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METAL-CHLORIDE COMPLEXES STUDIED BY ION EXCHANGE AND SOLVENT EXTRACTION METHODS

II* TRANSITION-METAL ELEMENTS AND THE HEXAVALENT ACTINIDES

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CONTENTS

ABBREVIATIONS

TBP	tri-n-butylphosphate	TIOA	tri-iso-octylamine
TOPO	tri-n-octylphosphine oxide	DVB	divinyl benzene

A. INTRODUCTION

In part I* data concerning chloride complexes formed in solution by non-transition-metal elements, obtained by solvent extraction and ion exchange distribution measurements, have been reviewed. For these elements, which usually form "hard" ions in the Pearson sense[1], the chloride complexes are rather weak, so that a large excess and a high concentration of ligand are required in order to obtain an appreciable fraction of the metal complexed. Under these conditions, the methods under discussion are advantageous, and sometimes the only ones

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* Part I, "Non-transition-metal ions, lanthanides, actinides and d^0 transition metal ions", *Coordin. Chem. Rev.* 2 (1967), 195. The symbols used in Part II are the same as defined in Part I.

suitable. The transition metals include those which form "soft" ions[1], and although for them the methods discussed here do not yield exclusive information, they have provided much useful information on the species formed.

B. COMPLEXES ACCORDING TO THE PERIODIC GROUPS

(i) Group VIb and the hexavalent actinides

Chromium(III) does not form strong chloride complexes in aqueous solutions, and anionic chloro complexes are apparently not formed at all. This is possibly due to the strong binding of water in the aquo-ion, and the inability to assume tetrahedral coordination, as do iron(III) and gallium(III), of comparable ionic radius. The non-formation of anionic complexes is seen in the non-sorption on anion exchangers from hydrochloric acid of any concentration[2-6], even not from ethanolic acid[7], nor is it extracted by the secondary amine Amberlite LA-1 hydrochloride[8]. It shows very low distribution coefficients when extracted by methyldioctylammonium chloride, 8% in trichlorethylene[9] ($D = 0.02$ in dilute HCl, $D = 0.09$, in 10 M HCl), and it is doubtful whether extraction as an anionic chlorocomplex occurs.

Chromate ion is, of course, a stable anion, and Cr^{VI} does not form chlorocomplexes in aqueous solutions. It is extracted well from dilute HCl solutions with tertiary amine hydrochlorides[10], and sorbed on anion exchangers; at high HCl concentrations it is reduced.

Molybdenum(VI), on the other hand, does form chlorocomplexes, and the extractability of Mo^{VI} from HCl above *ca.* 6 M by ether is well known. As molybdate solutions containing the anion MoO_4^{2-} are gradually acidified with HCl, polymeric anions are first formed, which are partly protonated as the pH decreases, so that the average negative charge per Mo^{VI} atom decreases until it reaches zero at the isoelectric point, about pH = 1.1. At sufficiently high Mo^{VI} concentration, hydrated MoO_3 precipitates at this pH. Above this pH, Mo^{VI} migrates to the anode, below it to the cathode, while below pH = 0.7 (*i.e.* above *ca.* 0.2 M HCl) the molybdenum is to a large part present[11-13] as MoO_2^{2+}. At still higher HCl concentrations, chlorocomplexes[13] start to form, as observed by the renewed anodic migration of Mo^{VI} above 2 M HCl, and from spectrophotometric studies[12,17]. At this stage, significant extraction with oxygenated solvents starts, and $d \log D / d \log c_{HCl}$ for anion exchange[16,18] or amine extraction[14,15] changes its sign from negative to positive (Fig. 1).

Extraction with neutral extractants (ethers and ketones[19-21], TBP[24], adiponitrile[22] and other solvents[23]), has been studied by a number of authors, the most thorough investigation being that of Diamond[20,21]. In some cases it was found that the ratio $H^+ : Mo^{VI} : Cl^-$ in the extracted species is 1:1:3 (*e.g.* for adiponitrile[22] and some other solvents[23]. A similar species, $MoO(OH)Cl_3 \cdot 7H_2O$ was found to be soluble in ether[17]. It has not been disproved conclusively that this species is the ion pair $H^+MoO_2Cl_3^-$. Most oxygenated solvents (ethers, esters, ketones), however, extract Mo^{VI} with the molar ratio Cl:Mo = 2:1. The behavior of D with Mo^{VI} concentration in the range 10^{-9}–10^{-2} M and with the presence of strong acid, points to the mononuclear species MoO_2Cl_2 in the organic phase, and mononuclear species in the aqueous phase[20,21]. With solvents such as β,β'-dichlorodiethylether, of relatively high dielectric constant, some ionic dissociation was found by conductivity measurements, and since the empirical formula has still Cl:Mo = 2:1, the species could be $H^+MoO_2(OH)Cl_2^-$.

The anion exchange data below 2 M HCl show considerable disagreement but above about 3 M HCl show surprising agreement, for different resins (Dowex-1[25], Dowex-2[16], Amberlite IR400[18]) and the liquid exchanger 0.1 M Hyamine 1622 in 1,2 dichloroethane[15]. Indeed, addition of 0.20, 0.40 and 0.80 units respectively to log D for the other systems brings them to the same curve of log D against log a as for Dowex-1 (Fig. 1). Since the invasion functions $\bar{a}$ for the different exchangers are expected to differ over the range 3–12 M HCl, it is concluded that p, the charge of the complex predominating in the resin, must be zero, to account for the observed parallelism in the D curves. Furthermore, the marked similarity of the D curve for anion exchange with α_2[17], the fraction of the molybdenum in the form of the second complex, also points to MoO_2Cl_2 being the predominant species in the resin, just as in ethers or ketones. The anion exchange data may be accounted for quantitatively by the expression

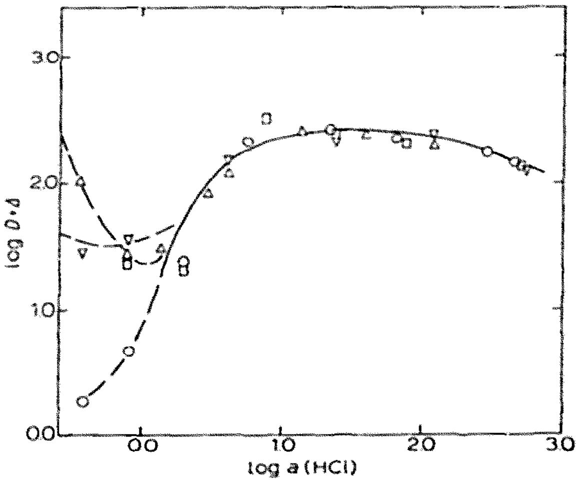

Fig. 1. Distribution data for molybdenum(VI). ○ ref. 25 Δ = 0.00, ref. 14 Δ = 0.20; △ ref. 18 Δ = 0.40; ▽ ref. 15 Δ = 0.80; —— calculated from eq. 1.

$$\log D = \log K^* - \Delta - \log(\beta'_{-2}{}^*a^{-2} + 1 + \beta'_1{}^*a) \tag{1}$$

with log $K^* = 2.45$, log $\beta'_{-2}{}^* = 1.3$ and log $\beta'_1{}^* = -2.69$ being the effective equilibrium constants for the reactions $MoO_2Cl_2 \rightleftharpoons \overline{MoO_2Cl_2}$, $MoO_2Cl_2 \rightleftharpoons MoO_2{}^{2+} + 2\,Cl^-$ and $MoO_2Cl_2 + Cl^- \rightleftharpoons MoO_2Cl_3{}^-$, and $\Delta = 0$ for Dowex-1, $\Delta = 0.20$ for Dowex-2, $\Delta = 0.40$ for Amberlite IR400 and $\Delta = 0.80$ for the Hyamine extractant. The constants $\beta'_{-2}{}^*$ and $\beta'_1{}^*$ also account well for the spectrophotometric data, which yield α_2 and α_3[17]. The presence of anionic chlorocomplexes in the aqueous phase above 6 *M* HCl is confirmed by electromigration results[13]. In the region where the cationic species are important 2–4 *M* HCl, the data scatter considerably and there are doubts about the mononuclearity of the species[11,21], so that the reaction $MoO_2{}^{2+} + 2\,Cl^- \rightleftharpoons MoO_2Cl_2$ (log $\beta_2{}^* = -1.3$) is only tentative.

There are very few data for W^{VI} in the literature. The anion exchange behavior resembles[25] that of Mo^{VI}, including a ratio of 8 between *D* for X-10 and X-1 resins. Below 6 *M* HCl W^{VI} is probably highly hydrolyzed and polymeric[25], and above 6 *M* HCl there are only three data points, so that a quantitative evaluation is impossible. The points are consistent with WO_2Cl_2 in the resin and WO_2Cl_2 along with $WO_2Cl_3{}^-$ in the aqueous phase, but many other combinations of species are of course as good.

The hexavalent actinides, U^{VI}, Np^{VI} and Pu^{VI}, have been studied rather extensively by means of ion-exchange and solvent extraction techniques. The cationic species $MO_2{}^{2+}$, stable in dilute acid solutions, are well established from other (*e.g.* spectroscopic) studies. In dilute HCl solutions they are known to complex with chloride ions to give MO_2Cl^+ and possibly also MO_2Cl_2, as obtained also from distribution[26] and cation exchange[27] studies. These elements are sorbed on anion exchangers from HCl solutions above about 0.5 *M*[16,25,28–31], are extracted into amine hydrochloride solutions[10,32–34], and into undiluted TBP[35,36–39], but are only little extracted into diluted TBP[34,40]. The spectra of these ions sorbed on anion exchangers[31,41] or extracted into amine[33] or TBP[39] solutions have been measured and some information on the species found in these phases is thus available. The spectrum of U^{VI} on an X10 resin resembles somewhat that in concentrated LiCl solutions[41], but differs from that of U^{VI} on a X4 resin[31] absorbed from either HCl or LiCl solutions, which is similar to that of tertiary amine hydrochloride extracts[33,39], and to a solid[31] $(C_3H_9N)_3H_3O(H_2O)_3(UO_2Cl_4)_2$. These, in turn, differ from the spectra of $UO_2Cl_4{}^{2-}$ in solids or solutions[31], or of U^{VI} extracted into TBP solutions, or in TBP containing additional dry HCl[39], which have been identified[42] with $UO_2Cl_3{}^-$. The structure and the bonding of the compound prepared by Ryan[31], having a spectrum resembling that of X4 resin and amine hydrochloride extracts, have not been established but Ryan proposed the hydrogen bonded structure $[UO_2Cl_4 \cdot H_3O(H_2O)_3 \cdot Cl_4UO_2]^{3-}$. This species is possibly too bulky to be absorbed on the more highly crosslinked resin which accounts for the different spectra. The spectrum of U^{VI} on the resins resembles also the spectra of UO_2Cl_2 and $UO_2Cl_3{}^-$, possibly hydrogen bonded, so that the presence of the tetrachloride species in the resin is by no means established. It does not agree with loading results, or with sorption from slightly acid concentrated LiCl solutions, which yields a resin (X-4) spectrum similar to that of the species sorbed from HCl.

Turning to the distribution measurements, it can be seen (Fig. 2) that there is good agreement between various authors' results for U^{VI}, for both anion exchange and extraction with undiluted TBP, the curves being displaced parallelly for different resin preparations or (low) concentrations of U^{VI}. The species in TBP having been identified[39] as $[H(H_2O)_x,2TBP)]^+UO_2Cl_3^-$ (The species $[H(H_2O)_3 \cdot 3TBP]^+ UO_2Cl_3^-$ has also been proposed[38]), the data could be fitted with the equation

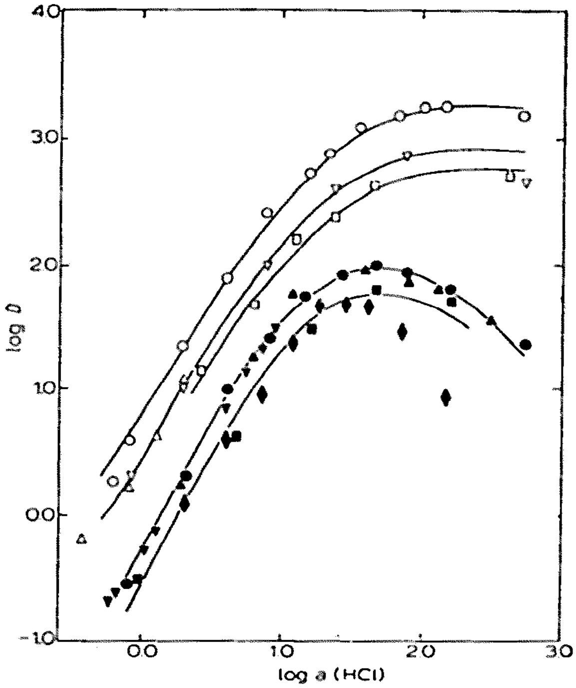

Fig. 2. Distribution data for uranium(VI). Empty symbols: anion exchange, filled symbols: TBP extraction. ○ ref. 25 log $K_U^* = 1.54$; $\varDelta$ ref. 29 (D_v), and ▽ ref. 14 (D) log $K_U^* = 1.19$; □ ref. 30 log $K_U^* = 1.09$; ● ref. 36 △ ref. 35, and ▼ ref. 39 log $K_U^* = 1.69$; ■ ref. 36 and ◆ ref. 38 log $K_U^* = 1.45$; —— calculated from eq. 2 with K_U^* values stated.

$$\log D = \log K^* + \log \bar{a} - \log(\beta_{-2}^{*\prime} a^{-2} + \beta_{-1}^{*\prime} a^{-1} + 1 + \beta_1^{*\prime} a) \qquad (2)$$

with the effective stability constants $\log \beta_{-2}^{*\prime} = 0.7$, $\log \beta_{-1}^{*\prime} = 1.0$, $\log \beta_1^{*\prime} = -1.7$, (or $\log k_1^* = 0.3$, $\log k_2^* = -1.0$, $\log k_3^* = -1.7$), and the distribution parameter $\log K^* = 1.69$ for data at tracer U^{VI} concentrations[35,37], and $\log K^* = 1.45$ at higher concentrations (0.02–0.09 M)[36–39]. The variable $\bar{a}$ is the concentration of HCl in the TBP[36,38]. The same equation, with the same values for the effective stability constants in the aqueous phase, was found to account very well also for the anion exchange data, with the appropriate values of log K^* (1.54 for the data of Kraus[25] for Dowex-1, 1.19 for D_v data of Marcus[29] and for the data for Dowex-2[16], and 1.09 for the data for Ishimori[30]), and of $\bar{a}$, the invasion function of the resin. This good agreement would indicate that the species in the highly crosslinked resins is $UO_2Cl_3^-$, possibly hydrated (it differs from anhydrous acetone solutions of $UO_2Cl_3^-$). A species with unit charge is compatible also with available loading data[31]. The increase in D by a factor of 23 for U^{VI} in 3 M HCl, compared with 19 for Fe^{III}, sorbed most probably as $FeCl_4^-$, as crosslinking varies[12] from X1 to X10, also points to a mononegative resin species. At 12 M HCl this factor becomes 37, and a more highly charged species might be formed in the slightly crosslinked resin of high effective dieletric constant; this could be the bulky hydrogen bonded triply charged dimer proposed by Ryan[31].

