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CHROMATOGRAPHIC TECHNIQUES USING LIQUID ANION EXCHANGERS
V. H₂SO₄ SYSTEMS*

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SUMMARY

Using thin-layer chromatography on silica gel impregnated with Aliquat 336, Alamine 336, Amberlite LA-1 or Primene JM-T, and on non-impregnated silica gel, the behaviour of 25 ions in H₂SO₄ and sulphate salt systems has been systematically investigated. The chromatographic data confirm earlier work on liquid-liquid extractions regarding the sorption sequence of the exchangers. A number of successful separations is reported.

Two general patterns of dependence of metal extraction on exchanger class exist, *viz.* the sequence primary < secondary < tertiary \approx quaternary (the sequence also encountered in monobasic acid systems); and primary > secondary \approx tertiary \approx quaternary. In the latter case, the low sorption strength of secondary-quaternary exchangers is attributed to steric effects.

INTRODUCTION

High-molecular-weight amines and substituted quaternary ammonium salts have proved very useful in extraction techniques and especially in reversed-phase extraction chromatography. Many interesting qualitative separations have been achieved on paper and thin-layer material impregnated with these so-called liquid anion exchangers. Solutions of nearly all conventional inorganic monobasic acids have been used as eluants; polybasic acids have not yet been employed, with the exception of sulphuric acid. However, even for this acid, only a few data have been reported¹⁻⁴. An interesting result is the successful separation of Zr and Hf, described by YAGODIN AND CHEKMAREV³.

In the present paper, results on a systematic study of liquid anion exchanger-H₂SO₄ systems are reported.

MATERIALS AND METHODS

The exchangers selected were Aliquat 336 (General Mills, Kankakee, Ill., U.S.A.), a C₂₇-C₃₃ methyl-tri-*n*-alkylammonium chloride with a molecular weight of approx. 475; Alamine 336-S (General Mills), a C₈-C₁₀ straight-chain alkylamine with a ter-

* For Part IV of this series, see ref. 20.

