicted and found. Elution time is also intermediate between those found with the separate components.

With TiOA, correspondence between paper (Fig. 5) and thin-layer data is as good as in the case of Amberlite LA-1.

Tri-n-octylamine. TnOA, the only amine used until now to a significant extent (cf. ref. 6 and Table I), yields thin layers of reasonable quality and its adsorption power is fairly high (Fig. 7).

Tetrahexylammonium chloride. This ammonium salt has approximately the same adsorbing power as TiOA (Fig. 8), but it forms many badly tailing spots, especially with Cu, Mn and Bi. Moreover, the detection of some ions, e.g. Sb, is difficult. Here, as with some other amines, especially Zn and Cd form thinnish spots when 10 *M* or conc. HCl are used as eluants; there is hardly any reaction with reagents such as 8-hydroxyquinoline, but the thinnish spot—looking very much like a fingerprint—makes detection easy.

Hyamines 1622 and 10X. From these two very analogous quaternary ammonium salts Hyamine 1622 was chosen for thin-layer experiments. Some difficulties were encountered during equilibration, separation of the organic and aqueous layers being a time-consuming process, that took at least some hours. When preparing thin layers, the "twice dipping" technique (see under METHODS) was often used.

Fig. 9 shows that Hyamine 1622 adsorbs more strongly than the Amberlites, but cannot bear comparison with most of the other compounds tested. Results found with low normalities of HCl (0.5–2.0 *N*) looked somewhat less reliable, though no real difficulties were encountered.

Hyamine 2389. This mixture of quaternary salts yields very thin silica gel layers sometimes, but the average elution time is still fairly short, being 7.5 min only. Therefore, Hyamine 2389 may have advantages in this respect, but the experimental results are not too satisfactory, irreproducible R_F spectra being obtained for e.g. Sb and Bi (cf. legend to Fig. 10). Moreover, the adsorbing power is less than with the Amberlites, even though the 0.1 *M* solution has a higher effective strength as one of the components bears two functional groups.

As regards the problems met when using the Hyamines in paper chromatography, one is referred to the section on paper chromatography below.

Primene JM-T. This primary amine with which the migration rate of the eluant varies surprisingly little with HCl normality, has fairly weak adsorbing qualities. It contains quite a few impurities, that form a broad fluorescing zone at the solvent front with 8-hydroxyquinoline, which gives difficulties when detecting Mn. The identification of Pb also proved difficult, probably partly due to the long tailing spots obtained at intermediate HCl strengths.

Primene yields deviating results with Bi (cf. Fig. 11 with e.g. Figs. 2, 6 and 12); similar deviations were found with the Hyamines (Figs. 9 and 10).

Aliquat 336. The Aliquat-silica gel suspension is remarkably unstable and the silica gel settles faster than with any of the other amines tested: within a few hours a hard cake forms on the bottom of the container, which can, however, be suspended again by thoroughly mixing for some minutes, so that this phenomenon causes no

real trouble. The silica gel layers are more or less scaly in character, unlike those found with *e.g.* the Amberlites and Adogen 368, which are more even with some small clots superimposed. With Aliquat, the "twice-dipping" technique was repeatedly used. Fe, present as an impurity, may be partly removed by washing with 3 vol. of 0.1 N HCl (ref. 26).

Fig. 12 shows that Aliquat has good adsorbing qualities and it may therefore be recommended for chromatographic work (*cf.* ref. 26).

Adogen 364. Adogen 364, like Adogen 368, gives excellent thin layers, that resemble those obtained with the Amberlites. The data summarized in Fig. 13 show that Adogen 364 has high adsorption strength and may be compared with TiOA in this respect.

Adogen 368. Fig. 14 shows that the adsorption behaviour of Adogen 368 is almost identical with that of Adogen 364; on the other hand, the migration rate of the eluant *vs.* HCl normality diagrams are quite unlike, Adogen 368 giving a surprisingly low movement for 0.5–2.0 N HCl. The colour of the Adogen 368·HCl solution turns to pink-yellow within a few hours.

Adogen 464. This fairly dark coloured quaternary ammonium salt forms scaly layers, and the suspensions in CHCl₃ settle fairly rapidly. Adogen 464 combines the advantages of fairly high adsorption power (Fig. 15), comparable with that of Aliquat, and short elution time (7.5–10 min).

