

THE NATURE OF SOME METAL-CHLORO ANIONS PRESENT IN THE ORGANIC PHASE IN REVERSED-PHASE CHROMATOGRAPHY INVOLVING LIQUID ANION-EXCHANGERS

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INTRODUCTION

In a recent series of papers¹⁻³ attention has been paid to the behaviour of cations in reversed-phase thin-layer chromatography using liquid anion-exchangers, with special emphasis on the chloride system. Ample demonstration has been given of the analogy between our chromatographic method and other similar techniques on the one hand, and liquid-liquid extractions using the same liquid anion-exchangers dissolved in an organic diluent, on the other.

At a later stage, attention was focussed on the nature of the metal-chloro species present in the organic phase in extractions, and in the impregnated thin layer in chromatography⁴. Methods of investigation included spectral measurements of the extracts and so-called maximum-loading experiments, in which the maximum metal/exchanger ratio in the organic phase is determined at constant exchanger and increasing metal concentration. The present paper is a continuation of this research in order to obtain information on the nature of the species present in the thin layer in reversed-phase chromatography.

MATERIALS AND METHODS

Liquid anion-exchangers

Three liquid anion-exchangers were currently investigated, *viz.* the quaternary Adogen 464, the tertiary Alamine 336 and the secondary Amberlite LA-1. For details concerning these compounds and some other anion-exchangers, which were incidentally introduced for reasons outlined below, one is referred to refs. 1-3.

Chemicals

All reagents were of normal analytical reagent grade; tetraphenylarsonium chloride was a product from Th. Schuchardt (München, Germany) and tetrabutylammonium bromide was obtained from Fluka (Buchs, S.G., Switzerland). Anhydrous CoCl_2 and CuCl_2 were prepared from the corresponding water-containing chlorides by allowing them to react with thionyl chloride⁵.

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

Determination of the cations

In liquid-liquid extraction experiments, the metals were determined (a) in an aliquot of the aqueous phase after removal of HCl by evaporation or (b) by stripping the organic phase with 0.1 *M* HNO₃ and subsequent analysis of the aqueous extract. The latter technique was employed with extractions involving the use of LiCl and with experiments where the percentage extraction was low.

Quantitative determination of Cu(II), Co(II), Mn(II), Zn(II) and Cd(II) was carried out using EDTA as a titrant. With the former two ions murexide served as the indicator, while eriochrome black T was selected for the titrations of manganese, zinc and cadmium.

Fe(III) was determined either using the iodometric procedure involving titration with thiosulphate, or by titration with MnO₄⁻ using ferroin as an indicator, after previous reduction to Fe(II) with a silver reductor.

Chromatography

Thin-layer chromatography was carried out on silica gel impregnated with a 0.1 *M* solution of the anion-exchanger selected in chloroform; in paper chromatography, Whatman paper No. 1 was employed, which was treated with a 0.15 *M* solution of the exchanger. For a full description of techniques, apparatus, identification etc. one is referred to refs. 1 and 3.

Spectra

Ultraviolet and visible spectra were recorded on an Optica CF-4 or a Zeiss PMQ II spectrophotometer, using 1- and 10-mm quartz and 30-mm glass cuvettes.

Liquid-liquid extraction

Experiments on liquid-liquid extractions were carried out at room temperature by shaking an aqueous chloride solution of the cation to be investigated in a separatory funnel with an equal volume of the selected liquid anion-exchanger in toluene; generally, 10 or 15 ml of each phase were employed. All solutions of the anion-exchangers in toluene were equilibrated beforehand with 3 vol. of 2 *N* HCl. Shaking was done on an E. Bühler Type Sm-2 apparatus for times varying between 10 and 30 min. In a few cases, it was demonstrated that this was ample time for reaching equilibrium (*cf.* ref. 6).

In investigations involving undiluted anion-exchangers, prolonged centrifugation was necessary to achieve a satisfactory separation of the viscous organic mass from the aqueous phase. Therefore, thick-walled 15-ml test tubes were employed to carry out these extractions, and accordingly smaller volumes of the two phases were used. Moreover, the ratio $v_{\text{aq.}}/v_{\text{org.}}$ was not always 1/1, though it was kept constant in every series of experiments. This did not introduce complications, because the organic phases were exclusively used for qualitative, *i.e.* spectral measurements.

RESULTS

Reversed-phase chromatography

Reversed-phase chromatography was carried out on silica gel impregnated

with Adogen 464, Alamine 336 and Amberlite LA-1, using LiCl solutions of varying molarity—and slightly acidified with HCl to prevent hydrolysis of the cations tested—as an eluant. R_F vs. M Cl⁻ spectra for 5 ions are presented in Fig. 1, where curves pertaining to the use of HCl as an eluant (*cf.* ref. 1) have been included for comparison. Data on Cd(II) strongly resembled those on Zn(II) and have therefore been omitted. Because the sorption strength of Alamine is too high to show distinctly the characteristic differences between the R_F spectra obtained with LiCl and HCl, respectively, some experiments on the silica gel-0.05 M Alamine system have been included in Fig. 1.