The amine hydrochloride extraction data[32,33] yield consistently a value of two for $(\partial \log D/\partial \log c_{R_3NCHL})c_{Cl}$. In view of the spectral data, it is unlikely that the tertiary amine solutions contain $UO_2Cl_4^{2-}$ species as such. If the species are the hydrogen-bonded $[UO_2Cl_4 \cdot H_3O(H_2O)_3Cl_4UO_2]^{3-}$ proposed by Ryan[31], ion-paired with the trialkylammonium cation in some manner, the slope of two remains unexplained. Species as $R_3NHCl \cdot R_3NHUO_2Cl_3$ account for the slope in the same manner as postulated for the trivalent actinides and Fe^{III} (see below). A composition $(R_4NCl)_2[R_4N]UO_2Cl_3 \cdot [(H_3O)_3O]UO_2Cl_3$ for the solid having the same spectrum as the amine extract and the resin may be an alternative formulation, the spectrum being in between these of $UO_2Cl_4^{2-}$ and $UO_2Cl_3^-$. Non-availability of $\bar{a}$ data for the amines used at their respective concentrations precluded a detailed analysis of the distribution data along the lines employed for the anion exchange and TBP extraction data.

Neptunium(VI) and Pu^{VI} are somewhat better sorbed[29] by the anion exchanger than is U^{VI}, and are also more highly extracted by TBP[35] or tertiary amine hydrochlorides[33]. The shape of the curves is similar, and the stability constants should therefore be not very different.

The only stable MO_2^+ ion among the actinides is Np^V. It does not show sorption on anion exchangers from HCl solutions[29], and is extracted with undiluted TBP a hundred-fold poorer than Np^{VI} in the range 4–7 M HCl. At higher HCl concentrations, D for Np^V continues to increase, whereas that for Np^{VI} decreases, so that they show comparable D at 10 M HCl[35].

The sorption of U^{VI} on anion exchangers from mixed solvent solutions of HCl has been studied[5,42–45]. The sorption of U^{VI} from HCl up to 0.1 M in diethyl or dipropyl ether with the same D, irrespective of the acidity[44] probably indicates the resin species being UO_2Cl_2. The sorption from alcoholic HCl (on anion exchange resin impregnated paper[45] and on resin itself[5,42,43]) seems, however, to involve an anionic species in the resin. Loading experiments showed that it is difficult to attain more than 0.5 mole U^{VI} per equivalent of resin, but the data presented do not prove that this is not due to slowness of sorption, or that the species are not mixtures of chloride and chlorouranate anions. The formation of $UO_2Cl_4^{2-}$ in the resin cannot, therefore, be considered established, in particular as the spectrum of U^{VI} sorbed from ethanolic HCl (containing water) is more similar to that sorbed from aqueous solutions (hydrated $UO_2Cl_3^-$?, see above) than to $UO_2Cl_4^{2-}$. The distribution coefficients increase up to a thousandfold as the water concentration of the solutions decreases from 30% to zero, very high D values being attained.

(ii) Group VIIb

The higher valency states, Mn^{VII}, Tc^{VII} and Re^{VII} do not form chloride complexes, but are well sorbed by anion exchangers, extracted with TBP etc., or by amine hydrochlorides from HCl solutions (unless reduced, as for Mn^{VII}). The species TcO_4^- and ReO_4^- seem to be stable both in chloride solutions as on anion exchangers, and may serve to define the invasion functions $\bar{a}$.

Divalent manganese was found by the cation exchange method[46] to form weak chloride complexes, and $\bar{n} = 2$ is reached at about 2.5 M HCl, above which concentration anionic species, $MnCl_3^-$, start to predominate. Extraction with an amine (Amberlite LA-1) hydrochloride starts above *ca.* 4 M HCl[8] reaching maximal D (0.14 for 10% amine in xylene) at 6.5 M HCl. Anion exchangers were variously reported to require 6.5 M HCl for efficient elution[6,47], distribution coefficients being however quite low (about 4) even in concentrated HCl[4,48,49]. Extraction with quaternary amine chlorides[14], and other amines or neutral phosphorus esters[7,50,51] from HCl is also quite low. For LiCl solutions, however, D values are much higher, being about 550 for anion exchange for 12 M chloride[53] and 180 for undiluted TBP and 10 M chloride[52], compared with 4 and 0.13 respectively for the same concentrations of HCl. Enhanced extraction by tertiary amines from LiCl solutions has also been observed[54]. Indeed, 1 M TOA · HCl extracted sufficient Mn^{II} from 11.4 M LiCl–0.6 M $MnCl_2$ so that its spectrum could be measured, and the organic species could be identified with $MnCl_4^{2-}$. The formation of this species in the aqueous phase, however, is very slight. If it is the main species in the resin phase, an analysis of the data[48] according to the Marcus–Coryell method shows a slope $(\partial (\log D - 2 \log \bar{a})/\partial \log a)$ of about -2 in the range 4–12 M HCl, corresponding to $MnCl_4^{2-}$ in the aqueous phase. If this is rejected in the light of the spectral data[54], and the resin species is selected as $MnCl_3^-$, then the slope $(\partial(\log D - \log \bar{a})/\partial \log a)$ becomes -1, corresponding to $MnCl_3^-$ predominating in solution above about 6 M HCl, in rough agreement with the chloride stability constants[46].

Enhanced anion exchange distribution, compared with HCl solutions, is observed not only with LiCl solutions but also with alcoholic HCl solutions[5,7].

Manganese(II) shows the curious behavior of D increasing first when a little water is added to anhydrous ethanolic HCl, and then decreasing strongly when more water is added[7]. Most elements show an immediate decrease. Distribution coefficients of a few thousands are exhibited in 95% ethanol or isopropanol $0.1-0.3$ M in HCl[5]. Smaller D values are observed in methanol, or at lower alcohol concentrations.

(iii) Group VIII

One of the earliest (1892) applications of the solvent extraction technique to inorganic complexes was the extraction of $\mathrm{Fe^{III}}$ with ether from HCl solutions[55]. Similarly, the usefulness of anion exchangers for the removal of metal complexes from concentrated electrolyte solutions was demonstrated for $\mathrm{Fe^{III}}$ and HCl in the earliest days of the development of stable strongly basic anion exchangers[56]. The $\mathrm{Fe^{III}}$-chloride complex system has been studied very thoroughly since then. The extraction of $\mathrm{Fe^{III}}$ with various oxygenated solvents (ethers, ketones, etc.) has been summarized by Diamond and Tuck[57], and their conclusions concerning the species present in the different phases and the effects of several concentration variables on the distribution are quite acceptable.

Solutions of anhydrous $\mathrm{Fe^{III}}$ chloride in anhydrous solvents (such as ethers, ketones, etc.) have been shown spectrophotometrically to contain only iron trichloride molecules, solvated with one solvent molecule[58,59], $\mathrm{FeCl_3 \cdot S}$. When anhydrous HCl is added, disolvated tetrachloroferric acid forms, $\mathrm{HFeCl_4 \cdot 2S}$, which has a low solubility in the solvent[59]. The appearance of isosbestic points in the spectrum show that only two species are present. Equilibrium constants were calculated for the reaction $\mathrm{FeCl_3 + HCl \rightleftarrows HFeCl_4}$ in a number of solvents[58].

When water is added gradually to a suspension of solvated tetrachloroferric acid in the solvent, the solid dissolves, and complete dissolution is attained when 3–5 moles water per mole $\mathrm{Fe^{III}}$ are added[59,60]. The spectrum of this solution is identical to that of $\mathrm{Fe^{III}}$ extracted by the same solvent from HCl solutions and these spectra have been studied by several authors[61–65]. They were found in every case to be similar to the spectrum of solid tetrachloroferrates, or to solutions of the potassium or ammonium salts in ethers[66]. Furthermore, an infrared study showed the $\mathrm{C{=}O}$ band shifts for the solvent in $\mathrm{Fe^{III}}$ extracts to be the same as in HCl extracts with no other shifts, for a large number of solvents, and observed no shift in anhydrous $\mathrm{KFeCl_4}$ solutions[65]. Finally, a Raman spectroscopic study showed the ether extracted iron to be bound tetrahedrally to four chlorine atoms[67]. All this proves that the extracted species[71–74] is $\mathrm{H}(x\mathrm{H_2O}, y\mathrm{S})^+\mathrm{FeCl_4}^-$, contrary to earlier beliefs that $\mathrm{FeCl_3}$ (or $\mathrm{Fe_2Cl_6}$)[68], $\mathrm{H_2FeCl_5}$ and $\mathrm{H_3FeCl_6}$[69] or $\mathrm{H}(x\mathrm{H_2O})^+$-$\mathrm{FeCl_4S_2}^-$[70] are the extracted species.

The dissociation of the ion pair $\mathrm{H}(x\mathrm{H_2O}, y\mathrm{S})^+\mathrm{FeCl_4}^-$ and its association to higher aggregates obviously depends on the dielectric constant of the solvent, saturated[57,75–83] with water and HCl. This problem is strongly connected with the dependence of D on the $\mathrm{Fe^{III}}$ concentration. In solvents of low dielectric constant, association to ion triplets and higher aggregates occurs[75–77], and therefore an increase of c_{Fe} will increase D. In solvents of relatively high dielectric constant ($\varepsilon > 10$), ionic dissociation occurs, as shown by the conductivity of the organic phase, and the anodic migration[79,81,82] of $\mathrm{Fe^{III}}$.

In addition to the oxygenated solvents, such as ethers, ketones, carbinol, etc., many other types of solvents have been used to extract $\mathrm{Fe^{III}}$ from aqueous HCl solutions. The extraction into inert solvents (benzene, $\mathrm{CCl_4}$, $\mathrm{C_2H_2Cl_2}$, etc.) was found to be negligible[84]. Solvents with donor atoms other than oxygen, such as sulfur in dibutylsulfide[85] or nitrogen in adiponitrile[22] show behavior similar to oxygenated solvents, the donor atoms associating with the hydrogen ion of the extracted species. Extraction with TBP has been claimed to be an exception, in that the solvent was thought to coordinate directly with the $\mathrm{Fe^{III}}$, in order to assure a coordination number of six[73,74,86]. At low HCl concentrations a third power dependence of D on c_{TBP} was observed, and at high c_{HCl}, a second power dependence, and this was taken to indicate the formation of $\mathrm{FeCl_3 \cdot 3TBP}$ and $\mathrm{H(FeCl_4 \cdot 2TBP)}$. It was however shown that in all cases non-solvated $\mathrm{FeCl_4^-}$ is the $\mathrm{Fe^{III}}$ species, and the TBP associates, like the other solvents, with the hydrogen ions[65,87]. The change in solvation number, also observed with other solvents, is due to competition of coextracted HCl. The published data for undiluted TBP[36,74,87,88], are unfortunately in disagreement, so that no useful analysis of these data can be made, until a dependable set of data is available.

The extraction of $\mathrm{Fe^{III}}$ with amine hydrochlorides has recently been studied by several authors[54,89–96], and summarized by Duyckaerts *et al.*[95]. The spectra of the organic phases show[54,89,95] that the $\mathrm{Fe^{III}}$ species is $\mathrm{FeCl_4^-}$, and not $\mathrm{FeCl_5^{2-}}$, as with the solvents discussed previously. This is so under conditions where the slope $(\partial \log D/\partial \log c_{\mathrm{R_3NHCl}})c_{\mathrm{HCl}},c_{\mathrm{Fe}}$ is both one (high c_{Fe})[92,94] or two (tracer $\mathrm{Fe^{III}}$)[91,92]. At high $\mathrm{Fe^{III}}$ concentrations saturation experiments[89], as well as the slope, indicate the formation[95] of $\mathrm{R_3NH^+FeCl_4^-}$. At low c_{Fe} the second power dependence could be interpreted as an association of this species with excess $\mathrm{R_3NHCl}$ to give $\mathrm{R_3NHCl \cdot HNR_3^+ + FeCl_4^-}$, with two $\mathrm{R_3NH^+}$ cations hydrogen-bonded to the chloride anion, or as a dipole–dipole association of $\mathrm{R_3NH^+Cl^-}$ with $\mathrm{R_3NH^+FeCl_4^-}$.

As mentioned above strong sorption of $\mathrm{Fe^{III}}$ on anion exchangers from concentrated HCl was demonstrated a long time ago[56] and several authors have studied the distribution of $\mathrm{Fe^{III}}$ and its dependence on c_{Fe}, c_{Cl} and c_{H}[47,49,56,97,98], giving data with fairly good agreement. Distribution coefficients were found to be independent of c_{Fe} up to a loading[97] as high as 10%, and independent of substitution of LiCl for HCl at constant a up to 9 M chloride[97]. Above this concentration D was lower in HCl than in LiCl solutions of the same a. In view of a similar behavior of the light absorption properties of the aqueous solutions, the decrease in D was interpreted as due to the formation of the non-absorbed ion-pair $HFeCl_4$ in the aqueous phase. The constant $\log K^* = -4.6$ has been calculated for the reaction $FeCl_3+H^++Cl^- \rightleftarrows HFeCl_4$ in the aqueous phase from data of D for HCl solutions. Using this constant for mixed LiCl-HCl solutions (using the same $y_{\pm HCl}$ and $\bar{a}$ as in pure HCl, as an approximation) gave good agreement with the data. The distribution results fitted well the expression

$$\begin{aligned}\log D = \log K^*+p\log\bar{a}-\log(\beta'_{-2}{}^*a^{-2}+\beta'_{-1}{}^*a^{-1}\\ +1+\beta'_1{}^*a+K^*c_H+c_{Cl}-y_{\pm HCl}{}^2)\end{aligned} \tag{3}$$

with $p = 1$ for $FeCl_4{}^-$ as the resin species, $\log\beta'_{-2}{}^* \leq 2.1$ (for $FeCl_3 \rightleftarrows FeCl^{2+}+2Cl^-$), $\log\beta'_{-1}{}^* = 1.40$ (for $FeCl_3 \rightleftarrows FeCl_2{}^++Cl^-$) and $\log\beta'_1{}^* = -1.92$ (for $FeCl_3+Cl^- \rightleftarrows FeCl_4{}^-$). The value $p = 1$ was selected in view of the tendency of Fe^{III} to form $FeCl_4{}^-$, and this is confirmed by the reflectance spectrum of Fe^{III} on the resin[99].