All the Adogens form rapidly drying thin layers and detection rarely causes difficulties; the Fe(III)-8-hydroxyquinoline reaction is, however, not too distinct. Moreover, the Fe-spots form comets at higher HCl normalities, a phenomenon not found with other amines of comparable strength.

Alamine 336. Results obtained with Alamine (Fig. 16) are satisfactory: the adsorption strength is high and is comparable with that of Adogens 364 and 368, while the elution time is reasonably short.

TABLE III

R_F VALUES OF SOME CATIONS ON PAPER IMPREGNATED WITH LIQUID ANION-EXCHANGER·HCl SYSTEMS

All experiments were carried out at room temperature using 6.5 N HCl as eluting agent.

Ion-exchanger	<i>R_F</i> values found for							
	Al	Pb	Ag	Mn	Cu	Co	Zn	Cd
Amberlite LA-1	0.97	0.95	0.67	0.95	0.69	0.90	0.20	0.09
Amberlite LA-2	0.98	0.95	0.70	—	0.66	0.88	0.20	0.10
TiOA	0.98	0.75	0.53	0.45	0.04	0.07	0.00	0.00
TnOA	0.95	0.69	0.55	0.60	0.07	0.11	0.00	0.00
Tetrahexylammonium chloride	0.97	0.77	0.61	0.57	0.18	0.08	0.00	0.00
0.15 M Hyamine 1622-decanol (4:1, v/v)	0.93	0.83	0.70	0.91	0.65	—	0.20	—
0.15 M Hyamine 10X-decanol (1:1, v/v)	0.96	0.70	0.63	0.89	0.69	—	0.24	0.23
Primene JM-T	0.95	0.88	—	0.97	0.83	0.92	0.78	—
Aliquat 336	0.96	0.83	0.70	0.87	0.33	—	0.03	0.00
Adogen 364	0.97	0.75	0.54	0.67	0.07	0.08	0.00	0.00
Adogen 368	0.95	0.75	0.55	0.71	0.06	0.08	0.00	0.00
Adogen 464	0.97	0.84	0.67	0.88	0.35	0.51	0.02	0.00
Alamine 336	—	0.73	0.56	0.60	0.06	0.10	0.00	0.00

Tribenzylamine. This aromatic amine forms thin layers that can hardly be used: the solvent fronts are very irregular and the eluting agents move only slowly. To improve the character of the thin layers, viscous substances (see below) were added to the suspension. This gave slightly better results, but the general picture was still unsatisfactory. We therefore only mention that Fe had R_F values of approx. 0.8 and 0.0 with 2 and 4 N HCl, respectively. Zn and Cd gave elongated spots with R_F 0.0–0.4 at both normalities. These results and those mentioned in the section on paper chromatography clearly indicate that tribenzylamine has only low adsorption power and is not suitable for our purposes.

Paper chromatography

As mentioned above in the paragraphs on Amberlite LA-1 and TiOA, R_F spectra obtained in paper chromatography are very analogous to those found using thin-layer techniques. We therefore omitted further systematic work on paper and limited ourselves to a short test on the usefulness of the amines by eluting 5–6 cations at one normality of HCl using papers, impregnated with each of these ion-exchangers.

Apart from a fairly good correspondence between the data so obtained (Table III) and those found in thin-layer work, our research showed as the more important aspect an overall usefulness of the basic liquid ion-exchangers in paper chromatography, excepting the three Hyamines and tribenzylamine, which yielded highly irregular solvent fronts and very elongated badly formed spots.

It is highly probable that these difficulties are brought about by the crystalline character of the ion-exchangers in question. Therefore, certain substances, *viz.* decanol and the condensation product of glycerol and benzhydryl chloride (synthesized according to ref. 30), were selected in order to retard the crystallisation of these compounds on the paper and were added to their solutions in CHCl_3 . The experiments showed that the results were improved to a considerable extent in this way, especially in the presence of the benzhydryl ether. However, the enormously increased elution time (7 h against 3 h normally) completely offsets this advantage. Therefore, these ion-exchangers are not suitable for use in the paper (and/or thin-layer) techniques described by us.