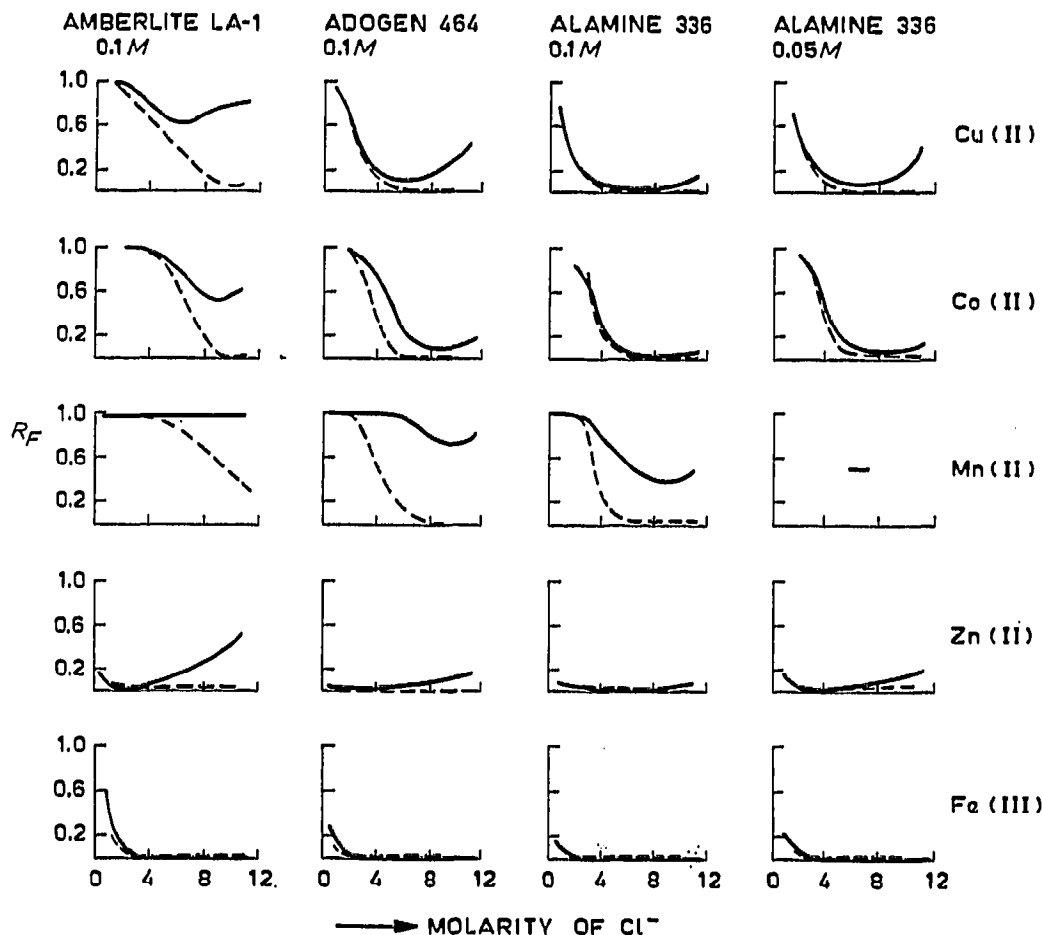


Fig. 1. R_F spectra for 5 ions using various amine·HCl and quaternary ammonium chloride systems in thin-layer chromatography. 0.1 M and 0.05 M pertain to the concentration of the exchanger in the CHCl_3 solution used for impregnation of the silica gel. Eluants: —, HCl; ---, slightly acidified LiCl.

In thin-layer chromatography involving LiCl, the elution times were fairly long, especially with Adogen 464, and on an average took approx. 30 min in the case of the lower molarities and up to several hours for 9–11 M LiCl solutions. Moreover, at high LiCl strengths detection of the ions was somewhat complicated owing to the hygroscopic character of the LiCl-containing thin layers. These practical difficulties were less pronounced in paper chromatography, where the substitution of HCl by LiCl also led to a distinct, though smaller, lowering of the R_F values. Similar results were obtained here for some other ions, *e.g.* In(III), ReO_4^- and Br^- .

Parenthetically, it may be remarked that our results agree with those of BAGLIANO *et al.*⁷, who used the strong-base solid resin paper Amberlite SB-2.

Liquid-liquid extraction

For the cations systematically investigated in chromatography, several series of extraction experiments were performed, using both HCl and slightly acidified LiCl solutions as aqueous phases. Adogen 464, Alamine 336 and Amberlite LA-1 were selected as liquid anion-exchangers; triisooctylamine and Adogen 368 were incidentally tested, *viz.* with Zn(II), and gave results nearly identical with those obtained with Alamine 336. Our results, pictured in Fig. 2, are in good agreement with literature data, *e.g.* those recently published by SEELEY AND CROUSE⁸.