Very little has been published about the Fe^{II} chloride complex system. This ion is removed within the first 10 column volumes when eluted even with 12 M HCl[100], its D not exceeding 8. The limiting slope of $\partial(\log D-p\log\bar{a})/\partial\log a$ at high a is +0.3, −0.6 and −1.5 for $p = 0$, $p = 1$ and $p = 2$, respectively. There is no certainty that Fe^{II} is sorbed as an anionic complex at all. There is no information for deciding on the resin species, and too few data for analyzing the D *vs.* a curve. The secondary amine Amberlite LA-1 hydrochloride was found to extract Fe^{II} slightly from concentrated HCl[101].

The chloride complexes of cobalt(II) are less stable than those of iron(III), but the striking color change from the pink, octahedral Co^{2+} to the blue, tetrahedral cobalt(II) species has led to many studies of this system.

The stability of the cationic complex species $CoCl^+$ has been studied by a cation exchange method by Trémillon[102], using an ingenious frontal analysis method to amplify small differences in the resin affinities of two similar divalent cations, such as nickel and calcium or cobalt and nickel. Assuming that cationic complexes are not sorbed by the resin, that calcium does not form chloride complexes and that only monochloride complexes are formed, the constant $\log\beta_1 = -0.6$ was found for $CoCl^+$ in a 1 N divalent metal medium (chloride and nitrate of nickel (or calcium) and cobalt, ionic strength 1.5 M). A more detailed study at 0.691 M ionic strength, maintained by perchloric acid, and tracer cobalt concentrations showed[103] the formation of both $CoCl^+$ and $CoCl_2$, using Fronaeus' method. At the concentrations of chloride used (below 0.6 M) there was no evidence for the formation of species higher than $CoCl_2$. The formation constants found are rather high ($\log\beta_1 = 0.69$, $\log\beta_2 = 0.51$), and since unreasonably high affinities for the resin of $CoCl^+$ were found in this study, the results require being checked. Results more in keeping with the known low stability of the cobalt complexes were obtained by using cation exchange paper[104] ($\log\beta_1 = 0.21$, $\log\beta_2 = -1.0$), but the low precision possible with measurements of R_F make this method rather unsatisfactory.

The extractability of cobalt chloride by organic solvents is slight[105,106]. Alcohols, such as butanol or octanol as well as some ketones, such as cyclohexanone, are capable of extracting cobalt chloride to some extent, although much less successfully than cobalt perchlorate[107]. The combination 3 *M* HCl+ 4 *M* $CaCl_2$ has been found a useful salting agent[106]. The distribution follows the rules expected when $CoCl_2$ is the species in the organic phase[106]. More basic oxygenated solvents have also been examined. Contrary to qualitative indications obtained by White and Ross[108], tri-n-octyl-phosphine oxide does extract cobalt from hydrochloric acid solutions with a maximal $D = 1$ at 8 *M* HCl for 0.13 *M* TOPO in toluene[51].

Considerably more detailed information is available about extraction of cobalt chloride with TBP. It is extracted to some extent from its concentrated aqueous solution ($D = 0.033$ for a 3.2 *M* aqueous solution, at 25°)[109], and it has been suggested that a dimer $(CoCl_2)_2$ is formed, in order to explain the increase of *D* with cobalt concentration[109]. The solutions studied do not behave ideally, however, and the deviations from Nernst's partition law need not be due to dimerization. The extraction of small concentrations of cobalt from concentrated hydrochloric acid or lithium chloride solutions has been studied by several authors[88,110-113]. The distribution coefficient of tracer cobalt rises sharply with hydrochloric acid concentration, the slope $d \log D/d \log a = 2.00$ for the range 2–7 *M* HCl[110,111] (the data of Weidemann[88] are in disagreement with the others), and show a flat maximum at higher chloride concentration, 8–10 *M*. In the former region, the species in the organic phase has been identified as $CoCl_2 \cdot 2TBP$ from spectrophotometric measurements[110-112] and the dependence of *D* on TBP concentration. Hence the slope of two for $d \log D/d \log a$ (Fig. 3) indicates that cobalt is complexed hardly at all by chloride in the aqueous phase, the major species being Co^{2+} aq. At the higher chloride concentrations the spectrum of the organic species changes, as also does the TBP concentration dependence of *D*, and the organic species is $[H \cdot TBP_x(H_2O)_y]_2{}^+ \; CoCl_4{}^{2-}$, with *x* and *y* possibly being one and three respectively[112]. This change in organic phase species would call for a steep increase in $d \log D/d \log a$, and the actual decrease of the slope, to zero and slightly negative values, is due to formation of cobalt chloride complexes in the aqueous phase on the one hand, compensated by competition of hydrochloric acid for the TBP on the other, as discussed previously above (*e.g.* for uranium(VI)). Since such competition is absent in lithium chloride solutions[110,112], cobalt(II) shows much higher *D* values when extracted from such solutions than from hydrochloric acid (a factor of 2000 around 10 *M*). Furthermore, more TBP seems to associate with the cobalt complex extracted from the former solutions than from the latter ($d \log D/d \log (TBP) = 2.75$ at 8 *M* LiCl)[112].

The extraction curves for TBP are similar to the anion exchange distribution

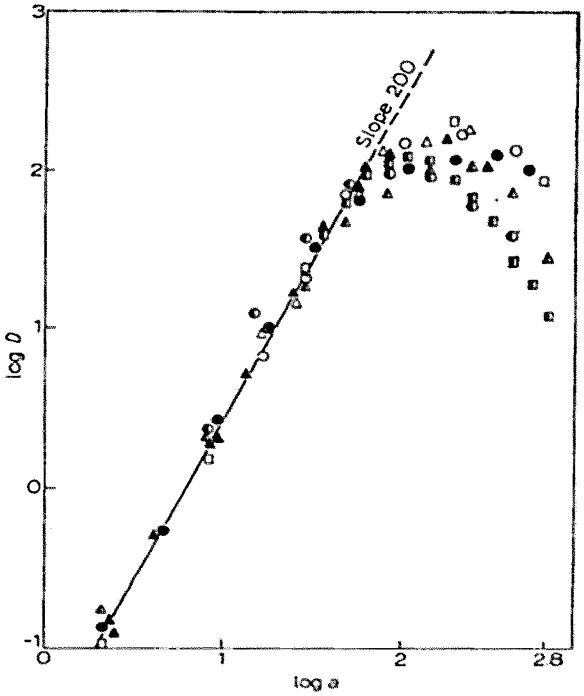

Fig. 3. Distribution data for cobalt(II). Full symbols: TBP extraction, empty symbols: anion exchange, half-filled symbols: amine extraction, plotted log $D+\Delta$. ● ref. 110, ▲ ref. 111, $\Delta = 2.00$; □ ref. 116, × 4 resin, $\Delta = 0.59$, ○ ref. 116, × 10 resin, $\Delta = 0.37$, △ ref. 114, $\Delta = 0.70$; ◭ ref. 15, $\Delta = 1.90$, ◐ ref. 90, $\Delta = 2.35$; ◧ ref. 121, $\Delta = 1.70$. —— line with slope 2.00

curves for both hydrochloric acid and lithium chloride. As for TBP extraction[110], the distribution coefficients are not strongly dependent on the cobalt concentration, since elutions at practically 100% loading (at the position of the blue colored band on the anion exchange resin column) show the same elution constants $E = (i+D_v)^{-1}$, where i is the fractional interstitial volume as elutions at tracer cobalt concentrations[114]. Unfortunately, whilst this early work[114] contains only four experimental points where D is appreciably larger than zero, subsequent papers quoting these results[48,115], treat them as a continuous curve with apparently more significant information. Some more information was subsequently published for both hydrochloric acid[47,116] and lithium chloride solutions[53,116], and their mixtures at constant total chloride concentrations[117]. It was found, as for other elements, and as for TBP extraction, that D in 12 M lithium chloride is about a hundred-fold higher than for 12 M hydrochloric acid[53,116], and at constant chloride concentration, D falls smoothly with increasing acidity[117]. This was attributed[117] to formation of $HCoCl_4^-$ in the aqueous phase, not absorbable by the resin, but other explanations of the "HCl effect" are also possible[116].

The cobalt species in the resin is generally believed to be tetrahedral $CoCl_4^{2-}$, as evidenced by the intense blue color[99,118]. Blue tetrahedral cobalt(II) chloride species include[119] besides $CoCl_4^{2-}$, also $CoCl_2(H_2O)_2$ and $CoCl_3(H_2O)^-$. The distribution curve from hydrochloric acid (Fig. 3) was found[115] to parallel the optical absorbance curve at 624 mμ, attributed to the species $CoCl_2(H_2O)_2$, but this fact cannot throw light on the species in the resin. The reflection spectrum of cobalt(II) on the anion exchanger[118] shows that $CoCl_4^{2-}$ is probably the major species in the resin[119]. A complication arises from the apparent ability of the cobalt species sorbed from hydrochloric acid to hydrogen-bond with acid[120], but this observation has not yet been presented in detail. The possibility that $CoCl_3(H_2O)^-$, rather than $CoCl_4^{2-}$, is the major species in the resin, already suggested by Moore and Kraus[114], is supported by the small crosslinking effect (a factor of about 1.7 between 10% and 4% crosslinked resin[116], characteristic more of mononegative than of dinegative resin species). Loading of the resin from hydrochloric acid also does not support the species $CoCl_4^{2-}$ as the predominant cobalt species in the resin[120]. More work is needed to settle these points.

The amine extraction behavior of cobalt(II) follows in general the same lines as its anion exchange[9,15,90,121,122]. In the case of hydrochloric acid, part of the amine salt becomes unavailable for the cobalt because of its being found as the bichloride, $R_3NH^+HCl_2^-$. The spectra of the organic solutions correspond closely[54,122] to $CoCl_4^{2-}$, and loading of the amine salt phase[121] also shows that $CoCl_4^{2-}$ is the principal cobalt species in the organic phase. The "hydrogen ion effect", *i.e.* the binding of ligand by bichloride formation, is of similar magnitude in anion exchange and amine extraction from hydrochloric acid. Hence, the presumed formation of $Co(H_2O)Cl_3^-$ in the former and $CoCl_4^{2-}$ in the latter case, requiring respectively one and two organic phase ligands would cause the amine extraction curve to show a more negative slope than the anion exchange curve at high hydrochloric acid concentrations. This is the actually observed behavior (Fig. 3).

Cobalt chloride is sorbed on an anion exchange resin from nonaqueous media both in the presence[5] and in the absence of excess chloride[123,124]. Both a strongly basic resin such as Dowex-1[5,123] or Deacidite FF[124], and a weakly basic one, such as Deacidite H[124] may be used with solvents such as alcohols[5], acetone[123,124] or dimethylformamide[124]. In the absence of excess chloride the metal is sorbed as the neutral chloride, $CoCl_2$, and no ions are released into the solution in exchange. The attainable loading of the resin under these conditions[123] increases with water content, reaching about 1.25 m*M* cobalt per g. resin with 22% water in acetone. No cobalt is sorbed in a completely anhydrous system[123]. Again, there is no information on the actual species in the resin or in the equilibrium solutions.

Hexamine cobalt(III) ions are slightly, though definitely, sorbed on an anion exchanger (Dowex-1 × 4) from chloride solutions[125], showing a maximal $D \sim 0.5$ at about 5 *M* lithium or sodium chloride, and for high concentrations of the former, a slight increase after a shallow minimum. The results are taken as indicating the formation of chloride complexes, although they are hardly conclusive.

Nickel(II), although resembling cobalt(II) in dilute aqueous solutions, differs from it in concentrated chloride solutions by forming chloride complexes much more reluctantly. This is reflected above all by its poor sorbability on anion exchangers, and its poor extractability by solvents that extract cobalt(II) well.

The cation exchange technique of Trémillon[102] shows nickel to complex somewhat with chloride ions to yield $NiCl^+$, $\log \beta_1 = -0.66$ at an ionic strength of 1.5 *M* (1 *M* nickel-calcium chloride–nitrate mixtures). Application of Fronaeus' cation exchange method, at 0.69 *M* perchloric–hydrochloric acid media, shows[126] the formation of $NiCl^+$, $\log \beta_1 = 0.23$, $NiCl_2$, $\log \beta_1 = -0.04$. The almost complete exchange of the medium anions for ligand anions, and the unreasonably large distribution ratio of $NiCl^+$ between the resin and solution, however, cast some doubt on the validity of the conclusions regarding the species formed and their stability (*cf.* the case of cobalt(II), above). The values found by chromatography on cation exchange paper[104], $\log \beta_1 = -0.64$ and $\log \beta_2 = -2.2$ are more reasonable.

Nickel chloride is poorly extracted by most organic solvents[107,108]. It is however, extracted from its concentrated aqueous solutions by undiluted TBP. It was found[127] that $\log D$ is linear with $\log c_{MCl_2}$, and from this it was concluded that the aqueous species is dissociated $Ni^{2+}aq$, while the organic species is (solvated) $NiCl_2$. Such a definite conclusion, however, is not warranted by the data, the solutions being far from ideal. Tracer Ni^{II} shows very low distribution coefficients (maximal $D = 0.0053$ at 7.3 *M* HCl)[110] with TBP, but in saturated lithium chloride solutions (about 13 *M*), a value $D = 2$ is attained, permitting sufficient nickel to be extracted for its absorption spectrum to be determined[112]. The species existing in the TBP phase was found to be tetrahedral $NiCl_4{}^{2-}$. No spectral data are available on nickel extracted from concentrated nickel chloride solutions, where the organic species may be $NiCl_2 \cdot 2TBP$, in analogy with cobalt.

Nickel(II) is not extracted to an appreciable extent from hydrochloric acid solutions by long-chain ammonium chlorides[90]. Using 8% methyldioctylamine hydrochloride in trichloroethylene, Mahlman, Leddicotte and Moore[128] found $D \sim 0.01$ for nickel(II) in 8 *M* HCl. As with other systems, extraction from lithium chloride solutions is more appreciable, and absorption spectral measurements show that $NiCl_4{}^{2-}$ is the species in the organic phase at equilibrium[54] with 13 *M* LiCl.