DISCUSSION

In the last decade liquid ion-exchangers⁶ have been introduced in paper and column chromatography, and it has been shown that all the advantages of selectivity and versatility of these compounds can be transferred into the field of thin-layer chromatography, where these processes can be understood by assuming that the supports treated with ion-exchangers behave like a thin film of ion resin.

Therefore, the great similarity between the processes in extraction using liquid ion-exchangers, in resinous ion-exchange and in the chromatographic techniques considered here may be emphasized: they can all be expressed either as ion-exchange, implying transport of ions, or as adduct formation, implying transport of neutral species, alternatives which are thermodynamically equivalent². On the other hand, this comparison should not be carried too far, since the physical aspects of these systems are obviously substantially different⁶.

We have now studied more systematically high-molecular-weight amines and

substituted ammonium salts, starting with HCl systems, because more data are available here for comparison. From the experiments carried out with a number of cations selected with regard to their different behaviour in HCl media, we may conclude (see Figs. 1-16 and RESULTS) that nearly all the exchangers tested gave satisfactory results. Difficulties were encountered only with some crystalline compounds—which are therefore not true liquid ion-exchangers. In these cases addition of viscous substances only moderately improved the results (see *Paper chromatography*).

Figs. 1-16 and Table III reveal a very satisfactory correspondence between paper and thin-layer experiments, especially when taking into account the difference in support and in concentration of the ion-exchangers in the equilibration solution (0.15 vs. 0.10 M). The discrepancies sometimes occurring do not severely detract from this general picture, as may be established by comparing *e.g.* Co in Figs. 1 and 2 and Mn and Bi in Figs. 5 and 6.

Our data moreover indicate that each of the ions investigated shows more or less the same behaviour with all exchangers. For most ions the analogy is even very pronounced (*cf.* the analogous results of CERRAI AND GHERSINI²⁰ when using TnOA and Aliquat 336) and it follows clearly from the figures that the exchangers may be classified according to their adsorption strength in HCl medium as follows:

TiOA > Adogen 364 ~ Adogen 368 ~ Alamine 336 ~ tetrahexylammonium
 ~ TnOA > Aliquat 336 ~ Adogen 464 > Hyamine 1622 > Amberlite LA-1
 ~ Amberlite LA-2 > Hyamine 2389 > Primene JM-T.

Despite the apparent presence of a certain sequence, it is not yet possible to obtain far-reaching conclusions as regards *e.g.* the correspondence between structure and adsorption strength, owing to the complicated composition of some of the products used and possibly the moderate reproducibility of some of the experiments.

However, it may be tentatively assumed that tertiary and quaternary compounds are generally superior in HCl media; on the other hand their adsorption strength does not show much variability in the range of 24 to 30 carbon atoms. Reference may be made here to a paper by PANG AND LIANG²¹, who did not find a distinct relationship between the number of carbon atoms in the amines and the R_F values of 6 elements studied, when using tri-*n*-alkylamines ranging from 12 to 27 carbon atoms.

The correspondence of our data and those on extraction using liquid ion-exchangers (see review by COLEMAN²) seems to indicate that the sequence proposed above also holds in liquid-liquid extraction—at least in HCl media—Primene JM-T being a weaker extractant than Amberlite LA-1, which in its turn is clearly surpassed by Aliquat 336, TiOA and Alamine 336. A less satisfactory result is obtained for Hyamine 1622, but here the diluent, dichloroethane, possibly plays an important role, because the other exchangers were used dissolved in xylene, kerosene or diethylbenzene, which are probably less suitable in extracting ionic species.