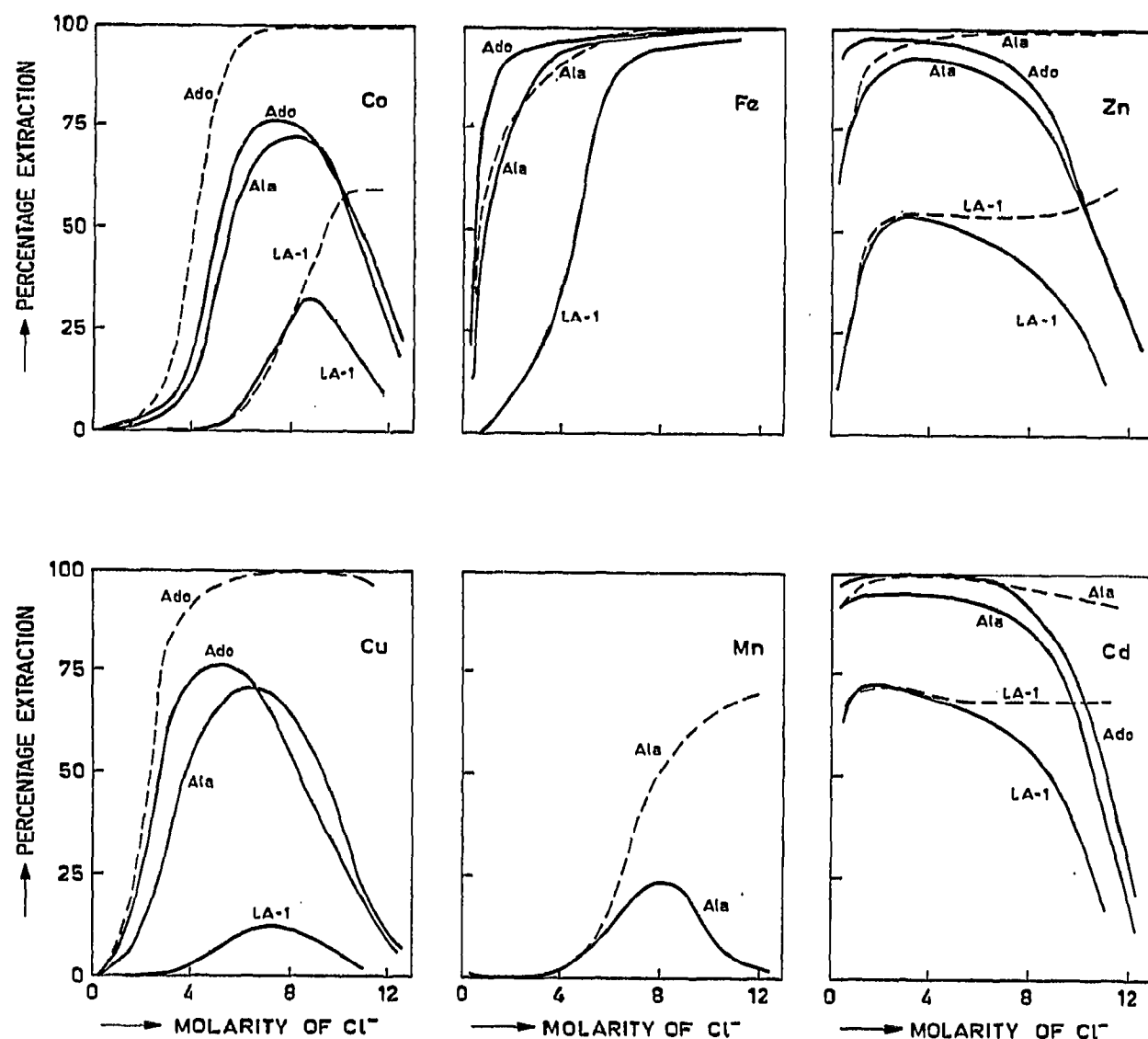


Fig. 2. Percentage extraction *vs.* M Cl^- curves for 6 ions using various amine·HCl and quaternary ammonium chloride salts dissolved in toluene as the organic phase. In the starting solutions the molarity of the exchangers was 0.10 M and that of the cations approx. 0.04 M ; $v_{aq.} = v_{org.}$. Aqueous phase: —, HCl; ---, slightly acidified LiCl. Abbreviations: Ado = Adogen 464; Ala = Alamine 336; LA-1 = Amberlite LA-1.

Job curves

In investigations exclusively concerned with the stoichiometric composition of complex species A_nB_m , it suffices to prepare mixtures of A and B subject to the condition that the total molar concentration of the two components remains constant. For each mixture a property characteristic for A_nB_m , e.g. its absorbance, is determined and from this is subtracted the corresponding quantity calculated on the assumption that no complex formation has taken place. In this so-called method of continuous variation⁹, a plot of the resulting value vs. the mole fraction will have an extremum for $c_A/c_B = n/m$.

When trying to determine the composition of the complex metal-chloro anions MCl_p^{n-} , it is sufficient to evaluate the ratio (metal/exchanger)_{org.}, because the number of monovalent exchanger cations present per atom M corresponds with the negative charge on the complex anion (however, see the DISCUSSION). We therefore introduced the method of continuous variation in our investigations by varying the metal/exchanger ratio at a constant high Cl^- concentration. It has been shown by IRVING AND PIERCE¹⁰ that JOB'S method may be applied to such two-phase systems.

Experiments were carried out using the Adogens 464 and 368, and Amberlite LA-1; Fe(III), Cu(II) and Co(II) were the metals selected. 0.1 M stock solutions of the cations and the exchangers were made in aqueous HCl of appropriate normality (see legend to Fig. 3) and toluene, respectively. The experiments were performed by shaking suitable amounts of the stock solutions diluted in such a way that variable metal/exchanger ratios were obtained while the total molar concentration ($c_{\text{metal}} + c_{\text{exchanger}}$) was kept constant; $v_{\text{aq.}}/v_{\text{org.}}$ was 1/1 in all experiments.