Nickel(II) is not sorbed on an anion exchanger from hydrochloric or lithium chloride solutions[48,114,129]. This holds even for highly crosslinked resins, containing 16 or 24% DVB[129]. It is, therefore, concluded that anionic complexes of nickel are not formed in aqueous hydrochloric acid or lithium chloride solutions[114,129]. Use of ethanolic hydrochloric acid does not improve the sorbability of nickel(II)[7], but in 95% isopropanol, 0.2 *M* in HCl, $D = 100$ is obtained[5], while from 96% acetone 0.05–0.1 M in HCl nickel(II) is sorbed with D values[5] exceeding 1000. (Note that the figures quoted in various parts of reference 5 are inconsistent). However, nothing is known about the species formed by nickel(II) in the resin under these conditions.

Among the platinum metals, cation exchange has been applied particularly to the study of Ru^{III} and Rh^{III} chloride complex species. The cationic species can be separated from each other, including the resolution of geometrical (*cis-trans*) isomers, and from the neutral and anionic species[130–132]. The ruthenium species were identified[130,131] as Ru^{3+}, $RuCl^{2+}$ and *cis* and *trans* $RuCl_2{}^+$ by determining the charge per ruthenium atom by accounting for the amount of eluting cation required to displace a given amount of ruthenium from the resin, and the charge per species from the dependence of the distribution coefficient on concentration. Similar methods were used to identify the analogous rhodium species[132]. Contrary to some statements in the literature[133], Rh^{III} does sorb on a cation exchanger from perchloric acid solutions, provided it is in a cationic form, *i.e.* the solution does not contain more than two chloride ions per rhodium ion[134]. Chromatography on a cation exchanger impregnated paper[135] follows the same behavior as does elution from a cation exchange resin column, and a bivalent and a monovalent cation, $RhCl^{2+}$ and $RhCl_2{}^+$, could be identified by elution with 0.1–0.5 M HCl.

Paramonova[136] applied her method of relative absorption curves to a study of Ru^{IV} species in perchloric–hydrochloric acid mixtures. Below 0.07 M chloride $Ru(OH)_2{}^{2+}$ was found to predominate, while $Ru(OH)_2Cl_2$ is also an important species. This method, however, is not reliable, and the species found need confirmation.

The platinum metal ions are not extracted well from chloride solutions by most solvents. Thus diethyl ether extracts only traces of Pt^{IV} but larger amounts of iridium ($D \sim 0.05$) (oxidation state unspecified) from 6 M HCl[19]. More appreciable distribution coefficients are obtained with TBP and TOPO[24,137,138], but even with these reagents D hardly exceeds 10. With TBP extractant, D increases from low values at 1 M HCl to a flat maximum at 4–9 M HCl for all metals studied, increasing in the order Rh^{III}, Pd^{II}, Ir^{IV} and Pt^{IV}. The oxidation states of the species actually extracted were, however, not checked and it was found that part of the iridium in the system was Ir^{III}. The species extracted are thought to be complex chloro acids (the TBP solvating the hydrogen ions), rather than solvated neutral metal complexes, however without any substantiating data. Chloride complexes of the nitrosyl ruthenium(III) cation are also extracted by TBP from hydrochloric acid solutions, the extracted species[139] being probably $(HTBP_n,aq)_2{}^+$ $RuNOCl_5{}^{2-}$. Dialkylphosphate dithioic acid extracts palladium(II) very efficiently from hydrochloric acid[140] solutions, even better than it does other elements which form acid insoluble sulfides, such as gold(III), copper or mercury. Other thio derivatives of phosphorus esters are expected to behave similarly.

Published data concerning the anion exchange behavior of the platinum metal chloride complexes is relatively more abundant (Fig. 4).

The distribution of $\mathrm{Pd^{II}}$ and $\mathrm{Pt^{IV}}$ was studied at high resin loadings[141], but the results for Dowex-1 × 10 at 4–12 M HCl (3–28 % loading) are surprisingly similar to those obtained at low loadings (<2%) for a different resin, Amberlite IR-400, in this range[142]. These latter data extend down to 0.1 *M* HCl, and cover also $\mathrm{Rh^{III}}$, $\mathrm{Ir^{III}}$, $\mathrm{Ir^{IV}}$ and ruthenium, at an unspecified oxidation state. Data have also been presented[2] for $\mathrm{Rh^{III}}$, $\mathrm{Ir^{III}}$, $\mathrm{Pd^{II}}$, $\mathrm{Ru^{IV}}$, $\mathrm{Pt^{IV}}$, $\mathrm{Ir^{IV}}$, and $\mathrm{Os^{III}}$ in graphical form, unfortunately on a scale which does not permit accurate reading of the results. Those for $\mathrm{Ir^{IV}}$, $\mathrm{Pt^{IV}}$ and $\mathrm{Pd^{II}}$ are in agreement with the others published, those for $\mathrm{Ir^{III}}$ only up to 0.5 *M* HCl, and those for $\mathrm{Ru^{IV}}$ agree above 4 *M* HCl with data obtained for Dowex-2[16], but below 4 *M* HCl the latter show *D* increasing with hydrochloric acid concentrations, contrary to the behavior of the other platinum metals, but $\mathrm{Ru^{IV}}$ may be extensively hydrolyzed in this range[136]. The data for $\mathrm{Rh^{III}}$, however, are in complete disagreement among the various authors[2,142], and those given by Shimogima[133] are widely scattered and cannot be used. There exist in addition, data for $\mathrm{Ir^{III}}$ in sodium chloride solutions[143], and some observations on the kinetics of ligand exchange between the resin and chloride complexes[144] of $\mathrm{Ir^{III}}$, $\mathrm{Ir^{IV}}$ and $\mathrm{Pt^{IV}}$. The latter two were found to sorb on the resin as the anionic chloride complexes, $\mathrm{IrCl_6^{2-}}$ and $\mathrm{PtCl_6^{2-}}$, each releasing two chloride ions into the solution, *e.g.*

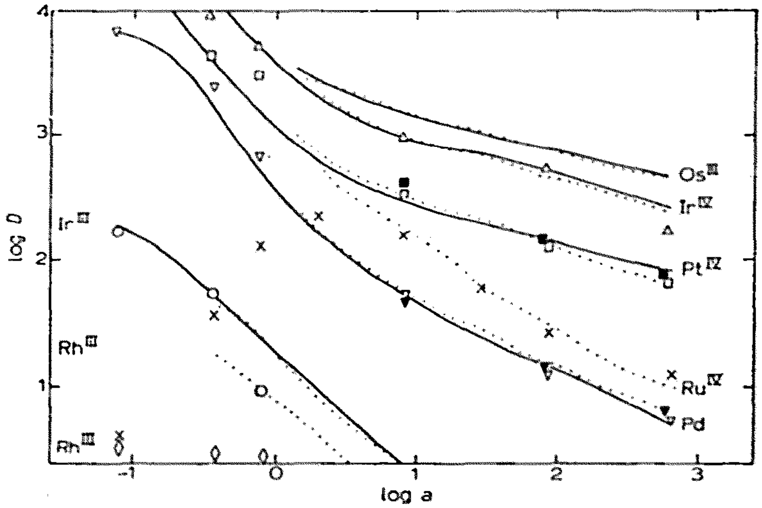

Fig. 4. Distribution data for the platinum metals. ...... ref. 100, open symbols: ref. 142, △ $\mathrm{Ir^{IV}}$, □ $\mathrm{Pt^{IV}}$, ▽ $\mathrm{Pd^{II}}$, ○ $\mathrm{Ir^{III}}$; filled symbols: ref. 51, ■ $\mathrm{Pt^{IV}}$, ▼ $\mathrm{Pd^{II}}$; × ref. 14; —— calculated from eq. 6, 7 and 8.

$$\mathrm{IrCl_6^{2-}} + 2\overline{\mathrm{Cl^-}} \rightleftarrows \overline{\mathrm{IrCl_6^{2-}}} + 2\mathrm{Cl^-} \qquad (4)$$

rather than sorbing as a neutral species and then reacting with ligands in the resin to yield an anionic complex. That this is the case with the robust iridium and platinum complexes does not imply that all systems behave in this way. Indeed, Ir^{III} readily exchanges its ligands both with those in solution and in the resin, so that the kinetic measurements with labelled chloride could not be used to determine the sorption reaction. In sodium chloride solutions it appears[143] that Ir^{III} is in the form of $Ir(H_2O)_2Cl_4^-$, and sorbs as such on the anion exchanger. The very small crosslinking effect on the distribution of this metal certainly indicates the sorption of a mononegative species. The distribution coefficients obey the relationship:

$$\log D_{Ir^{III}} = \log K_{Ir^{III}} + \log \bar{a} - \log a \text{ (NaCl)} \tag{5}$$

predicted for such a case. The data in hydrochloric acid obey a similar expression, but they extend to a somewhat higher range of chloride concentration (or effective activity), where the species $Ir(H_2O)Cl_5^{2-}$ becomes important[145], and the data can be represented by Fig. 4.

$$\log D_{Ir^{III}} = \log K_{Ir^{III}} + \log \bar{a} - \log a(1+k_5^*a) \quad \text{(in HCl)} \tag{6}$$

with the constant $k_5^* = 2 \pm 1$, which is not too far from $k_5 = 4.7$ determined at 40–50° in $\gtrsim 3.75\ M$ $HClO_4$ medium[145].

Analysis of the other systems studied shows agreement between the data and the expressions (Fig. 4)

$$\log D_M = \log K_M + 2 \log \bar{a} - 2 \log a \tag{7}$$

for $M = Pt^{IV}$, Ir^{IV} and, surprisingly, also $M = Os^{III}$, signifying the predominance of the species $PtCl_6^{2-}$, $IrCl_6^{2-}$ and $OsCl_5^{2-}$ in both phases. The former two are in agreement with the chloride ligand exchange data[144], and the latter, which should perhaps be written as $Os(H_2O)Cl_5^{2-}$, is in line with the results for Ir^{III}, where, however, $Ir(H_2O)_2Cl_4^-$ predominates. Since no details were given, it is not excluded that the osmium was present as Os^{IV}, *i.e.* the species $OsCl_6^{2-}$, more in line as regards the order of sorbabilities (*i.e.* K_M) with Ir^{IV} and Pt^{IV}.

The data for Pd^{II}, which might be expected to form $PdCl_4^{2-}$ in both phases and, therefore, also conform to eq. (7), do not do so, but apparently they conform to (Fig. 4)

$$\log D_{Pd^{II}} = \log K_{Pd^{II}} + 4 \log \bar{a} - \log a^2(1+k_5^*k_6^*a^2) \tag{8}$$

instead. Thus the main species in the resin appears to be $PdCl_6^{4-}$ while in the solution it is $PdCl_4^{2-}$ at low, and $PdCl_6^{4-}$ at high, hydrochloric acid concentrations. This result was obtained by combining the data of Kraus and Nelson[2,16] and of Berman and McBryde[142], using different K_{Pd}^{II} values to account for differences in resin crosslinking, water content, etc. This makes the analysis of the data somewhat uncertain. Still, the suggestion that $PdCl_6^{4-}$ is stable at high chloride activities has already been made by several authors[146-148], and although it has been criticized for concentrations lower than 1 *M*, it may be true for the resin and high hydrochloric acid concentrations ($\log k_5{}^*k_6{}^* \sim 0.3$.)

The data for the other platinum metal chloride complexes are either insufficient or conflicting (*e.g.* Rh^{III}, Ru^{IV}) to be amenable to analysis.

Amine extraction has not been applied extensively to the platinum metal chloride complexes, although they should be readily extractable, since they occur mainly as anionic species. The extraction of Ru^{IV} by 5% TiOA in xylene from hydrochloric acid solution has been studied[10], *D* being found to decrease somewhat with increasing acidity (from 4.6 at 0.1 *M* to 0.42 at 10.6 *M*). The extraction of Rh^{III} by 20% TiOA in xylene[149] is much lower (*D* decreases from 1.3 at 0.1 *M* to 0.06 at 8 *M* HCl), considering the higher extractant concentration. A long chain aliphatic primary amine ($C_{>10}H_{>20}NH_2$) and triamylamine have also been applied[150]. It has not been stated whether the amines were neutralized to ammonium chloride salts previous to the metal extractions, since at the concentration levels used (*e.g.* 0.82 *M* triamylamine in chloroform, with 0.3 *M* hydrochloric acid) part of the amine could remain free, and act as a strong extractant by direct coordination to the platinum metal ions. Thus in the range 0.3–3 *M* HCl Pt^{IV} shows $D > 100$, and even Ir^{III} shows $D > 1$ below 2 *M* HCl. Definite extraction by long-chain alkyl-ammonium salts, however, has been demonstrated[150,151,152] Long-chain ammonium sulfates in organic diluents exchange the sulfate anion for chlorocomplex anions, which have been identified by analysis of the organic phase as $PtCl_6{}^{2-}$, $IrCl_6{}^{3-}$ and $RhCl_6{}^{3-}$, extractability decreasing in this order. The secondary amine Amberlite 2A-2 has been applied in carbon tetrachloride and in cyclohexane solutions to extract chloroplatinate(IV) from both chloride and perchlorate solutions[153]. In the former, it was shown that the expected expression $\log D_{Pt} = \log K + 2\log \bar{c}_{RCl} - 2\log c_{Cl^-}$ is obeyed. However, for extraction from perchlorate solutions, a 3/2 power dependence of *D* on $\bar{c}_{RClO_4}$ was found, but could not be adequately explained by any distribution mechanisms. Trioctylamine behaves like Amberlite LA-2 in this system. The spectrum of the extracted species shows it to be $PtCl_6{}^{2-}$ in all the systems, and loading of unneutralized amine by excess chloroplatinic(IV) acid shows 0.5 platinum atom per each amine, corresponding to $(R_2NH)_2H_2PtCl_6$ or $(R_2NH_2)_2{}^+PtCl_6{}^{2-}$. Quaternary ammonium extractants[152], as also triphenylpropylphosphonium chloride[154] were found to extract Ru^{III}, Rh^{III}, Pd^{II}, Ir^{IV}, and Os^{IV} well from chloride solutions into such diluents as chloroform, alcohols, ketones, esters, etc. The distribution data for the amine and analogous systems reported are, however, insufficient for a detailed analysis.

(iv) Group Ib

Like the platinum metal ions, copper(I), silver and gold form strong complexes with chloride ions, though not robust, *i.e.* they are in rapid equilibrium with the solution. Copper(II), on the other hand, behaves as the other bivalent metal ions of the first transition group, and forms rather weak chloride complexes in solution. Ion exchange and solvent extraction methods have contributed some information about these systems.