The fundamental aspects of liquid-liquid extraction and chromatography on treated papers may be correlated through the quantitative relationship^{9,31}:

$$\log E_a^0 = k \cdot R_M$$

where E_a^0 is the extraction coefficient, k a constant and $R_M = \log (1/R_F - 1)$, where the R_F values have been obtained using the same extractant and aqueous phase. As an illustration, Fig. 17 gives a comparison of data on Amberlite LA-1, which indeed

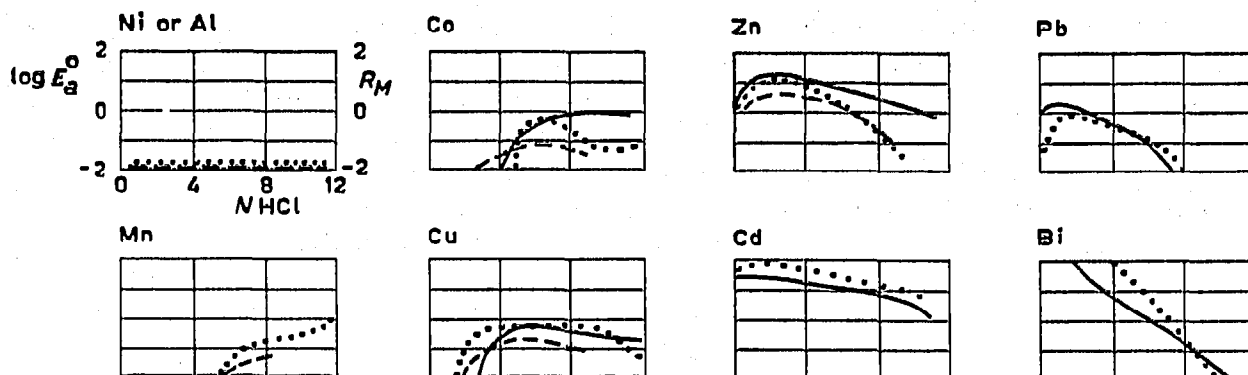


Fig. 17. Comparison of $\log E_a^0$ and R_M for Amberlite LA-1, when plotted against normality of HCl. E_a^0 data have been extracted from ref. 2: (---) 0.3 *M* Amberlite in xylene; (···) 0.1 *M* Amberlite in diethylbenzene. R_M values (—) have been calculated using the data in Fig. 2 and in ref. 28. The 0.3 *M* Amberlite curve for Co has a curvature more pronounced than that normally found. With Mn, we found appreciable adsorption only when using amines stronger adsorbing than Amberlite LA-1; in these cases, the R_M curves resembled the $\log E_a^0$ data.

show a satisfactory resemblance of the $\log E_a^0$ and the R_M curve. Similar results were obtained for the other liquid ion-exchangers mentioned above. In view of the many theoretical difficulties inherent in these problems, a quantitative discussion of the data seems premature at this stage of our investigation.

As regards comparison with ion-exchange data, one is mostly referred to the papers by KRAUS, NELSON and coworkers³², but it is also worthwhile to call attention to the publications by LEDERER AND OSSICINI³³. Our data (also see ref. 28) show an agreeable correspondence with the results of LEDERER who used the strong base resin paper Amberlite SB-2 (containing Amberlite IRA-400, a polystyrene resin). Supports impregnated with Aliquat 336 and all stronger adsorbing amines generally give the same or lower R_F values as SB-2 paper, while the Amberlites LA-1 and LA-2 are still more strongly adsorbing than both DE-20 and AE-30 cellulose anion-exchange paper³³. It may be remarked that the curvature in LEDERER's diagrams is mostly less pronounced than in ours.

Reference may also be made to work^{7,34} on the use of tri-*n*-butyl phosphate, tri-*n*-octylphosphine oxide and bis-(di-*n*-hexylphosphinyl)methane, which are generally more powerful extractants in the order given. Two conclusions reached there are worth mentioning as they correspond with our experiences: (a) the large amounts of the weak extractant tri-*n*-butyl phosphate required on the paper alter its physical characteristics and thereby cause an uneven and slow flow of the mobile phase; (b) tri-*n*-octylphosphine oxide is not too suitable in concentrated (0.2 *M*) solution⁷, because it is a solid which tends to crystallize on the paper, but a more dilute, e.g. 0.025 *M*, equilibration solution is very satisfactory³⁴. The most interesting observation is, however, that the curves found for these three organophosphorus compounds in HCl media closely resemble those obtained by us when using basic liquid ion-exchangers. Therefore, it seems that these neutral compounds—which are assumed to react via a coordination through the phosphoryl oxygen directly to the metal ion displacing water of hydration⁷—may also be described as anion-exchangers (*cf.* ref. 7, p. 71).