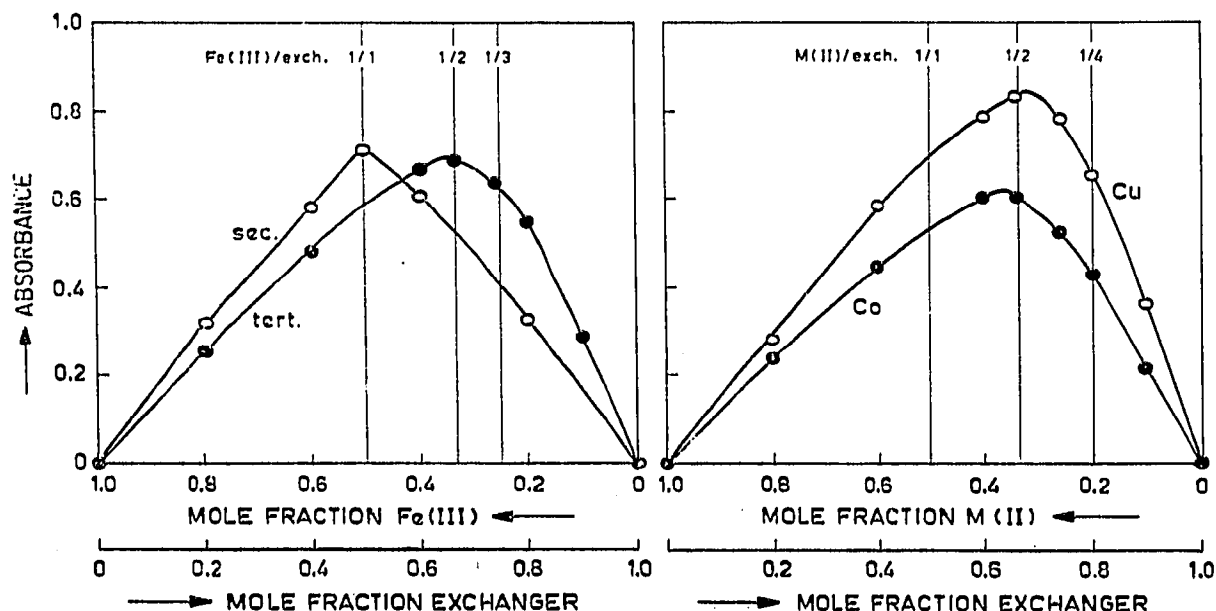


Fig. 3. JOB curves for various metal-chloride systems; $c_{\text{metal}}/c_{\text{exch.}}$ was varied at constant ($c_{\text{metal}} + c_{\text{exch.}}$) and at constant Cl^- concentration. Cobalt: Adogen 464, 7.5 N HCl; $\lambda_{\text{max.}} = 698$ nm; Copper: Adogen 368, 7.0 N HCl; $\lambda_{\text{max.}} = 410$ nm. Iron: \circ — \circ , Amberlite LA-1, 8 M LiCl + 1 N HCl; \bullet — \bullet , Adogen 368, 2 N HCl; $\lambda_{\text{max.}} = 366$ nm in both cases. All spectra pertain to the organic phases.

From the results represented in Fig. 3 we may conclude that with Co(II) and Cu(II) maximum absorption occurs at a metal/exchanger = 1/2 ratio, so that the complex species present in the organic phase may be tentatively formulated as $(R_2R'_2N^+)_2MCl_4^{2-}$, where R stands for an alkyl group and R' represents either an alkyl group or an H atom. With Fe(III), on the other hand, where a fairly large number of experiments was performed, the picture is more complicated, the results being dependent on the class of the anion-exchanger tested. Using the quaternary Adogen 464, maximum absorption is found at a metal/exchanger = 1/1 ratio irrespective of the Cl^- concentration in the aqueous phase. With tertiary and secondary compounds, however, maximum absorption shifts from a metal/exchanger = 1/2 to a metal/exchanger = 1/1 ratio when substituting a low aqueous Cl^- concentration, e.g. 2 M, by a high one, e.g. 8 M; two representative curves are given in Fig. 3. The interpretation of these results will be given in the DISCUSSION.

Assignment of spectra

In order to be able to interpret our spectral data, preliminary experiments were carried out for the Co(II)-, Cu(II)- and Mn(II)-chloride systems. The spectrum of $FeCl_4^-$ is well known, so that in this case we may rely on literature data (see e.g. refs. 11 and 12).

With Co(II) and Cu(II), constant amounts of either anhydrous $CoCl_2$ or $CuCl_2$ were shaken with variable amounts of Adogen 464 (occasionally Adogen 368) dissolved in toluene or acetonitrile. In combination with data reported in the literature¹³⁻¹⁵ our experimental results could be interpreted to yield the following conclusions of importance for our present work.

(a) The monovalent anion $CoCl_3^-$ is characterized by a peak at 590 nm*, which is completely absent from the spectrum of $CoCl_4^{2-}$, which may be identified on the basis of its 620-710-nm band showing three distinct peaks, at 633, 668 and 698 nm, respectively.

(b) When toluene is used as the solvent, in all cases—i.e., irrespective of the Cl/Co ratio—the same spectrum is observed, viz. that assigned to $CoCl_4^{2-}$. In accordance with this phenomenon, the anhydrous $CoCl_2$ completely dissolves only when using toluene, if the ratio exchanger/ $CoCl_2$ exceeds a value of approx. 2/1.

(c) In the case of the Cu(II)-chloride system, the occurrence of peaks at 409 and 475 nm indicates the presence of $CuCl_4^{2-}$ and $CuCl_3^-$, respectively.

(d) Contrasting the results obtained with Co(II), in the case of Cu(II), at a Cl/cation ratio of approx. 3/1, the monovalent anion $CuCl_3^-$ is present in solutions in both acetonitrile and toluene, though to a distinctly lesser extent in the latter solvent. This phenomenon may be due to the formation of some dimeric $Cu_2Cl_6^{2-}$, in which every copper atom is still surrounded by four chlorine atoms.