The cation exchange behavior of copper(II) in dilute halide solutions has been studied alongside with that of Co^{II} and Ni^{II}, and the comments given above concerning the validity of the method apply also to the Cu^{II} systems. The value $\log \beta_1 = -0.40$ given by Trémillon[102] is in line with $\log \beta_1 = -0.02$ and $\log \beta_2 = -0.8$ given by Grimaldi and Alberti[104], both authors agreeing on the stability decreasing in the order Cu, Co, Ni, for the species MCl^+, even in widely differing media. The much higher constants found by Morris and Short[155]: $\log \beta_1 = 0.98$, $\log \beta_2 = 0.69$, $\log \beta_3 = 0.55$, $\log \beta_4 = 0.0$, are difficult to accept for reasons stated previously. Copper(II) is extracted into various acidic extractants, particularly long chain carboxylic acids, as a "soap" *i.e.* by exchanging for hydrogen ions[106,156]. However no information on chloride complex formation is available from these studies.

The extractability of copper(II) is, again, similar to that of cobalt(II). Oxygenated solvents such as butyl acetate[106,157] extract Cu^{II} only slightly, but more basic solvents, such as TBP, show much more appreciable extraction[24,88,110,112,124,158] The data for undiluted TBP given by different authors agree quite well, all showing a maximum around 7 *M* HCl of $D \sim 0.6$, with a steep increase from around 0.006 at 1 *M* HCl, and a slight decrease to around 0.3 at 11 *M* HCl. Within the scatter due to results of different authors, the data conform to the expression (Fig. 5)

$$\log D_{Cu} = \log K_{Cu} + \log(1+\bar{a}^2) - \log(a^{-2}+a^{-1}+10^{-2.6}a) \qquad (9)$$

where $\log K_{Cu} = -1.74$ and $\bar{a} = \bar{c}_{HCl}$, as used before for the HCl–TBP system. The dependence on the hydrogen chloride concentration in the TBP phase can be taken as indicating the occurence of the reaction

$$CuCl_2 \cdot xTBP + 2\,H(yTBP)^+Cl^- \rightleftarrows H(yTBP)^+{}_2CuCl_4 + xTBP \qquad (10)$$

in this phase. This is in agreement with the spectrophotometric data of Morris and Gardner[158], who find spectra similar to that of 0.6 m*M* copper (II) chloride dissolved in TBP (presumably solvated $CuCl_2$), in extracts from dilute HCl, and in extracts from concentrated HCl spectra similar to that of tetrahedral $CuCl_4{}^{2-}$). At intermediate HCl concentrations (3–4 *M*), the spectrum of the extract resembles that of a solution containing 0.7 m*M* $CuCl_2$ + 0.7 m*M* LiCl in TBP, said to contain the species $CuCl_3{}^-$ (absorbing around 480 mμ, compared with 395 mμ for $CuCl_4{}^{2-}$. The two species $CuCl_3{}^-$ and $CuCl_4{}^{2-}$ (associated with hydrogen ions solvated by TBP) were identified also in a continuous variation study[159] of the extraction of copper(II) chloride from chloride solutions by TBP. The distribution data permit the inclusion of another parameter, to account for the formation of $CuCl_3{}^-$, but do not require it. The formulation proposed[158] for this species: $(H \cdot TBP \cdot 3H_2O)^+$

$(CuCl_3 \cdot 2TBP)^-$, is, however, inacceptable, and $(H_3O \cdot 3TBP)^+CuCl_3^-$ is more probable, accounting equally well for the participation of three TBP molecules in the species (obtained from the TBP concentration dependence). The formulation of the cation is compatible with ideas on the extraction of hydrochloric acid by TBP. The TBP dependence study[151] yields $y = 1$ in eq. (10).

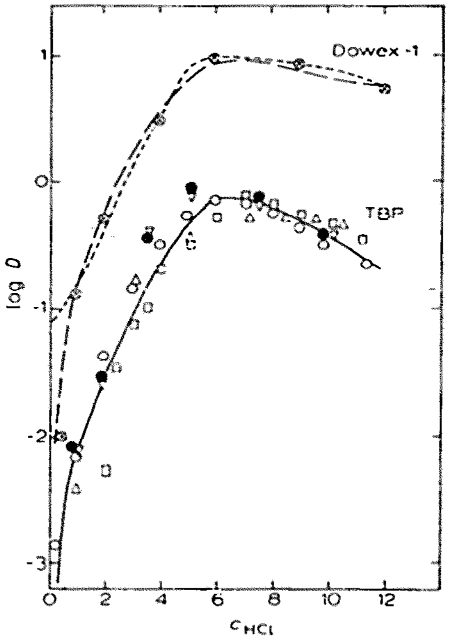

Fig. 5. Distribution data for copper(II). ⊗ ref. 48, anion exchange; – – – – calculated from eq. 9 with $\log K_{Cu} = -0.50$ and second term on the right being $\log(1+10^{-1.3}a)$; — — — calculated from eq. 11; ○ ref. 157, ● ref. 112, □ ref. 88, △ ref. 53, ▽ ref. 110, all for TBP extraction; calculated from eq. 9.

The dependence of the distribution coefficient on the hydrochloric acid concentration indicates [eq. (9)] the presence of Cu^{2+} and $CuCl^+$ in dilute HCl solutions, while $CuCl_3^-$ predominates in concentrated HCl solutions. Formation of appreciable quantities of $CuCl_4^{2-}$ is incompatible with the TBP extraction data according to eq. (9).

The extraction of copper(II) by TBP from lithium chloride solutions is much better than from hydrochloric acid solutions, as found for many other elements, D reaching a value of ~1000 in 12 M LiCl compared to ~0.2 in 12 M HCl. The spectra of the extracts resemble those of extracts from hydrochloric acid solutions, but much higher lithium chloride concentrations are required to convert the spectrum attributed to $CuCl_3^-$ to that due to $CuCl_4^{2-}$, probably because of the lower extractability of lithium compared to hydrogen chloride into TBP.

Copper(II) chloride is extracted from its concentrated solutions by TBP without excess of chloride present, and the species[127] in the organic phase is solvated $CuCl_2$.

The extraction of copper(II) by long-chain amine hydrochlorides and similar reagents has been studied by several authors[128,160], although not in detail. At high hydrochloric acid concentrations the negative slope is greater than in TBP extractions. Quaternary salts, such as triphenylpropylphosphonium chloride, also extract Cu^{II} from chloride solutions[154]. Extraction from concentrated lithium chloride solutions[54] is again much greater than from hydrochloric acid, and the species in toluene solutions of trisooctylammonium chloride has been identified spectrophotometrically as $CuCl_4^{2-}$. The distribution data are not sufficiently detailed to warrant numerical analysis.

There exist data on the sorption of copper(II) from chloride solutions on anion exchangers[2,4,6,16,48,100,117,160a,161,162]. Uptake of small amounts of Cu^{II} from sodium or calcium chloride solutions[161] on the exchangers Wofatit L-150 or MD was considered facilitated by the chloride ligands in the resin, which can interact with sorbed copper(II) chloride to form complex anions. There is no proof, however, that this is the sorption mechanism, rather than exchange of the chloride ions for pre-formed chlorocuprate anions. The sorption of Cu^{II} from mixed hydrochloric acid—lithium chloride solutions[117] has been interpreted in terms of the formation of undissociated $HCuCl_4^-$ in the aqueous phase. The ratio of $CuCl_4^{2-}$ to total copper(II) in 6 M LiCl has been estimated at 13%.

The sorption from hydrochloric acid solutions has been studied by Kraus and Moore[48], and the data conform to an expression similar to (9), except that $\log K_{Cu} = -0.50$, and the term for the organic phase is $\log(1+10^{-1.3}\,\bar{a})$ instead of $(1+\bar{a}^2)$, *cf.* the long-dashed curve in Fig. 5. Since the TBP and anion exchange distribution data deal with the same aqueous phase, the result that the same species, Cu^{2+}, $CuCl^+$ and $CuCl_3^-$ are consistent with both curves should naturally follow. The species in the exchanger are $CuCl_2$ at low, and $CuCl_3^-$ at high resin invasion. However, the anion exchange data are capable of being "explained" by a different set of species. Assuming the resin species to be[162] $CuCl_4^{2-}$, the solution species come out to be $CuCl_2$ and $CuCl_4^{2-}$, according to

$$\log D_{Cu} = \log K_{Cu} + 2\log \bar{a} - \log(1+10^{-2.55}a^2) \qquad (11)$$

with $\log K_{Cu} = -1.7$, *cf.* the short-dashed curve in Fig. 5. Since the data are very few, and since spectral data indicate[162] that the resin species is $CuCl_4^{2-}$, it is difficult to decide between the formation at high HCl concentrations of $CuCl_4^{2-}$, which is consistent with spectrophotometric data, but inconsistent with the TBP extraction data, or of $CuCl_3^-$, which does "explain" both the anion exchange and TBP extraction curves. In any case, the anion exchange distribution data[54] must be accepted with caution, since it has been shown[163] that copper(II) may be partly reduced on the anion exchanger, and that it is necessary to use a holding oxidant, such as chlorine, to attain equilibrium with copper(II). This ion may be loaded on a column from chlorinated 6 *M* HCl, and eluted quantitatively by chlorinated 0.1 *M* HCl, but is not eluted completely with plain HCl.

Some information on the anion exchange behavior of copper(II) in non-aqueous or mixed solutions has been published. Copper(II) chloride, like the cobalt salt, is sorbed on a weakly basic anion exchanger from acetone or dimethylformamide solutions[124], probably through complex formation with the resin functional groups. The sorption of Cu^{II} from organic aqueous hydrochloric acid solutions was found to be much larger than from pure aqueous hydrochloric acid[5,164]. The enhancing effect at <1 *M* HCl and $<35\%$ solvent is largest with acetone, and smaller with ethanol or isopropanol[5,164], but at high acidity or low organic solvent content an opposite effect of solvent on sorption enhancement is observed[5]. The distribution coefficients obtained in 95% isopropanol, 0.01–0.20 *M* HCl, $D = 79{,}000$ to 87,000, may be compared with those in aqueous 2–6 *M* HCl, $D = 2.2$ to 22, the latter being the maximal value. Reducing the isopropanol concentration from 95% to 90% reduces *D* by a factor[5] of about 100. No appreciable amount of acid is co-sorbed with the copper from a 0.005 *M* $CuCl_2$ – 0.010 *M* HCl solution in 95% alcohols[5], which rules out sorption of species such as $HCuCl_3$ or $HCuCl_4^-$.

Very little has been published concerning ion exchange or solvent extraction of copper(I) from chloride solutions. Sulfur containing reagents which have a high affinity for heavy metals will extract copper(I) from hydrochloric acid, where it is strongly, complexed, Thus *O,O'*dialkylphosphodithioic acids extract even from strong hydrochloric acid solutions in a decreasing order[165] of efficiency Pd^{II}, Au^{III}, Cu^{I}, Hg^{II}, Ag^{I} and Cu^{II}. Coordination with a phosphorus atom is involved in the extraction of copper(I) from aqueous halide solutions by triphenylphosphite[166] forming $(C_6H_5O)_3PCuCl$. The distribution curve has a maximum around 0.1 *M* HCl. Competition of chloride complexing probably decreases the distribution coefficients at higher concentrations. A combination of a tertiary amine (Bu_3N) and a tertiary amine salt (Bu_3NHCl) in methylene chloride is effective for extracting copper(I) from halide solutions[167]. Other long-chain ammonium chloride extractants are expected to extract copper(I) from hydrochloric acid solutions, although this has not been demonstrated yet, in analogy with its anion exchange behavior. This has been studied and reported very briefly only[2], the distribution coefficient for Dowex-1 × 10 decreasing from about 100 at 1 *M* HCl to about 2 at 12 *M* HCl, a decrease expected for metal ions forming stable anionic complexes in this range. This species $CuCl_2^-$, which is wellknown from other methods of studying metal complexes, is extractable from hydrochloric acid solutions into diethyl ether[168], and fairly high concentrations can be attained in this solvent. Raman spectroscopy of these ether extracts shows the copper to be in the form of the linear $CuCl_2^-$ species. Much more use could have been made of ion exchange and solvent extraction techniques for studying the copper(I) chloride complexes.

The low solubility of silver chloride in water, or even in chloride solutions where silver(I) forms complex chloride anions, has probably discouraged its study by ion exchange and solvent extraction methods, although they are well suited for the study of tracer concentrations. Distribution coefficients of Ag^I between a cation exchanger and chloride solutions are expected to be extremely low, both because of an intrinsic relatively low affinity of silver towards the resin, compared with multivalent ions, and because of its conversion to a neutral or to anionic species. Being a "soft" cation[1], *i.e.* highly polarizable, silver(I) is not strongly solvated by solvents having the "hard" oxygen as donor atom. On the other hand, it does not form a mononegative complex acid, $H^+AgCl_2^-$, since it is readily further complexed, and therefore is not extractable in this form. Hence its low extractability by oxygenated solvents.

Solvents containing the "softer" donor atoms are expected to coordinate strongly to silver and thus extract it from chloride solutions. Thus *O,O'*-dialkylphosphorothioic acid or -dithioic acid extract silver efficiently from acid solutions[165,169], and though trioctylthiophosphate shows $D < 10^{-3}$ for Ag^I in hydrochloric acid solutions[149], the more effective tributylphosphinesulfide[170] extracts silver with appreciable distribution coefficients. These extraction systems have, however, not been used to study chloride complex formation of silver.

Extractants containing a stable cation can extract anionic silver chloride complexes, *e.g.* triphenylpropylphosphonium chloride in chloroform or other solvents[154], or tributylammonium chloride in methylene chloride[167]. Longer chain ammonium chlorides were used for more detailed studies[149,160,171]. The distribution coefficient was found to decrease with increasing hydrochloric acid concentrations, using methyl dioctylammonium chloride in trichloroethylene[171] Amberlite LA-1 in xylene[160] or triisooctylammonium chloride in xylene[149]. Distribution coefficients in concentrated lithium chloride solutions are somewhat (a factor of 5 only, compared with the much higher effect of 100–1000 for other systems) higher, in cesium chloride solutions considerably lower, than in hydrochloric acid[171]. The distribution coefficients are proportional to the square of the amine concentration in the range 0.1–10% at constant HCl, LiCl or CsCl concentrations in the aqueous phase[171]. This is interpreted as due to the extraction of the silver as the species $(R_3NH)_2{}^+AgCl_3{}^{2-}$.