The form of the curves for the various ions (Figs. 1–16) may be tentatively interpreted (*cf.* ref. 32) by assuming the existence of a neutral (and/or positive) species

at low ligand concentration (R_F approx. 1.0); increased adsorption once a reasonable amount of the first negative ion has been formed (decreasing R_F); maximum adsorption of the same or a higher negative ion in or close to the minimum of the R_F curve, and lastly desorption owing to competition of excess ligand, or possibly other causes such as formation of less adsorbed higher charged negative complexes or decreasing dissociation of complex acids $H_n[MCl_p]$. Naturally, this simple picture can be considerably complicated by phenomena such as adsorption in the network of the support (e.g. with $AuCl_4^-$; cf. ref. 33) or precipitation. Parenthetically, experiments carried out with silica gel layers not treated with liquid ion-exchangers did not show any adsorption ($R_F \geq 0.9$) for the ions used, except for Sb(III) below 4 N HCl, probably due to hydrolysis.

CONCLUSIONS

The experimental results show that the application of the thin-layer chromatographic technique opens the route to quickly obtain a considerable amount of information, though the results are at best semi-quantitative as regards their value in theoretical calculations.

It is advantageous that the need for a diluent is eliminated; which is important, as it has been repeatedly shown that this so-called "inert" solvent plays a significant role in liquid-liquid extraction; moreover, prior acclimatisation can be omitted.

Our data indicate that the Adogens 364, 368 and 464, Alamine 336, Aliquat 336, TnOA and TiOA (and tetrahexylammonium chloride) all show an analogous behaviour, which also holds for the Amberlites LA-1 and LA-2 and lastly for Primene JM-T, though they adsorb more weakly. Inexpensive technical-grade products may therefore be chosen to replace more expensive ones, such as tetrahexylammonium salts and TnOA. By selecting a few amines with divergent adsorption strength the R_F values for a cation in a certain medium may be varied either by varying the molarity of the equilibration solution (cf. Table II; however, higher molarities will lengthen the elution time) or by mixing two or more of the selected amines (cf. Figs. 2, 3 and 6).

Moreover, our methods, in some respects, compare favourably with those involving the use of solid resin-impregnated papers. The latter are far more expensive and not so handy either, the use of HCl being limited to normalities up to 8 N HCl. On the other hand, the use of partly organic solvent mixtures (ref. 20 and own unpublished experiments) is possible only using the resin paper. LEDERER's investigations³⁵ using anionic, cationic and neutral papers may also be transferred into our field by using paper impregnated with e.g. HDEHP and DNS as cation exchange paper.

Our results show the necessity to test further some of the selected anion-exchangers with respect to their behaviour with other strong monobasic acids. This work, that is currently being done, may shed more light on the reliability of the adsorption sequence tentatively proposed above. Moreover, it may show which systems are most promising for further qualitative and quantitative separations. Lastly, despite the fair correspondence between chromatography, extraction and ion-exchange found until now, it will be necessary to support this evidence by collecting data on more ions.

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SUMMARY

Paper and thin-layer chromatography have been carried out in HCl media, using supports impregnated with basic liquid ion-exchangers. Approximately ten high-molecular-weight amines and substituted ammonium salts have been successfully investigated in combination with 9 cations. From the R_F spectra so obtained a sequence for the adsorption strength of these liquid ion-exchangers has been tentatively derived.

The R_F spectra are favourably compared with LEDERER's data on papers impregnated with solid anion resin; a remarkable correspondence with results obtained when using neutral organophosphorus compounds is also pointed out. The curves are discussed assuming among other things the formation of chloro anions and desorption owing to competition by the ligand ion.

Advantages of the chromatographic techniques with respect to speed, low cost, elimination of diluent and overall versatility are outlined. Some possible applications for practical and theoretical purposes are considered.