The chloro complexes of Mn(II) are not very stable and moreover have fairly low molar absorbances. Therefore, no systematic study of Mn(II)-chloro complexes was undertaken and work was limited to the preparation of the crystalline tetraphenylarsonium tetrachloromanganate(II), synthesized according to ref. 16. The spectrum of a solution of this compound in dichloroethane showed good analogy with that recorded by GILL AND NYHOLM¹⁶ as regards the peaks at 433 and 447 nm

* This and all other wavelengths given in this study are average values; when using different anion-exchangers, variations up to 3 nm were generally encountered.

and their molar absorption coefficients (see Table I). However, the peak at 358 nm was not observed by these authors and therefore our spectroscopic measurements were extended to MnBr_4^{2-} , which was prepared as the crystalline tetrabutylammonium salt. From a comparison of the data summarized in Table I it is evident that the peaks at 358, 433 and 447 nm all may be attributed to MnCl_4^{2-} .

TABLE I

WAVELENGTHS (nm) OF SOME IMPORTANT PEAKS IN THE ULTRAVIOLET AND VISIBLE SPECTRA OF MnCl_4^{2-} AND MnBr_4^{2-}

Numbers in parentheses give molar absorption coefficients.

MnCl_4^{2-}		MnBr_4^{2-}		
<i>This work</i>	<i>Ref. 16</i>	<i>This work</i>	<i>Ref. 16</i>	<i>Ref. 17</i>
358 (1.4)		362 (4.0)		363 (3.7)
380 (sh.)		375 (3.1)	371 (2.4)	374 (3.0)
433 (0.5)	430 (0.5)	437 (1.3)	437 (1.0)	437 (1.2)
447 (0.7)	445 (0.7)	453 (2.2)	452 (1.9)	455 (2.2)
458 (sh.)		470 (sh.)	465 (sh.)	466 (sh.)

Spectra

Ultraviolet and visible spectra were recorded for the Co(II)-, Cu(II)-, Fe(III)- and Mn(II)-chloride systems, using both liquid anion-exchangers dissolved in toluene and undiluted exchangers as the organic phases. Unless otherwise specified (*i.e.* with the undiluted quaternary exchangers), the exchangers were always equilibrated with a HCl solution of appropriate normality before being contacted with a metal-containing aqueous phase.

Diluted liquid anion-exchangers. As has been described in a previous section, various series of liquid-liquid extractions were performed in order to determine the percentage extraction. Spectral data were collected for a representative set of the organic extracts obtained in that way, *viz.* for toluene solutions of quaternary (Adogen 464), tertiary (Alamine 336) and secondary (Amberlite LA-1) exchangers, that had been contacted with metal-containing aqueous phases of widely divergent HCl and LiCl concentrations (2-3, 5-8 and approx. 11 N with respect to HCl, and 5-8 and approx. 10 M with respect to LiCl*).

For each of the four cations investigated, the spectra of its metal-containing organic extracts were identical, irrespective of the exchanger tested or the composition of the aqueous phase. The results may be summarized as follows (for complete spectra, *cf.* refs. 11, 13, 17 and 19).

(a) The spectra of the blue Co(II)-containing extracts were all characterized by the three peaks in the 620-710-nm band and the complete absence of the 590-nm peak, which points to the sole presence of CoCl_4^{2-} in the complex ammonium metal-chloro salts. The same results were obtained for organic extracts that had been shaken with aqueous solutions containing an excess of the cation as compared with the liquid anion-exchanger.

(b) In the case of Cu(II), all bright-orange coloured organic extracts showed only the peaks due to CuCl_4^{2-} (409 and 292 nm), while absorption at 475 nm was

* In these and all subsequent cases, the LiCl solutions were slightly acidified with HCl.

negligible. As was the case with the other cations investigated, the shape of the spectra did not alter when the samples were diluted with toluene.

(c) All Fe(III)-containing organic extracts, which had a yellow colour, showed characteristic absorption at 318 and 366 nm, while smaller peaks were observed at 535, and at approx. 615 and 690 nm. These results imply that even when working under conditions where tertiary and secondary amine hydrochlorides on the one hand, and quaternary ammonium salts on the other, form complex Fe(III)-chloro salts of different composition, all spectra still closely resemble the literature spectra ascribed to FeCl_4^- .

(d) The extraction of Mn(II) from aqueous chloride solutions is appreciable only when using fairly concentrated LiCl solutions (see Fig. 2); moreover, the molar absorbance of the yellow-green MnCl_4^{2-} is quite low. Therefore, only approx. 10 M LiCl aqueous solutions were used, in combination with an excess Mn(II) to further stimulate the extraction. The light-coloured exchangers Alamine 336 and the quaternary Aliquat 336 were selected as extractants. The spectra were completely analogous, showing peaks at 358, 434 and 447 nm, *i.e.* those assigned to MnCl_4^{2-} .

Undiluted anion-exchangers. To imitate thin-layer chromatographic conditions as much as possible, undiluted exchangers were shaken with metal-containing chloride solutions. These corresponded in composition to the aqueous phases that were used above.

Initially, quaternary compounds were selected only for experiments on undiluted exchangers, in view of the difficulty in handling these syrupy substances: the quaternary exchangers are purchased as the chloride salts and therefore may be used without prior equilibration. At a later stage, however, we still tried to use tertiary exchangers, *viz.* Adogen 368 and Alamine 336. However, when the former compound was equilibrated with aqueous HCl, a mass of extremely high viscosity was formed that could hardly be removed from the separation funnel. Therefore, Alamine 336 was selected whose chloride salt, although it also became very viscous, could still be handled. The investigations were further extended by studying a secondary amine as well. Amberlite LA-1 was initially used, but here the same difficulties were encountered as mentioned above for Adogen 368, especially at high HCl concentrations. Therefore, all work on secondary amines was carried out using the light-coloured, less viscous di-(2-ethylhexyl)-amine. Here, extraction with the undiluted exchanger could satisfactorily be carried out at 2–5 N HCl and 5–10 M LiCl, but with more concentrated HCl solutions an intense red colour developed* on equilibration, and in addition the organic mass became very viscous. Therefore, an 11 N HCl aqueous solution was used with Co(II) only, where rapid experimenting permitted us to record the expected 620–710 nm band.