The anion exchange behavior of silver(I) tracer in chloride solutions was studied by Kraus and Nelson[2] and by Marcus[172]. The former authors found distribution coefficients decreasing from about 1000 at 0.1 *M* HCl to about 1 in 12 *M* HCl, the absorption from lithium chloride solutions being only slightly higher than from hydrochloric acid solutions, (an effect comparable with that for bromide, about a factor of 5 at 12 *M* chloride, as for the amine extraction case, see above). The distribution coefficients were found[172] to be independent of the silver ion concentration over a range of about 100, the decrease in *D* with increasing hydrochloric acid concentration above *ca.* 0.1 *M* HCl being confirmed, the distribution curve having a maximum at 0.12 M HCl. The data were found[172] to conform to the expression

$$\log D = 4.78 + p \log \bar{a} - \log(1 + 10^{2.5}a + 10^{3.35}a^2 + 10^{2.25}a^3) \qquad (12)$$

with $p = 2$, signifying the sorption of $AgCl_3^{2-}$ in the resin, in analogy with the species in amine extracts discussed above. The power series in a shows the successive formation of AgCl, $AgCl_2^-$, $AgCl_3^{2-}$ and $AgCl_4^{3-}$ at increasing hydrochloric acid concentrations, the last mentioned species being formed only at very high concentrations. Thus $AgCl_3^{2-}$ is the major species in solution, over a wide concentration range, as it is in the resin.

Gold(III) has been known to be extractable from chloride solutions for a long time[173]. It hydrolyzes and precipitates unless strongly complexed by chloride, hence no attempts were made to sorb it on cation exchangers in a cationic form, nor to extract it with acidic extractants. However, from concentrated lithium chloride or hydrochloric acid solutions gold(III) sorbs strongly on a polystyrene sulfonate cation exchanger[174], although certainly not as the cation Au^{3+}. The gold(III) species in the cation exchanger is probably ion-paired Li^+AuCl_4 and H^+AuCl_4 respectively, but there is as yet no good explanation for this enhanced sorption.

The extraction of gold(III) was first studied in detail by Mylius and Huttner[173], who studied the distribution of chloroauric acid between diethyl ether and hydrochloric acid. They confirmed the formula $HAuCl_4$ for the species in the organic phase. It was also found that the distribution coefficients increase with increasing gold concentrations. Later, Poskanzer and coworkers[175,176] studied the similar system with bisdichlorodiethyl ether as solvent and other ethers[177], esters[177], and alcohols[82,178] were also used to extract both tracer and macro amounts of gold(III) from hydrochloric acid.

It was found that the variation of D with gold and hydrochloric acid concentrations depends strongly on whether the solvent has a low dielectric constant, *e.g.* diethyl ether, promoting association to ion multiplets at higher concentrations, or a relatively high dielectric constant, *e.g.* bisdichloroethyl ether, promoting ionic dissociation. Dissociation was proved by electromigration experiments[82] with diisopropyl carbinol in suitable diluents. It was found that gold is slightly extractable into aromatic solvents themselves, without an oxygenated extractant (benzene[82], $\log D = -2.0$, xylene[177], $\log D = -2.7$) this might involve some interaction of the gold with the π-electron systems of these solvents. In any case, extraction by oxygenated extractants (diisopropyl carbinol[82], TBP[179,180] TOPO[180], polyethyleneglycol[181]) is much higher than by the diluents themselves, and the extractant concentration dependence may be used to determine the solvation of the proton in the extracted species $(HS_x(H_2O)_y)^+AuCl_4^-$. For TBP it was found[179,180] that $x = 3$, while y varies from one to four. A similar species was found for TOPO, although hydration is less than with TBP. The association of hydrogen and chloroaurate ions, found in low dielectric constant solvents, was also assumed to occur in aqueous solutions at high acidities, to explain the acid dependence. Using some unrealistic assumptions, concerning species and activity coefficients, and not very accurate data, the value $\log K_H = \log K(H^+ + AuCl_4^- \rightleftarrows HAuCl_4) = -0.4 \pm 0.4$ was determined by ether extraction[182] from 0.1–2.5 M HCl. A value of $\log K_H = 0.04$ was obtained from solubility measurements of $(CH_3)_4NAuCl_4$ in HCl–LiCl mixtures, 10 M in chloride with c_{HCl} varying[183] between 0.01 and 1.8 M. In an organic solvent the constant is of course much higher, *e.g.* $\log K_H = 2.42$ for bisdichloroethylether (water saturated)[183], 3.4 in diisopropyl carbinol-*O*-dichlorobenzene mixtures[82] etc.

The anion exchange behavior of gold(III) has been studied by Kraus[2,53,184,185], and by Marcus[186] in hydrochloric acid, lithium chloride and mixed solutions. The data for hydrochloric acid can be reproduced by the equation

$$\log D = 5.40 + \log \bar{a} - \log (a + 10^{-1.0} a^2) \tag{13}$$

where the invasion correction is applied for a monovalent anion in the resin, $AuCl_4^-$, and $10^{-1.0}$ is the constant for the reaction $AuCl_3 + H^+ + Cl^- \rightleftarrows HAuCl_4$, since $a^2 = c_H{}^+ c_{Cl}{}^- y^2{}_{\pm HCl}$. The data for lithium chloride agree with equation (13) up to about 3 M chloride, above which concentration those of Marcus[186] continue to obey this relation omitting the term in a^2, but those of Kraus[185] deviate strongly upward. This strong deviation and high sorption finds its counterpart in the high sorption on cation exchange resins (*cf.* above). The results for mixed lithium chloride–hydrochloric acid solutions of constant molality (10 m) were interpreted in terms of association to $H^+AuCl_4^-$ in the aqueous phase, with $\log K_H = 1.0$. This value should be compared with the lower values quoted above. Summarizing, the anion exchange data are consistent with the species $AuCl_4^-$ sorbed in the resin and predominant in dilute aqueous solutions, while some $H^+AuCl_4^-$ ion-pairs are found in concentrated acid solutions.

Little work was done on the amine extraction of gold(III), probably because of the easy reducibility of gold(III) by the amine salt or impurities in the amine solutions. Still, gold(III) was found[186] to be extracted as $AuCl_4^-$ both by tertiary amine (*e.g.* tripropyl or tributylamine) salts, or by quaternary ammonium (*e.g.* tetrabutylammonium or hexadecyltrimethyl ammonium) chlorides, as also by other extractants involving large cations, such as triphenylpropylphosphonium[154] or tetraphenylarsonium[188]. The tetrachloroaurate anion is sufficiently stable so as to function as a large simple anion in such studies.

No application of ion exchange or solvent extraction methods to the study of gold(I) chloride complexes seems to have been made.

(v) Group IIb

Zinc, like the other bivalent first-row transition metal ions, forms rather weak chloride complexes, although somewhat stronger than those of *e.g.* cobalt or copper. At moderately high chloride concentrations, anionic species are formed in aqueous solutions. These have been studied extensively by ion exchange and solvent extraction methods. In fact, since the zinc ions are colourless, and a convenient radioactive tracer exists, these methods are of advantage, particularly at the higher ligand concentrations.

Cation exchange has been applied[189] in a 0.69 *M* perchloric–hydrochloric acid medium, and formation of the four successive complexes $ZnCl^+$, $ZnCl_2$, $ZnCl_3^-$ and $ZnCl_4^{2-}$ has been found, using Fronaeus' method. As mentioned earlier, the constants found ($\log \beta_1 = 0.72$, $\log \beta_2 = 0.49$, $\log \beta_3 = -0.19$, $\log \beta_4 = 0.18$) are too high, because of changing a too high fraction of the medium ions, and a too high apparent sorption of $ZnCl^+$ cations on the resin. There are no detailed corroborative studies, using either cation exchange or extraction with cation-exchanging (*i.e.* acidic) extractants. An indirect extraction method using the extraction of zinc thiocyanate by hexone has, however, been applied to a study of zinc chloride complexes in a 1 *M* sodium chloride–perchlorate medium[190]. Only approximate values of the stability constants could be obtained, however, ($\log \beta_1 = 0.2$, $\log \beta_2 = 0.3$), because of the limited range of ligand concentration.

Solvating extractants on the other hand, have been applied directly to zinc chloride extraction in a number of studies. Thus tracer zinc(II) was found to be coextracted with macro-quantities of iron(III) or gallium(III) from 6–7 *M* HCl into ether[191], although it shows negligible extractability by ether from 6 *M* HCl ($D \sim 0.002$) when it is alone[19]. Irving and Edgington[36] have studied the extraction of tracer zinc from hydrochloric acid with TBP while others have used tributoxyethyl phosphate[192], and dialkyldithioic acid[193], which are similar reagents. The results are not sufficiently detailed for drawing conclusions concerning the species formed. Detailed studies have been made by Morris, Short and coworkers[52,194], using TBP and solutions of zinc, both at trace and at macro concentrations in hydrochloric acid, lithium, sodium and cesium chloride solutions. The species found in the TBP phase depends on the concentration of coextracted bulk halide. When this is low, TBP solvates the metal ion directly, and the species formed is $ZnCl_2 \cdot 2TBP$, with the Cl–Zn–Cl axis linear (and hence the tetra-coordinated complex square planar), as revealed by a Raman-spectroscopic study[194]. At higher concentrations of coextracted bulk chloride, *e.g.* hydrochloric acid, the species $(H \cdot 2TBP)^+ZnCl_3 \cdot TBP$ which is also probably planar, is formed as an intermediate[194]. At the highest coextracted chloride concentrations, the species $(Li \cdot TBP)_2{}^+ZnCl_4{}^{2-}$ and $(H. TBP)_2{}^+ZnCl_4{}^{2-}$ are formed in the organic phase, in which the zinc is coordinated tetrahedrally by chloride ions, and the TBP solvates the monovalent hydrogen and lithium ions exclusively[52,194]. These conclusions are drawn from the solvent, acid and chloride ion concentration dependencies, as well as from the Raman data.

The distribution curves in hydrochloric acid, lithium and cesium chloride solutions with TBP have been found[52] to resemble closely those obtained with a long-chain amine (10% methyl dioctyl ammonium chloride in trichlorethylene)[171] and with a resin anion exchanger[195].

In contrast with its neighboring elements in the Periodic Table, the 3d transition elements and gallium and germanium, zinc(II) is sorbed well on anion exchangers, even from dilute chloride solutions. Its distribution curve for hydrochloric acid solutions has been given first by Kraus and Moore[48] and has since been essentially confirmed by many others[6,49,100,117,171,185,195–198]. Other authors have studied the sorption of zinc(II) from other aqueous chloride media[53,117,161,185,195,197,199], in non-aqueous or mixed media[5,164,200–203], and as a function of a large number of variables, such as resin cross-linking, temperature, zinc(II) concentration, etc.

The species sorbed from aqueous solutions seems to be $ZnCl_4^{2-}$, as found at macro-loading, both at saturation (where the chloride concentration in the resin is double the capacity, *i.e.* $ZnCl_2$ is added per each 2 RCl), and from the loading isotherm at increasing zinc(II) concentrations[200,201]. The same species has also been found to account for the results at tracer loadings, from the cross-linking dependence[143].

The tracer zinc(II)-chloride system is one of the not-so-numerous class, where both an ascending and a descending branch is found for the distribution curve in the accessible concentration range. This is true for hydrochloric acid solutions[2,117,171,195,197,198], as well as for potassium, cesium, ammonium and substituted ammonium chlorides[171,195,197], but not for lithium, sodium, calcium, magnesium and aluminium chloride solutions[185,195,197], where the distribution coefficients continuously increase with the chloride concentration. The general explanation of this "secondary cation effect" lies in the different effective activities the chlorides have in the resin phase, depending on the bulk cation. Taking this into account has been found to explain quantitatively the differences observed in lithium, sodium, potassium, ammonium and cesium chloride solutions[197]. The mono-, di-, and trimethyl substituted ammonium chlorides form a regular family of curves between the ammonium and the tetramethyl ammonium chloride curves[199], which in turn resemble the potassium and cesium chloride curves. It is expected that for these solutions too the differing amounts of resin invasion can account for the zinc distribution differences. The "invasion-corrected" curve for hydrochloric acid falls in line up to about 5 *M* HCl, but deviates at higher concentrations. At 6 *M* total chloride, for instance, D falls from about 4000 in pure LiCl, to about 2500 in 0.5 *M* HCl-5.5 *M* LiCl, to about 700 in 2 *M* HCl-4 *M* LiCl and to about 300 in 6 *M* HCl, Only a part of this decrease is explained by changes in the effective ligand activities in the solution, a, and in the resin, $\bar{a}$. The formation of non-adsorbable $HZnCl_4^-$ has been advanced as a possible cause for this effect[117].

The stability constants of the species formed in solution can be calculated from the dependence of D on a, and it was shown that the results conform to the expression[197]

$$\begin{aligned}\log D_{\mathrm{Zn}} = {} & \log K_{\mathrm{Zn}} + 2\log \bar{a} - \\ & -\log(10^{-0.61}a^{-2} + 10^{-0.18}a^{-1} + 1 + 10^{-0.08}a + 10^{-0.41}a^{2})\end{aligned} \tag{14}$$

irrespective of the bulk cation or the crosslinking (which affects K_{Zn} and $\bar{a}$ only, but not the β'^{i*} values, the coefficients in the power series in a). The constants β'^{i*} were calculated using the two-parameter approximation of Dyrssen and Sillen[204], but they agree well with independently determined constants[196]. The average charge of the zinc(II), species $\bar{i}$, varies from $+2$ in dilute solutions(<0.1 M) to -2 in concentrated solutions ($a > 10$, *e.g.* about 4 M HCl). Some other estimates of the average charge, using the Kraus and Nelson treatment[205] with different corrections for activity coefficients, lead to inconsistent results[197]. The fraction of zinc(II) in 6 M LiCl appearing as $ZnCl_4^{2-}$ is, according to (14) 88%, while Mizumachi has estimated about 67% from his results[117].

The distribution of the zinc has been studied as a function of the zinc(II) concentration. An early report has given the elution constant E as a function of loading[206]. The distribution curve at 2 M total chloride[201] is from three to six times lower at 0.01 M zinc(II) concentration level than at tracer concentrations, for 1–5 M HCl. As is mentioned above, the sorption isotherm, $\bar{c}_{\mathrm{Zn}}$ as a function of c_{Zn}, tends to a value of 0.5 $\bar{c}_{\mathrm{R}}$, *i.e.* half the resin capacity[200,201]. It does so at lower zinc chloride concentrations, the higher the concentration of the other chloride in the solution (*e.g.* sodium chloride). As $\bar{c}_{\mathrm{Zn}}$ is always less than 0.5 $\bar{c}_{\mathrm{R}}$, *i.e.* there are always more than two resin chloride ions per zinc chloride sorbed, the conclusions reached by Trémillon[200] that $ZnCl_3^-$ is sorbed along with $ZnCl_4^{2-}$, is not reasonable. The sorption of zinc from a sodium chloride–nitrate solution onto a chloride–nitrate resin has been interpreted[207] in terms of the presence of $ZnCl_4^{2-}$ in the resin, so that the concentration of free chloride ions in the resin is given by $\bar{c}_{\mathrm{Cl}} = \bar{c}_{\mathrm{Cl\,(tot)}} - 4\,\bar{c}_{\mathrm{Zn}} = \bar{c}_{\mathrm{R}} - \bar{c}_{\mathrm{NO3}} - 4\,\bar{c}_{\mathrm{Zn}}$. Using these calculated values in a mass-action-low-expression, and assuming constant activity coefficients at constant total solution concentrations of 0.4 and 3.0 M, the authors have concluded from their measurements that Zn^{2+} and $ZnCl^+$ predominate at 0.4 M NaCl, and $ZnCl_3^-$ and $ZnCl_4^{2-}$ predominate at 3.0 M NaCl, at zinc loadings of the resin up to 15%.