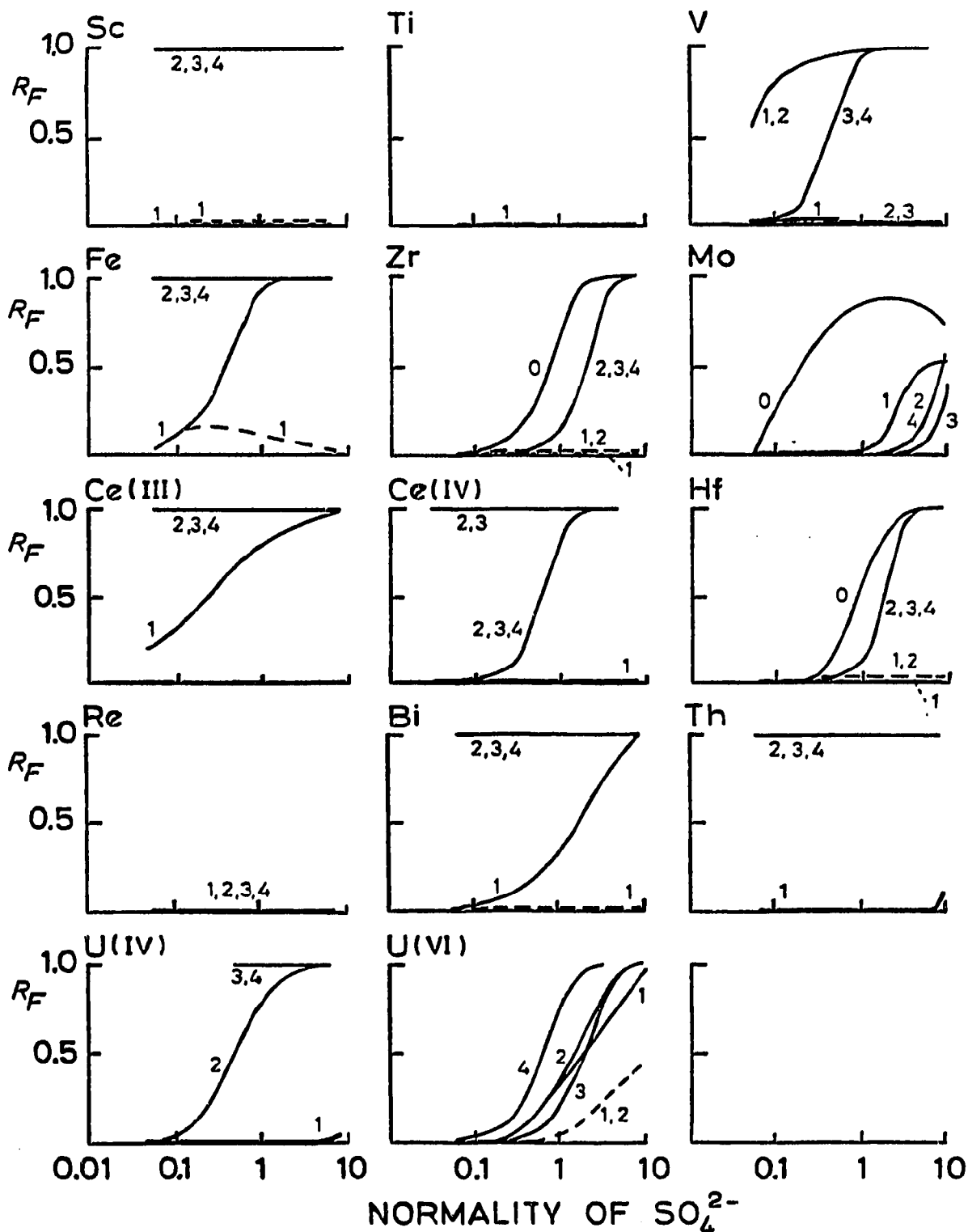


Fig. 1. R_F vs. SO_4^{2-} normality plots for fourteen ions on silica gel impregnated with Primene (1), Amberlite LA-1 (2), Alamine 336-S (3), Aliquat 336 (4), and on silica gel not treated with an anion exchanger (o). Eluants: —, H_2SO_4 ; - - - , $(\text{NH}_4)_2\text{SO}_4$. Details not mentioned in the text are as follows: Ti(IV) shows streaking spots (R_F 0.0–1.0) at all concentrations with Amberlite LA-1, Alamine and Aliquat, the mass centres moving to higher R_F values with increasing acid concentration. For 0.06–0.6 N H_2SO_4 , Ce(IV) and U(IV) show streaking with Amberlite, and Alamine and Aliquat, respectively.

tiary amine content of at least 99% and a molecular weight of 392; Amberlite LA-1 (Rohm and Haas, Philadelphia, Pa., U.S.A.), an unsaturated secondary dodecyltrialkylmethylamine with a mean molecular weight of 372; and Primene JM-T (Rohm and Haas), which consists of a relatively large number of primary amines; it was roughly purified by repeated vacuum distillation and collecting the middle fractions having a mean molecular weight of 300–310 (ref. 5).

Thin-layer plates were prepared as follows: 0.1 M solutions of the amines in CHCl_3 were equilibrated with 2 vol. of 2 N H_2SO_4 . The organic phase was separated and mixed thoroughly with silica gel (Type DO, Fluka, Buchs SG, Switzerland) (silica gel– CHCl_3 (0.6:1, v/v)). Ordinary microscope slides were dipped into the resulting suspension, superfluous material was wiped off the back of the slides, and four to six spots were applied on each plate. Ascending chromatography was carried out for a 3.0-cm run in suitable jars. The duration of the run was generally between 8 and 15 min; with Primene-treated silica gel, however, development may take up to 30–40 min. For details of the experimental procedure and the apparatus required, see refs. 4 and 6.