As regards the experimental results, the following observations may be made.

(a) The investigations were started with the system quaternary exchanger–Co(II)-Cl⁻. The spectra of the undiluted organic masses did not show any trace of the 590-nm (CoCl_3^-) peak, which was also absent after dilution with the liquid anion-exchanger itself. This dilution step had to be introduced because the high absorption of the original Co(II)-containing mass did not allow us to record the exact position of

* Equilibration of all secondary and tertiary exchangers investigated with more concentrated HCl solutions yielded fairly dark-coloured amine hydrochlorides, while heat was evolved in the reaction.

λ_{\max} . in the 620–710-nm region. Dilution using toluene did not seem appropriate, because in that case any CoCl_3^- present undoubtedly would have been converted into CoCl_4^{2-} . When dilution was carried out with acetonitrile instead of anion-exchanger, a very small peak at 590 nm could be observed next to the strong CoCl_4^{2-} band.

The experiments described here were initially carried out using Aliquat 336, because it is less viscous than Adogen 464 and moreover is lighter in colour. At a later stage, the experiments were repeated with Adogen 464 and di-(2-ethylhexyl)-amine was also investigated. In all cases, completely analogous spectra were obtained.

(b) With Cu(II), the spectra of all organic extracts again showed the peaks due to CuCl_4^{2-} only; Adogen 464, Alamine 336 and di-(2-ethylhexyl)-amine were investigated. In view of the results presented for Co(II), here and in all subsequent cases, dilution of the organic masses after the contacting step was done only using the exchangers themselves.

(c) With Fe(III), the earlier experiments⁴ gave the most satisfactory results. Therefore, work with undiluted compounds was limited to Aliquat 336 and di-(2-ethylhexyl)-amine. In all instances, the spectra were identical to those found above, showing the two characteristic peaks at 318 and 366 nm.

(d) Using the same arguments as presented above, we limited the research on Mn(II) to extractions from approx. 10 M LiCl aqueous solutions, using Aliquat 336 and Alamine 336 as extractants only. The spectra again indicated MnCl_4^{2-} to be the metal-containing species present in the organic phase.

DISCUSSION

In reversed-phase chromatography using liquid anion-exchangers the R_F vs. N acid (HCl) spectra of a great majority of the ions studied may be qualitatively explained in terms of anion-exchange and competition between the complex metal-chloro anions and the excess Cl^- present; hydrolysis and/or precipitation must occasionally be taken into account. On the basis of the analogy between results obtained in chromatography and liquid-liquid extraction, it has repeatedly been assumed that the mechanism describing the extraction process will also be valid in reversed-phase chromatography. We have already shown⁴ that with Co(II), Cu(II), Zn(II), Cd(II) and Fe(III), MCl_4^{2-} is the metal-containing species predominantly present in the organic phase in extraction analysis; this conclusion probably also holds for chromatography.

In the present paper special attention has been paid to the validity of the conclusions for chromatography. Moreover, the nature of the metal-containing species has been determined not only at the point of minimum R_F (maximum extraction), but over a considerable range of Cl^- concentrations.

Starting our discussion with the Co(II)-chloride system, we may conclude on the basis of the assignment of the 620–710-nm band to CoCl_4^{2-} , that in both liquid-liquid extraction and reversed-phase chromatography only one Co(II)-containing species, *i.e.* CoCl_4^{2-} , is present in the organic phase, irrespective of (a) the class of the liquid anion-exchanger used, (b) the complex Co(II)-chloride species predominantly present in the aqueous phase, which are undoubtedly different in *e.g.* 3 and 10 M Cl^- solutions²¹, and (c) the use of either HCl or LiCl in the aqueous phase. This result

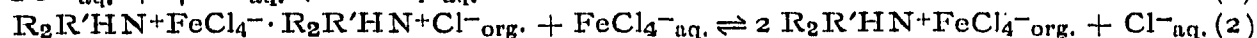
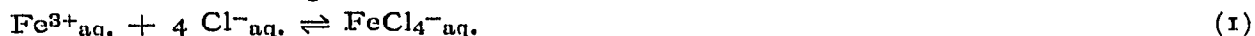
both confirms and extends the less firmly founded conclusions previously published⁴.

As regards liquid-liquid extraction, excellent agreement exists between the present results (including the exchanger/Co(II) = 2/1 maximum on the JOB curve) and the earlier data on maximum loading. Our quantitative and qualitative results moreover agree with those published by GOOD and coworkers^{19, 20} and, recently, by SATO²¹.

In this context it may be mentioned that our combined data seem to rule out the possibility that acidic species such as HCoCl_4^- are extracted into the organic phase, which concurs with the observation of GOOD AND SRIVASTAVA²² who could not detect any acidic Co(II)-containing species in their organic extracts. Because it may be assumed that the mononegative HCoCl_4^- will show reasonable extractability, the complete absence of acidic species from the organic phase does not favour the hypothesis²³ that desorption and decreased extractability at high HCl concentrations are due to the formation of HCoCl_4^- in the aqueous phase. Neither is desorption and decreased extractability owing to the formation of CoCl_6^{4-} —if existent—supported by our data, apart from the fact that it is highly questionable whether this species would have the same ultraviolet and visible spectrum as has CoCl_4^{2-} .