The distribution coefficient of zinc(II) varies strongly with the cross-linking of the resin, D, increasing by a factor of about 3 as the crosslinking increases from 2% DVB to 10 or 12% DVB, in hydrochloric acid[197,208] as well as[197] in lithium, sodium[143], potassium, ammonium and cesium[171,197], chloride solutions. This increase has been interpreted[197] in terms of the electrostatic interactions to form ion pairs between the negatively charged zinc chloride species and cations in the resin, being dependent on the effective dielectric constant in the resin. The relatively large cross-linking sensitivity is taken as indicating that the zinc is present as a doubly charged species, *i.e.* $ZnCl_4^{2-}$. Other structural features of the resin, such as changing the functional group from trimethyl methylene ammonium (Dowex-1) to dimethyl (β ethanol) methylene ammonium (Dowex-2) have relatively small effects[201] on D.

In the anion exchange of zinc(II), addition of anhydrous and mixed aqueous organic solvents enhances the distribution coefficients in dilute chloride solutions. The effectiveness of propanol, methanol, ethanol and acetone increases in this order[164]. The increase of D with ethanol content is slow up to about 80%, but is very rapid thereafter, *e.g.* from 80 in aqueous solution, to 500 at 30% ethanol, to 3000 at 80% to 6.8×10^4 at 95% and to 1.2×10^6 in absolute ethanol, in 0.3 M HCl solutions[5,202,203]. At higher chloride concentrations D decreases rapidly, the curves being steeper in organic media than in aqueous solutions, as, *e.g.*, the results for tetramethylammonium chloride in water and 50% ethanol show[199]. Even the curve for lithium chloride comes down, when sufficient ethanol has been added[202] the curve becoming steeper the higher the organic content of the solvent, the curves for lithium chloride and hydrochloric acid approaching each other[202,203]. Addition of acetone to macro concentrations of zinc chloride in water, in the absence of an added foreign chloride, again causes a large increase in the sorption at low concentrations, and to a slight decrease at concentrations above *ca.* 0.2 M. Up to 30% acetone, the higher the organic solvent content, the more pronounced is the tendency of the sorption isotherm ($\bar{c}_{Zn}$ *vs.* c_{Zn}) to level off at the value $0.5\ \bar{c}_R$, *i.e.* the higher the stability of $ZnCl_4^{2-}$ in the resin phase[200]. In absolute ethanol, on the other hand, the resin species seems to be $ZnCl_2$, since the distribution curve for tracer zinc(II), in both hydrochloric acid and lithium chloride solutions starts out with a horizontal portion, and decreases with increasing chloride concentrations[203]. These results are consistent with the uncharged $ZnCl_2$ being the predominant species in the resin, while the species in solution change from $ZnCl_2$ to $C^+ZnCl_3^-$ to $C^+_2ZnCl_4$ ion associates ($C^+ = H^+$ or Li^+), as the chloride concentration increases. Specifically, for ethanolic hydrogen chloride solutions, the distribution data follow the expression

$$\log D_{Zn} = \log K_{Zn} - \log(1 + 10^{2.92}a^2 + 10^{6.40}a^4) \qquad (15)$$

with $\log K_{Zn} = 6.60$. The crosslinking effect which is considerable in aqueous solutions (see above) becomes very slight in methanol solutions, and almost vanishes in ethanol solutions[209], again pointing to the importance of species with low charge in the resin.

As it has already been pointed out, the extraction of zinc(II) from chloride solutions by solutions of long-chain ammonium chlorides resembles strongly the anion exchange behavior[90,171,210]. From 0.1% up to 10% amine, there is a second power dependence of D on the methyldioctyalmmonium concentration in trichloroethylene for dilute as well as concentrated hydrochloric acid, lithium or cesium chloride[171]. It has been concluded from this that the extracted species is

$(R_3NH)_2{}^+ZnCl_4{}^{2-}$. A detailed analysis of the distribution curve for zinc(II) tracer between a quaternary ammonium chloride, Aliquat 336 in benzene, and lithium chloride solutions has been made[210], taking into account the considerable amount of invasion of electrolyte into the organic phase. Using essentially the Marcus–Coryell treatment, stability constants for the aqueous phase have been calculated, but agree poorly with those of other workers. No explanation for this discrepancy has been given.

The ion exchange and extraction behavior of cadmium(II) has received much less attention than that of zinc(II), although they are similar, and good sorbability and extractability can be expected. The cation exchange method has been applied to cadmium–calcium chloride–perchlorate solutions at a constant ionic strength of 0.1 M[211]. The apparent selectivity constant for the cadmium–calcium exchange depends on the chloride concentration, since the concentration of free cadmium ions decreases as complex formation proceeds. The sorption of $CdCl^+$ ions in the resin has been neglected, and an association constant $\log \beta_1 = 1.62$ at 25° (increasing with increasing temperature from 0° to 98°) has been found. Applying the cation exchange method, employing a cation-exchanger-impregnated paper, Grimaldi and coworkers[104] have found a much too low first association constant, $\log \beta_1 = 0.26$, but a reasonable value for $\log \beta_2 = 1.9$. The low precision of their method has been acknowledged by these authors.

Very little is known about the extraction of cadmium(II) from chloride solutions by solvating solvents, and no systematic study of this problem has been made. In survey-type studies D values for the extraction of cadmium(II) from hydrochloric acid similar to those for zinc were found for undiluted TBP[24], and somewhat lower values at low hydrochloric acid concentrations for 5% TOPO in toluene[51].

More information is available concerning the anion exchange sorption behavior of cadmium(II). Leden[212] has already long ago found that cadmium is sorbed on an anion exchanger from a 0.01 M $CdCl_2$ solution, and even better if 0.5 M NaCl is also present. He assumed that the species sorbed on the resin is $CdCl_3{}^-$. The same species has been assumed by Fomin and co-workers[213], who found that D varies little from 0.8 M to 1.2 M KCl but decreases somewhat at 2.0 M KCl. The choice of the resin species is, however, unimportant for calculating activity coefficient ratios at different chloride concentrations, as done by the authors. From the distribution of cadmium chloride between the two phases in the absence of added chloride, Harris[214] has calculated the stoichiometric activity coefficients of this salt, using the Donnan law. These are twenty to forty times lower than those of the comparable salts, cobalt and barium chlorides. The fraction of uncomplexed cadmium can, in principle, be estimated from these measurements, and is found low indeed. As the cadmium chloride concentration increases, its concentration in the resin reaches the definite limit $\bar{c}_{Cd} = 0.5\, \bar{c}_R$. When sodium chloride is present, this occurs at lower cadmium concentrations, the higher the concentration of this salt[200]. Thus the cadmium species in the resin appears to be $CdCl_4^{2-}$. From mixtures of sodium and cadmium chlorides of comparable concentrations cadmium(II) is sorbed in amounts proportional to α_2 the fraction of the uncharged $CdCl_2$ species, as estimated from known stability constants[200], as predicted by Fronaeus' treatment. The same observation has recently been made by Marple[215] for aqueous hydrochloric acid solutions and trace cadmium(II) concentrations, correcting the distribution data for invasion. Limiting his study to the range 0.4 *M* to 2.0 *M* HCl, he has found a good proportionality of $D^0 = D/\bar{a}^2$ and α_2.

The sorption of cadmium(II) from hydrochloric acid solutions has been measured in a number of studies[2,6,49,215,216], as well as that from lithium chloride solutions[217]. The latter results conform to the expression

$$\begin{aligned}\log D_{Cd} &= \log K_{Cd} + 2\log \bar{a} - \\ &- \log(10^{-2.50}a^{-2} + 10^{-0.55}a^{-1} + 1 + 10^{-0.15}a + 10^{-0.85}a^2)\end{aligned} \tag{16}$$

The corrected distribution curve, $\log D^0 = \log D - 2\log \bar{a}$, shows extended regions at low and high a values of slopes +2.00 and −2.00 respectively, denoting gradual transition from Cd^{2+} to $CdCl_4^{2-}$. The resin species assumed for this analysis is $CdCl_4^{2-}$, consistent with the loading data given above. The data for hydrochloric acid diverge, starting from about 0.2 *M* chloride, and can be accounted for if the formation of unsorbable $HCdCl_3$ is assumed (*i.e.* the uncharged $HCdCl_3$ is salted out from the resin phase with its high ionic concentration). Other explanations for the acid effect are, of course, also possible.

Mixed and non-aqueous media have also been used for anion exchange studies of the cadmium(II)-chloride system. The behavior of cadmium in aqueous ethanol is similar to that described for zinc above, *D* increasing slowly up to 80% ethanol and more rapidly at higher ethanol contents. But whereas in aqueous solutions[218] and mixed aqueous-ethanolic solutions[5,219] cadmium has higher *D* values at given hydrochloric acid or lithium chloride concentrations, in anhydrous ethanol zinc has the higher *D* values[203]. No explanation for this inversion is immediately apparent. The distribution of cadmium(II) tracer between the anion exchanger and mixed aqueous-ethanolic solutions exhibits an interesting feature: at constant mole fraction of lithium chloride in the mixture *D* shows a minimum as the fraction of ethanol is increased[219]. This demonstrates the difficulties of selective resin swelling and ion solvation on the one hand, and the necessity of selecting a reasonable concentration scale on the other, since such a minimum apparently is not found when the lithium chloride concentration on the molar scale is held constant (*cf.* data for zinc at 0.5 *M* LiCl)[202]. In anhydrous ethanol[203] the data for hydrogen chloride solutions have been found to follow the expression

$$\log D_{Cd} = \log K_{Cd} - \log(1 + 10^{2.69}a^2) \tag{17}$$

but they can equally well be fitted to the expression

$$\log D_{Cd} = \log K_{Cd}\bar{\beta}_1\gamma_{\pm}{}^{-1} + 2\log \bar{a} - \log(1 + \beta'{}_1{}^*a^2 + \beta'{}_2{}^*a^4) \tag{18}$$

The first expression, with $\log K_{Cd} = 5.20$, signifies that $CdCl_2$ is the species in the resin throughout the concentration range, where the solution species vary from $CdCl_2$ to $H^+CdCl_3{}^-$ as the concentration increases. This is analogous with the cases of zinc(II) and mercury(II). The second expression, however, allows for the formation of the species $H^+CdCl_3{}^-$ in the resin, with $\beta_1 y_{\pm 1}{}^{-1} = (\overline{H^+CdCl_3{}^-})\, \bar{y}_{\pm HCdCl3}/\bar{a}_{CdCl_2}\, \bar{a}^2$, and the solution species are then $CdCl_2$, $H^+CdCl_3{}^-$ and $H_2{}^+CdCl_4{}^{2-}$, as the chloride concentration increases. The experimental data do not permit a choice between these possibilities. From lithium chloride solutions, however, the data indicate that $CdCl_2$ is the resin species, while $Li_2{}^+CdCl_4{}^{2-}$ is formed in solution at the highest concentrations.

Little has been published concerning extraction of cadmium(II) with long chain ammonium chloride solutions. In survey-type studies, its behavior was found to resemble[50,51] that of zinc(II). Specifically, extraction with 10% Amberlite LA-1 in xylene shows $D \sim 30$ between[160] 1 and 8 M HCl, and 20% TIOA in xylene also shows good extractability[149].

Mercury(II) forms strong complexes with chloride ions, so that if a concentration of chloride about 10^{-5} M and stoichiometrically equivalent to that of the mercury is present in a solution, practically all of the latter will be bound. Thus although tracer mercury(II) is sorbed on a cation exchanger from perchloric acid ($D = 110$ at 1 M $HClO_4$ on Dowex 50×4), very small concentrations of hydrochloric acid suffice to decrease the distribution coefficients drastically, D being negligible[220] above 0.1 M HCl. In lithium chloride solutions, however, D starts to increase again above 2.4 M ($D = 0.12$) but reaches only rather low values even at 8.4 M ($D = 1.60$)[221]. Sorption here is possibly due to invasion of the resin by undissociated $HgCl_2$, although it is only a very minor species in the aqueous phase at these concentrations of chloride.

The species $HgCl_2$ formed at stoichiometric concentrations, although very stable, can still undergo reactions to form other species. The distribution method has been used to study the reactions

$$HgCl_2 + Hg^{2+} \rightarrow 2\,HgCl^+ \tag{19}$$

$$HgCl_2 \rightleftarrows HgCl^+ + Cl^- \tag{20}$$

$$2HgCl_2 \rightleftarrows Hg_2Cl_4 \tag{21}$$

$$HgCl_2 + nCl^- \rightleftarrows HgCl_{2+n}{}^{n-} \quad (n = 1, 2) \tag{22}$$

$$HgCl_2 + HgA_2 \rightleftarrows 2\,HgClA \quad (A = Br^-, I^-) \tag{23}$$

$$HgCl_2 + nA^- \rightleftarrows HgCl_mA_n + (2-m)Cl^-$$
$$(n = 1, 2, 3, 4, \quad m = 0, 1, 2, \quad n+m \leq 4) \tag{24}$$

utilizing the distribution of "molecular" $HgCl_2$ between an "inert" organic solvent and aqueous or molten nitrate solutions. The results of more recent investigations[222–228] agree well with those of older studies[229–233].

In addition to being extractable by inert solvents, mercury(II) chloride can, of course, be extracted also by a variety of other solvents. Diethyl ether extracts mercury(II) slightly from hydrochloric acid, giving $D = 0.2$ at 0.5 M HCl and $D = 0.002$ at 6 M HCl[19]. TBP extracts mercury(II) chloride quantitatively from dilute solution, but does not extract excess chloride present, contrary to the behavior of bromide and iodide ions where $Li^+HgBr_3^-$ and $Li^+HgI_3^-$ are also extractable[234]. However, when dissolved in pure TBP, there is a maximum in a continuous variation plot for mercury(II) and lithium chloride, corresponding to the formation of $Li^+HgCl_3^-$. When lithium bromide or iodide are added to mercury(II) chloride in TBP, similar mixed species are formed, and lithium iodide in addition also causes HgICl to be formed in the TBP solution[234]. The distribution curve with TBP from hydrochloric acid shows a maximal $D = 200$ around 3 M HCl, increasing from $D = 60$ at 0.01 M HCl, and decreasing steeply at concentrations[235] above 3 M HCl. The Raman spectrum in TBP of the individual species $HgCl_2$ (linear, solvated by TBP), $Li^+HgCl_3^-$ and $HgCl_4^{2-}$, extracted from concentrated hydrochloric acid, have also been measured[236].