In the case of Aliquat, equilibration with aqueous H_2SO_4 does not easily lead to complete conversion of the chloride into the sulphate salt form. Therefore, two alternative procedures were investigated, *viz.* (a) equilibration with an aqueous suspension of Ag_2SO_4 , and (b) equilibration with an aqueous suspension of Ag_2SO_4 , and subsequently with 2 vol. of 2 N H_2SO_4 . The R_F vs. N H_2SO_4 plots obtained in chromatography on Aliquat-loaded silica gel are largely independent of the method used for the preparation of the sulphate salt for concentrations of H_2SO_4 of approx. 1 N and higher. However, when Aliquat sulphate is formed according to method (a) and dilute H_2SO_4 solutions are used as eluants, streaking of the spots of some metal ions is observed. Moreover, the R_F data do not fit in with those obtained with the amines as exchangers. No such difficulties are encountered when method (b) is applied for the preparation of the Aliquat sulphate.

Most probably, the diverging results observed with Aliquat sulphate prepared according to methods (a) and (b) are due to the formation of $(\text{R}_4\text{N}^+)_2\text{SO}_4^{2-}$ and $\text{R}_4\text{N}^+\text{HSO}_4^-$, respectively. In the former case, conversion to the hydrogen sulphate salt occurs gradually during development of the chromatogram. This conversion, which will slightly decrease the normality of the aqueous acid eluant and thus will be particularly manifest with dilute solutions, may well account for the irregular R_F spectra obtained with $(\text{R}_4\text{N}^+)_2\text{SO}_4^{2-}$. Since the amines are equilibrated with H_2SO_4 to hydrogen sulphate salts also, a mutual agreement of the R_F data found with these exchangers and with Aliquat hydrogen sulphate can be expected. Method (b) is therefore preferred for the conversion of Aliquat chloride.

The ions investigated were applied using solutions of their sulphates, containing 2–10 mg of ion per ml. The solutions were acidified as far as necessary to prevent hydrolysis. For the visualisation procedures, see refs. 6 and 7. Several elements, *e.g.* Al, Sc, Y, rare earths, and Th, are not easily detected when they move with the solvent front; in these cases, concentrated sample solutions were employed.

RESULTS

A large number of the 25 ions investigated do not show appreciable sorption ($R_F > 0.8$) over the whole H_2SO_4 concentration range employed with any of the four

exchangers. These are: Be(II), Mg(II), Al(III), V(IV), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Ga(III), Y(III), Cd(II) and In(III). For all other ions, the R_F vs. N H_2SO_4 plots are given in Fig. 1.

Chromatography on layers of silica gel slurried with $CHCl_3$ only (without liquid exchanger) results in high R_F values (> 0.8) for all ions with the exception of Ti(IV) and V(V) (streaking), and Zr(IV), Hf(IV) and Mo(VI). The R_F spectra for the latter three ions are included in Fig. 1.

For a limited number of ions, chromatography has been carried out using acidified Li_2SO_4 and $(NH_4)_2SO_4$ solutions as eluants. Ions which do not show appreciable sorption with any of the four liquid anion exchanger- H_2SO_4 systems investigated, e.g. Co(II), Cu(II) and Zn(II), show high R_F values in the salt systems also. However, a distinctly increasing sorption is observed with e.g. Fe(III), Bi(III) and U(VI) on Primene-treated silica gel, and with Zr(IV), Hf(IV) and U(VI) in the Amberlite LA-1 system, the effect being slightly more pronounced with Li_2SO_4 than with $(NH_4)_2SO_4$. Ions such as Sc(III), Zr(IV) and Hf(IV), which consistently show R_F 0 with Primene- H_2SO_4 , also remain at the origin in the salt systems. A few examples have been included in Fig. 1.

Although streaking of the spots occurs rather more frequently with sulphuric acid than with most other inorganic acids used as eluants, various interesting separations are obtained with H_2SO_4 . The results are presented in Fig. 2. The R_F values of some ions, notably Fe(III), are sensitive to changes in the H_2SO_4 concentration in the sample solution. This phenomenon explains the diverging results recorded for iron in Figs. 1 and 2.