As regards Cu(II), the spectra of all organic extracts, whether originating from liquid-liquid extractions or from experiments approaching chromatographic conditions, were identical—this in good analogy with Co(II). The sole presence of the 409-nm peak, irrespective of the class of the exchanger and the composition of the aqueous phase, points to at least the predominance of CuCl_4^{2-} in the organic extracts. This conclusion is confirmed by our other results. Using the same arguments as presented above, we may further state that species such as HCuCl_4^- and CuCl_6^{4-} definitely do not play an important role. However, it must be mentioned here, that in one or two experiments irregularities were observed, *viz.* when working at high Cu(II)/exchanger ratios. In these cases some CuCl_3^- ($\text{Cu}_2\text{Cl}_6^{2-}$) probably was present besides CuCl_4^{2-} , but as the conditions employed did not correspond with those in normal chromatographic or extraction analysis, this complication does not seriously invalidate our conclusions.

As has been pointed out above, with Fe(III) previous data⁴ regarding the nature of the metal-containing species in the organic phase were more conclusive than with Cu(II) and Co(II). Our present experiments—extending the field investigated—agreeably confirm the earlier results, pointing to the presence of FeCl_4^- in the organic phase in all cases. Here, however, a single point must be emphasized once more. With quaternary anion-exchangers, maximum-loading data, JOB curves and spectral measurements all indicate that the species extracted may be formulated as $\text{R}_4\text{N}^+\text{FeCl}_4^-$ and the same holds for tertiary and secondary amines at high Cl^- concentrations ($\text{R}_2\text{R}'\text{HN}^+\text{FeCl}_4^-$). However, when using the latter classes of compounds at low Cl^- concentrations, *e.g.* 2 N HCl, an Fe(III)/exchanger ratio of 1/2 is invariably found in JOB curves and with maximum-loading data, while the ultraviolet and visible spectra on the other hand still point to the presence of FeCl_4^- . This phenomenon may be explained by assuming that an extra molecule $\text{R}_2\text{R}'\text{HN}^+\text{Cl}^-$ is now attached to the species extracted, thereby forming $\text{R}_2\text{R}'\text{HN}^+\text{FeCl}_4^- \cdot \text{R}_2\text{R}'\text{HN}^+\text{Cl}^-$, while at higher Cl^- concentrations the equilibria



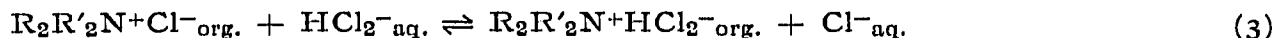
shift to the right (*cf.* refs. 4 and 6, p. 105).

As has been pointed out before, this different behaviour of quaternary from other exchangers—also found²⁴ with In(III)—may possibly be ascribed to hydrogen bonding *via* the hydrogen atom directly bound to the central nitrogen; definite proof, however, is still lacking.

Lastly, we may mention that the data on the Mn(II)–LiCl systems again point to the presence of a metal-tetrachloro anion in the organic phase. The analogous behaviour of Mn(II), Co(II) and Cu(II) repeatedly observed seems to justify the assumption that MnCl_4^{2-} is also the anion extracted from aqueous HCl solutions.

It has been shown in the foregoing paragraphs that the different behaviour of elements such as Co(II), Cu(II) and Mn(II) in reversed-phase chromatography and extraction, when using aqueous phases containing high concentrations of HCl and LiCl, respectively, cannot be ascribed to the formation of different metal-containing species; this conclusion probably also holds for *e.g.* Zn(II), Cd(II) and In(III).

As has been proposed^{20,25}, the solution of this problem may be looked for in the extraction of HCl_2^- according to the equation



which occurs at high aqueous HCl concentrations. This implies that under these circumstances the extraction—and therefore most probably also the sorption in reversed-phase chromatography (*cf.* Fig. 1)—of the metal-chloro anions is partially inhibited by the competition according to reaction (3). It is self-evident that this effect hardly plays a role when using slightly acidified LiCl solutions, so that here desorption and decreasing extraction at high Cl^- concentrations will be much less apparent, which satisfactorily explains the curves presented in Figs. 1 and 2. It may be mentioned here that GOOD *et al.*²⁰ have shown that more HCl is absorbed in the organic phase than can be accounted for by the formation of one HCl_2^- per salt molecule; they suggest that some excess molecular HCl may be present, probably hydrogen-bound to HCl_2^- .

Our conclusions may also be applied to the experimental results of LEDERER and coworkers^{7,20}, who used HCl and LiCl as eluants in chromatography on the solid resin paper Amberlite SB-2*. These authors also observed a considerable lowering of the R_F values for *e.g.* Fe(III), Co(II), Cu(II) and Ga(III), when substituting HCl by LiCl, while no such phenomenon was found with Ag(I) and Pb(II). They explain these experimental results by stating that “the differences between HCl and LiCl may be interpreted as a “salting-out effect”, affecting those ions which are held by adsorption”. As regards the deviating results for silver and lead, they suppose “...that these two ions seem to be retained almost entirely by ion exchange and not by adsorption. The results with LiCl seem to confirm these findings since in ion exchange the cation of the eluant should theoretically have no effect”.