REFERENCES

- 1 E. L. SMITH AND J. E. PAGE, *J. Soc. Chem. Ind.*, 67 (1948) 48.
- 2 C. F. COLEMAN, *Nucl. Sci. Eng.*, 17 (1963) 274.
- 3 C. F. COLEMAN, C. L. BLAKE, JR. AND K. B. BROWN, *Talanta*, 9 (1962) 297.
- 4 H. GREEN, *Talanta*, 11 (1964) 1561.
- 5 F. L. MOORE, *U.S. At. Energy Comm. Rept.*, NAS-NS 3101, 1960.
- 6 E. CERRAI, in M. LEDERER (Editor), *Chromatographic Reviews*, Vol. 6, Elsevier, Amsterdam, 1964, p. 129.
- 7 J. W. O'LAUGHLIN AND C. V. BANKS, *U.S. At. Energy Comm. Rept.*, IS-737, 1963.
- 8 T. B. PIERCE AND R. F. FLINT, *Anal. Chim. Acta*, 31 (1964) 595.
- 9 T. B. PIERCE AND P. F. PECK, *Analyst*, 89 (1964) 662.
- 10 S.-W. PANG AND S.-C. LIANG, *Hua Hsueh Hsueh Pao*, 29 (1963) 319; and 30 (1964) 237.
- 11 H.-W. CHENG, C.-H. KE, C.-Y. LIN AND J. W. WINCHESTER, *J. Chinese Chem. Soc. (Taiwan)*, 10 (1963) 80.
- 12 H. GROSSE-RUYKEN AND J. BOSHOLM, *J. Prakt. Chem.*, 25 (1964) 79; and 26 (1964) 83.
- 13 S. SIEKIERSKI AND R. J. SOCHACKA, *J. Chromatog.*, 16 (1964) 376 and 385.
- 14 M. N. SASTRI AND A. P. RAO, *Z. Anal. Chem.*, 196 (1963) 166; and 207 (1965) 409.
- 15 G. WERNER, *Z. Chem.*, 5 (1965) 147.
- 16 C. TESTA, *J. Chromatog.*, 5 (1961) 236.
- 17 E. CERRAI AND C. TESTA, *J. Chromatog.*, 5 (1961) 442.
- 18 E. CERRAI AND C. TESTA, *J. Chromatog.*, 6 (1961) 443.
- 19 C. TESTA, *Anal. Chem.*, 34 (1962) 1556.
- 20 E. CERRAI AND C. TRIULZI, *J. Chromatog.*, 16 (1964) 365.
- 21 S.-W. PANG AND S.-C. LIANG, *Hua Hsueh Hsueh Pao*, 30 (1964) 401.
- 22 S.-W. PANG AND S.-C. LIANG, *K'o Hsueh T'ung Pao*, (1964) 156; *C.A.*, 61 (1964) 15324f.
- 23 A. G. HAMLIN, B. J. ROBERTS, W. LOUGHLIN AND S. G. WALKER, *Anal. Chem.*, 33 (1961) 1547.
- 24 J. MIKULSKI AND I. STROŃSKI, *J. Chromatog.*, 17 (1965) 197.
- 25 E. CERRAI AND C. TESTA, *J. Chromatog.*, 8 (1962) 232.
- 26 E. CERRAI AND G. GHERSINI, *Energia Nucl. Milan*, 11 (1964) 441.

- 27 P. MARKL AND F. HECHT, *Mikrochim. Acta*, (1963) 970.
- 28 U. A. TH. BRINKMAN AND G. DE VRIES, *J. Chromatog.*, 18 (1965) 142.
- 29 F. FEIGL, *Spot Tests in Inorganic Analysis*, 5th Ed., Elsevier, Amsterdam, 1958.
- 30 P. E. VERKADE, J. VAN DER LEE AND W. MEERBURG, *Rec. Trav. Chim.*, 54 (1935) 716.
- 31 A. J. P. MARTIN AND R. L. M. SYNGE, *Biochem. J.*, 35 (1941) 1358.
- 32 K. A. KRAUS AND F. NELSON, *Proc. Intern. Conf. Peaceful Uses At. Energy, Geneva, 1955*, 7 (1956) 113.
- 33 M. LEDERER AND L. OSSICINI, *J. Chromatog.*, 13 (1964) 188.
- 34 E. CERRAI AND C. TESTA, *J. Chromatog.*, 7 (1962) 112.
- 35 M. LEDERER AND F. RALLO, *J. Chromatog.*, 7 (1962) 552.

J. Chromatog., 22 (1966) 407-424