DISCUSSION

The R_F spectra presented in Fig. 1 reveal that the ions concerned may be classified in two groups. Group I consists of Sc(III), Ti(IV), Fe(III), Zr(IV), Ce(III), Ce(IV), Hf(IV), Bi(III), Th(IV) and U(IV). For all these ions, sorption is stronger on silica gel impregnated with Primene than on silica gel treated with any of the other exchangers, which do not show significant differences amongst each other. (With U(IV), however, Amberlite LA-1 seems to surpass Alamine and Aliquat.) With the ions of Group II — V(V), Mo(VI), Re(VII) and U(VI) — Primene does not give the strongest sorption, and in fact no distinct sequence in the sorption strength can be observed. Obviously, the sorption sequence primary $<$ secondary $<$ tertiary \approx quaternary, repeatedly reported^{4,8} when solutions of monobasic acids have been employed as eluants, does not hold with sulphuric acid. This result is in agreement with data previously obtained⁴ for Fe(III), Zr(IV), Th(IV) and U(VI) in reversed-phase extraction chromatography on paper loaded with Primene, Amberlite LA-1, and Adogen 368, a tri-*n*-alkylamine of which the alkyl groups consist principally of octyl (40%), decyl (25%) and dodecyl (30%) chains.

The results of reversed-phase chromatography may be compared with data obtained in liquid-liquid extraction, since the distribution coefficient D (= concentration of element in organic phase/concentration of element in aqueous phase) of an extraction system, and the R_F value obtained with an exchanger fixed on an inert support and with the aqueous phase as eluant, are related by^{4,9,10}:

$$D = k(\tau/R_F - \tau)$$

where k is a constant. However, in deriving this equation, several assumptions have been made which are not fulfilled in practice. Only a semi-quantitative correlation can therefore be expected between the changes in the values of $1/R_F - 1$ and of D with varying normality of the aqueous acid solution. This correlation, verified experimentally for various acid eluant systems^{4,10}, also holds for the H_2SO_4 system: (i) the surprisingly high extraction efficiency of Primene towards Group I ions has repeatedly been observed¹¹⁻¹³ in liquid-liquid extraction; (ii) the existence of two general patterns of dependence of metal extraction on exchanger class in extraction analysis has already been noted by COLEMAN *et al.*¹¹. Y(III) and In(III) are the only exceptions and do not show sorption on Primene-treated silica gel, although high distribution coefficients have been reported for these ions at low aqueous H_2SO_4 concentrations by ISHIMORI *et al.*¹³. Surprisingly, sorption is observed for Y(III) and In(III) (R_F approx. 0.7 at 0.06 $N H_2SO_4$) when thin layers are prepared with aged (> two days) silica gel suspensions. This phenomenon, which is also observed with some of the rare earth elements, has not been investigated further.

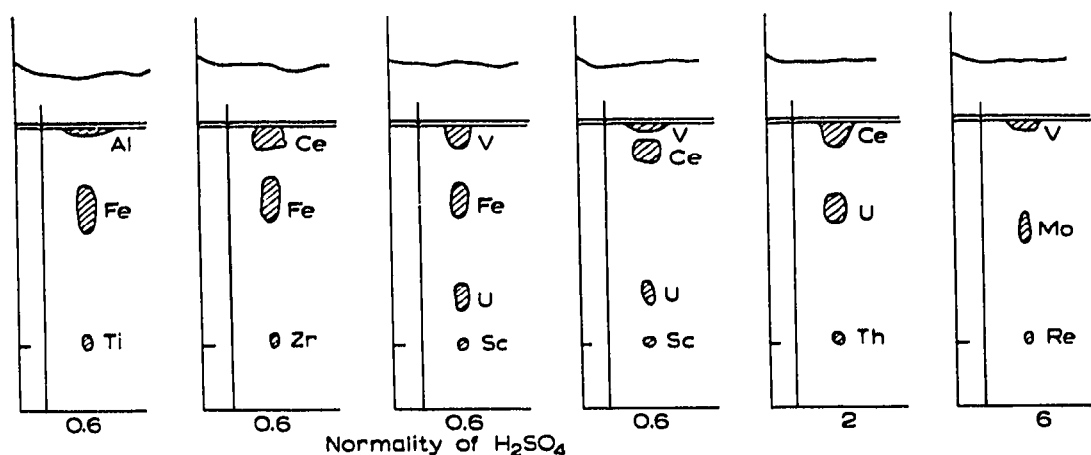


Fig. 2. Examples of qualitative separations in the Primene- H_2SO_4 system. Ce = Ce(III); U = U(VI).