However, recent data in the literature and those obtained by us in both chromatography and extraction imply that with an anion-exchange mechanism substitution of H^+ by Li^+ does affect the results, which satisfactorily explains the behaviour of Co(II), Fe(III), etc. On the other hand, with silver and lead, we must take into

* In this discussion the behaviour of the cellulose anion-exchange papers, which is quite different from that of the SB-2 paper, is not taken into account. It seems probable to us that factors other than anion-exchange play a role here.

account that here a distinct increase of the R_F values already starts at low HCl concentrations, *i.e.* in the region where sorption (extraction) of HCl_2^- is not yet important: substitution of HCl by LiCl will therefore have hardly any influence.

CONCLUSION

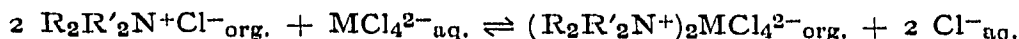
Combination of the data presented above and those previously published clearly shows that the same mechanism governs both the liquid-liquid extraction and the reversed-phase chromatographic process for the systems considered in our study. With Co(II), Cu(II), Mn(II) and Fe(III)—and probably also with Zn(II) and Cd(II)—the metal-tetrachloro anions are the predominant or even sole species sorbed on the impregnated thin layer and extracted into the organic phase over the whole concentration range studied. Desorption and decreasing extractability at high HCl (but not LiCl!) strengths—for both complex metal-chloro anions and *e.g.* ReO_4^- and Br^- —are brought about by the competing action of HCl_2^- . The sorption and extraction of metals by liquid anion-exchangers can therefore be

TABLE II

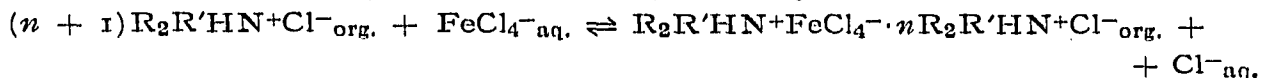
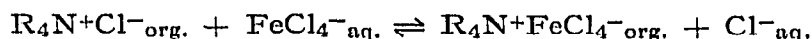
SUMMARY OF MECHANISMS GOVERNING REVERSED-PHASE CHROMATOGRAPHY AND LIQUID-LIQUID EXTRACTION FOR SOME LIQUID ANION-EXCHANGER-METAL-CHLORIDE SYSTEMS

R' denotes either an alkyl group or an H atom. Attention is called to two aspects: (a) Interchange of anions has been assumed in preference to the addition of neutral species, which alternatives are, however, thermodynamically equivalent and cannot be distinguished by any measurements made at equilibrium (*cf.* ref. 27). (b) Monomeric species have been written, though it is known that association of the (complex) salts occurs.

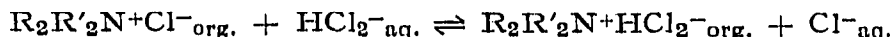
Divalent metals



Tervalent iron



HCl_2^- competition



* $n = 1$ or 0 dependent on the Cl^- concentration in the aqueous phase; see text and ref. 4 for details.

formulated as is done in Table II. It may be emphasized here that some of our results on liquid-liquid extraction, *viz.* those on Co(II), Fe(III) and HCl_2^- , are in good accord with the data published by GOOD and coworkers.

On the basis of our results, for future research on extractions preliminary experiments using thin-layer chromatography may be recommended. On the other hand, investigations regarding the nature of the extracted metal-containing species may well be carried out by combining maximum-loading (and continuous-variation) results and spectral data obtained in extraction analysis. Spectroscopic measurements seem preferable, especially when a comparative research concerning undiluted exchangers is requested; this method is currently being applied to the Co(II)-bromide

system, where it has already been found that CoBr_4^{2-} is the species extracted into the organic phase²⁸. However, in this way only the composition of the metal-halogeno anions can be found; research regarding the attachment of extra molecules of exchanger, as *e.g.* found with Fe(III), necessitates the use of the other methods. Moreover, many metal-containing anions lack characteristic ultraviolet and visible spectra; therefore, the introduction of *e.g.* Raman and infrared spectra may be valuable²².

Regarding the use of other methods suitable for elucidating the mechanism etc., especially in chromatography, attention may be called to a direct application of the maximum-loading technique to reversed-phase chromatography³⁰. Preliminary experiments carried out in our laboratory on the Fe(III)-chloride system using the Adogens 464 and 368 have met with various practical difficulties, but nevertheless it was clearly indicated that the maximum amount of Fe(III) taken up by the impregnated support at a 2 *N* HCl aqueous concentration was approximately twice as high in the case of the quaternary liquid anion-exchanger.

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SUMMARY

An analysis has been made of the metal-chloro species sorbed onto an impregnated thin layer in reversed-phase chromatography and extracted into the organic phase in liquid-liquid extractions, when using substituted quaternary ammonium chlorides or high-molecular-weight amine hydrochlorides. In all cases, *i.e.* irrespective of (1) the class of the anion-exchangers, (2) the concentration of Cl^- in the aqueous phase and (3) the use of either HCl or LiCl as the source of Cl^- , the sole metal-containing species present in the organic phase are CoCl_4^{2-} , CuCl_4^{2-} , MnCl_4^{2-} and FeCl_4^- . With Fe(III), however, in experiments involving the use of secondary or tertiary amine hydrochlorides, at low aqueous Cl^- concentration an extra molecule of the exchanger is attached to the Fe(III)-containing species, which then may be formulated as $\text{R}_2\text{R}'\text{HN}^+\text{FeCl}_4^- \cdot \text{R}_2\text{R}'\text{HN}^+\text{Cl}^-$ (R, alkyl; R', alkyl or H).

Desorption and decreasing extraction, which occur for many elements at high HCl—but not LiCl—aqueous concentrations, may be ascribed to the competitive sorption and extraction of the hydrogen dihalide anion HCl_2^- .

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