Regarding the mechanism of sorption/extraction in sulphate systems, the following remarks can be made:

(1) The increasing R_F values and decreasing distribution coefficients obtained for all ions when the aqueous H_2SO_4 concentration is increased, are most probably due to a shift of the $SO_4^{2-} \rightleftharpoons HSO_4^-$ equilibrium to the right: the HSO_4^- ions are held less tightly in the aqueous phase, and thus displace other anions better from the organic phase. When the solutions of H_2SO_4 are substituted by sulphate salt solutions, however, exchange is again with SO_4^{2-} rather than HSO_4^- and sorption of the anionic metal complexes increases (Fig. 1; *cf.* ref. 14).

(2) In the last decade, steric factors have repeatedly been suggested^{4,15,16} as a probable cause of the reversal of the normal sorption sequence. The subject has recently been discussed by SHEVCHUK *et al.*¹⁶. The steric-compatibility theory may be summarised as follows. Association of the alkylamine $\cdot H^+$ cations with singly and doubly charged complex anions is not sterically hindered, irrespective of the class of exchanger used. With triply and more highly charged anionic complexes, however,

the attachment of three tertiary or secondary alkylamine·H⁺ cations is hindered; sorption/extraction by means of a primary amine will therefore now be favoured over that involving the more bulky exchangers. The hypothesis is confirmed by data^{15, 17, 18} on the extraction of *e.g.* M(C₂O₄)₃³⁻ and M(CN)₆³⁻ (M = Fe(III) or Co(III)), Fe(CN)₆⁴⁻ and Fe(PO₄)₂³⁻, primary amines being the best extractants in all cases. The superior extraction efficiency of primary amines towards FeF₆³⁻ and various other fluoro complexes in both extraction¹⁹ and reversed-phase chromatography²⁰ has also been noted.

For the sulphate system, a considerable amount of information became available recently. As regards trivalent rare earths, Zr (and Hf), and Sc — all showing the strongest sorption in the presence of a primary amine — the identification of the highly charged anions La(SO₄)₃³⁻, Zr(SO₄)₄⁴⁻ and ScOH(SO₄)₃⁴⁻ (at pH 2.3)^{16, 21, 22} supports the hypothesis mentioned. The same holds true for Th: for this element, the extraction of a compound showing the stoichiometry (R₂NH₂)₆Th(SO₄)₅(H₂O)₃ has been claimed²³ in a study of the dioctylamine–Th(IV)–H₂SO₄ system. On the other hand, the isolation of (RR'₂NH⁺)₂FeOH(SO₄)₂²⁻ after extraction of iron from aqueous sulphate solutions (pH 2.3) by primary and secondary amines^{24, 25}, and the identification of the UO₂(SO₄)₃⁴⁻ moiety²⁶ cannot easily be fitted into the picture. As regards the extraction of U(VI), it must be added that there is no agreement between authors on the identity of the metal-containing anion in the organic phase^{26–29}.

In summary, for the large majority of the metal ions investigated, sorption/extraction from aqueous sulphate solutions is determined by anion-exchange only. High *R_F* values are consistently observed for cations which do not form anionic metal-sulphato complexes — sorption is recorded for the rest. The influence of phenomena other than ion exchange, which is manifest in the *R_F* spectra for Mo, Zr and Hf (Fig. 1), needs further investigation.

The present chromatographic data confirm earlier work on liquid–liquid extraction satisfactorily as regards the sorption sequence of the liquid anion exchangers. The occurrence of the sequence primary > secondary ≈ tertiary ≈ quaternary, the reverse of that normally encountered with monobasic acids as eluants, is largely due to steric effects, which cause a lowering of the extraction efficiency of bulky exchangers towards highly charged anions. However, although there is a large amount of supporting evidence, exceptions to the rule have been reported; moreover, the influence of *e.g.* aqueous phase acidity on the composition of the extracted metal-containing anions, and the actual structure of the alkylammonium salts, are only incompletely known. Therefore, more research will be necessary before a generally valid conclusion regarding the influence of steric effects can be drawn.

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