The anion exchange sorption of mercury(II) from hydrochloric acid has been demonstrated by Kraus and Nelson[2], but no details were given. Very high distribution coefficients were observed even with very dilute chloride solutions, and mercury(II) cannot be eluted from the anion exchanger with chloride[6]. Some further information is available in work concerning sorption of mercury(II) on the polyfunctional resin EDE-IOP, with $\log D = 3.8$ at 0.1 M HCl, decreasing to $\log D = 1.5$ at 6 M HCl[237]. Mizumachi[238] measured the distribution of mercury(II) between Dowex-1 × 8 and solutions of hydrochloric acid, lithium chloride and mixtures of the two. Whereas up to about 2 M chloride there is little effect of the cation, there is considerable difference between the curves above this concentration, that for hydrochloric acid showing a continuous decrease, that for lithium chloride showing a shallow minimum[218]. Even 25% substitution of H^+ for Li^+ in the lithium chloride solutions already causes a great decrease in D. Mizumachi assumed that both $HgCl_4^{2-}$ and $HHgCl_4^-$ are sorbed in the resin while the species $HgCl_4^{2-}$, $HHgCl_4^-$ and H_2HgCl_4 exist in solution, (above 2 M HCl), in order to explain his results. Using concentrations in the mass-action-law expressions at constant acquous chloride concentration, he obtained values for the equilibrium constants. That $HHgCl_4^-$ is an important species in the resin phase was also concluded by Marcus and Eliezer[218] who showed that the species must be mononegative, since they found the relationship

$$\log D_{Hg} - \log D_{ReO_4} = const. \tag{25}$$

to hold for hydrochloric acid solutions. For sodium or lithium chloride solutions, on the other hand, they found the expected relationship

$$\log D_{Hg} = \log K_{Hg} + 2 \log \bar{a} - 2 \log a \tag{26}$$

showing, in agreement with the data and conclusions of Mizumachi, that $HgCl_4^{2-}$ is the only species important in the resin and in the solution (above 1 M HCl; below that $HgCl_3^-$ is also present). The formation of $HgCl_4^{2-}$ and of $HgCl_3^-$ from $HgCl_2$ in a perchlorate-form anion exchanger in the presence of low concentrations of chloride ions could be studied, using a constant ionic medium technique[239]. Thus for the resin $\log K_3 = 2.15$ (kg resin mole^{-1}) $= 1.55$ (M^{-1}) (internal solution ~ 12 M perchlorate), compared with values ranging from 1.1 (M^{-1}) to 0.7 (M^{-1}) in 0.3 to 3.0 M sodium perchlorate respectively. Both in solution and in the resin, independent of ionic strength or concentration units used, K_3 was found to be approximately equal to K_4. Thus in a perchlorate form resin there is a range of concentration where $HgCl_3^-$ predominates, while in a chloride-form resin $HgCl_4^{2-}$ is by far the more important species. For the exchange reaction

$$HgCl_4^{2-} + 2\,\overline{Cl^-} \rightleftarrows \overline{HgCl_4^{2-}} + 2\,Cl^- \tag{27}$$

Mizumachi found for 4 M chloride medium and chloride resin $\log K = 4.73$ (l kg^{-1}), while Eliezer and Marcus found for a 3 M perchlorate medium and perchlorate resin $\log K = 2.50$ (l kg^{-1}). Thus it is much more difficult to exchange the small chloride ion for the large tetrachloromercurate anion in the tight, slightly swollen perchlorate resin than in the loose chloride resin.

The species $HgCl_4^{2-}$ loses its predominating role as the resin species not only when the chloride concentration in the resin decreases, by exchange for perchlorate ions, but also as the mercury(II) concentration increases from tracer to macro concentrations. Trémillon[200] showed that although D decreases from $\sim 10^5$ at tracer mercury(II) chloride (with no added chloride) to 42 at 0.1 M $HgCl_2$, the concentration of mercury in the resin, (4.2 M) is higher than accountable by complete conversion to the $HgCl_4^{2-}$ form (1.6 M), or even the $HgCl_3^-$ form (3.2 M). Considerable quantities of free $HgCl_2$ must be present in the resin, along with anionic forms, unless polynuclear anionic complexes are formed (*cf.* eq. (21)).

Uncharged $HgCl_2$ seems to be the major species in the resin when tracer mercury(II) is sorbed from an anhydrous ethanolic solution of hydrogen or lithium chloride. The distribution in the former medium follows the expression

$$\log D_{Hg} = \log K_{Hg} - \log (1 + 10^{2.00} a^2 + 10^{5.50} a^4) \tag{28}$$

with $\log K_{Hg} = 6.30$. In concentrated solutions, as is the case with zinc(II), the ion pairs $(Li, H)^+HgCl_3^-$ and $(Li,H^+)_2HgCl_4^{2-}$ are formed in the ethanolic solutions.

Mercury(II) is expected to be extractable from chloride solutions with organic long-chain ammonium chloride solutions, but very little work in this direction has been reported. Nakagawa[160] found very good extractability for mercury(II) with 10% Amberlite LA-1 in xylene ($D > 100$ in the range 2–8 M HCl, but lower outside this range). These results were confirmed by other workers with the same extractant and also with tri-iso-octylamine[51].

C. REVIEW OF CHLORIDE SPECIES FORMED

The data reviewed both in Part I and in the present part often lead to definite information concerning the species which are important at various chloride concentrations. In many cases equations could be found, relating D with a or with c_{HCl} through appropriate stability constants.

For most metals it has been possible to tabulate the species predominating at various concentrations of hydrochloric acid, as shown in Table 1. Such a tabulation gives information of more immediate use than the stability constants, as compiled *e.g.* in ref. 1, Part I. In many cases, however, there are uncertainties concerning the predominant species, particularly when hydrolysis is important. The text should be consulted for detailed information, as far as it is available.

TABLE 1

METAL CHLORIDE COMPLEX SPECIES PREDOMINANT IN HYDROCHLORIC ACID SOLUTIONS OF VARIOUS CONCENTRATIONS, AS OBTAINED FROM ION EXCHANGE AND SOLVENT EXTRACTION DATA

	HCl, *M*						
M	*0.1–0.5*	*0.5–2*	*2–4*	*4–6*	*6–9*	*9–12*	*resin*
M^{I} (Li–Cs)	M^+	M^+	M^+	M^+	M^+	M^+	—
M^{II} (Be–Ba)	M^{2+}	M^{2+}	M^{2+}	M^{2+}	M^{2+}	M^{2+}	—
Al^{III}	Al^{3+}	Al^{3+}	Al^{3+}	Al^{3+}	Al^{3+}	Al^{3+}	—
Sc^{III}	Sc^{3+}	Sc^{3+}	Sc^{3+}	Sc^{3+}	$ScCl^{2+}$	$ScCl_2^+$	?
Y^{III}	Y^{3+}	YCl^{2+}					
La^{III}	La^{3+}		$LaCl^{2+}$		$LaCl_2^+$	$LaCl_3$	
Lu^{III}	Lu^{3+}		$LuCl^{2+}$		$LuCl_2^+$	$LuCl_2^+$	
Am^{III}	Am^{3+}		$AmCl^{2+}$			$AmCl_2^+$	
Cf^{III}	Cf^{3+}		$CfCl^{2+}$			$CfCl_2^+$	
Zr, Hf^{IV}	$[M(OH)_2]_n^{2n}$	$M(OH)_2Cl^+$		$M(OH)_2Cl_2$	$M(OH)Cl_3$	$M(OH)Cl_5^{2-}$	MCl_6^{2-}
Th^{IV}		Th^{4+}	$ThCl^{3+}$	$ThCl_2^{2+}$			—
U^{IV}		U^{4+}	UCl^{3+}	UCl^{3+}	UCl_2^{2+}		UCl_6^{2-}
Pu^{IV}		Pu^{4+}	$PuCl^{3+}$	$PuCl_2^{2+}$	$PuCl_3^+$	$PuCl_6^{2-}$	$PuCl_6^{2-}$
V^{V}		VO^{3+}					
Nb, Ta^{V}					$M(OH)_2Cl_4^-$		?
Pa^{V}		$Pa(OH)_3^{2+}$	$Pa(OH)_2Cl_3$	$Pa(OH)_2Cl_4^-$	$PaCl_6^-$	$PaCl_7^{2-}$	?
Mo^{VI}			MoO_2^{2+}	MoO_2Cl_2	MoO_2Cl_2	$MoO_2Cl_3^-$	MoO_2Cl_2
W^{VI}					WO_2Cl_2	$WO_2Cl_3^-$	WO_2Cl_2
U^{VI}	UO_2^{2+}	UO_2Cl^+	UO_2Cl^+	UO_2Cl_2	$UO_2Cl_3^-$	$UO_2Cl_3^-$	$UO_2Cl_3^-$
Mn^{II}	Mn^{2+}		$MnCl_2$	$MnCl_2$	$MnCl_3^-$	$MnCl_3^-$	$MnCl_3^-$
Fe^{III}	Fe^{3+}	$FeCl^{2+}$	$FeCl_2^+$	$FeCl_2^+$	$FeCl_3$	$FeCl_4^-$	$FeCl_4^-$
Co^{II}	Co^{2+}	Co^{2+}	$CoCl^+$	$CoCl^+$			$CoCl_3^-$
Ni^{II}	Ni^{2+}	Ni^{2+}	Ni^{2+}	$NiCl^+$	$NiCl^+$		—
Ru^{III}	$RuCl_2^+$						
Ru^{IV}	$Ru(OH)_2Cl_2$						
Rh^{III}	$RhCl_2^+$						

TABEL I *(continued)*

	HCl, *M*						
M	*0.1–0.5*	*0.5–2*	*2–4*	*4–6*	*6–9*	*9–12*	*resin*
Pd^{II}		$PdCl_4^{2-}$	$PdCl_6^{4-}$	$PdCl_6^{4-}$	$PdCl_6^{4-}$	$PdCl_6^{4-}$	$PdCl_6^{4-}$
Ir^{III}	$IrCl_4^-$	$IrCl_5^{2-}$					$IrCl_4^-$
Ir^{IV}		$IrCl_6^{2-}$	$IrCl_6^{2-}$	$IrCl_6^{2-}$	$IrCl_6^{2-}$	$IrCl_6^{2-}$	$IrCl_6^{2-}$
Os^{III}		$OsCl_5^{2-}$	$OsCl_5^{2-}$	$OsCl_5^{2-}$	$OsCl_5^{2-}$	$OsCl_5^{2-}$	$OsCl_5^{2-}$
Pt^{IV}		$PtCl_6^{2-}$	$PtCl_6^{2-}$	$PtCl_6^{2-}$	$PtCl_6^{2-}$	$PtCl_6^{2-}$	$PtCl_6^{2-}$
Cu^{II}	Cu^{2+}	Cu^{2+}	$CuCl^+$	$CuCl_2$	$CuCl_3^-$	$CuCl_3^-$	$CuCl_3^-$
Ag^{I}	$AgCl_2^-$	$AgCl_3^{2-}$	$AgCl_3^{2-}$	$AgCl_3^{2-}$	$AgCl_4^{3-}$	$AgCl_4^{3-}$	$AgCl_3^{2-}$
Au^{III}	$AuCl_4^-$	$AuCl_4^-$	$HAuCl_4$	$HAuCl_4$	$HAuCl_4$	$HAucl_4$	$AuCl_4^-$
Zn^{II}	$ZnCl^+$	$ZnCl_2$	$ZnCl_3^-$	$ZnCl_4^{2-}$	$HZnCl_4^-$		$ZnCl_4^{2-}$
Cd^{II}	$CdCl_2$	$CdCl_3^-$	$HCdCl_3$	$CdCl_4^{2-}$			$CdCl_4^{2-}$
Hg^{II}	$HgCl_3^-$	$HgCl_4^{2-}$	$HHgCl_4^-$	H_2HgCl_4			$HHgCl_4^-$
Ga^{III}	Ga^{3+}	Ga^{3+}	Ga^{3+}	Ga^{3+}	$GaCl_4^-$	$GaCl_4^-$	$GaCl_4^-$
In^{III}	$InCl^{2+}$	$InCl_2^+$	$InCl_3$	$InCl_3$	$InCl_4^-$	$InCl_4^-$	$InCl_4^-$
Tl^{III}	$TlCl_4^-$	$TlCl_4^-$	$TlCl_4^-$	$TlCl_5^{2-}$	$TlCl_5^{2-}$	$TlCl_5^{2-}$	$TlCl_4^-$
Ge^{IV}					GeO_2aq	$GeCl_4$	$Ge(OH)_4Cl_2^{2-}$ $GeCl_6^{2-}$
Sn^{IV}		$(SnCl_4)$	$SnCl_5^-$	$SnCl_5^-$	$SnCl_6^{2-}$	$SnCl_6^{2-}$	$SnCl_6^{2-}$
Pb^{II}	$PbCl^+$	$PbCl_2$	$PbCl_3^-$	$PbCl_4^{2-}$	$PbCl_4^{2-}$	$PbCl_4^{2-}$	$PbCl_3^-$
As^{III}	H_3AsO_3	H_3AsO_3	$As(OH)_2Cl$	$As(OH)_2Cl$	$AsOHCl_2$	$AsCl_3$	?
Sb^{III}						$SbCl_4^-$	$SbCl_4^-$
Sb^{V}						$SbCl_6^-$	$SbCl_6^-$
Bi^{III}		$BiCl_5^{2-}$	$BiCl_6^{3-}$	$BiCl_6^{3-}$	$BiCl_6^{3-}$	$BiCl_6^{3-}$	$BiCl_5^{2-}$
Te^{IV}		TeO^{2+}		$TeOCl_4^{2-}$		$TeCl_6^{2-}$	$TeCl_6^{2-}$
Po^{IV}	$Po(OH)_2^{2+}$	$Po(OH)Cl_5^{2-}$	$PoCl_6^{2-}$	$PoCl_6^{2-}$	$PoCl_6^{2-}$	$PoCl_6^{2-}$	$PoCl_6^{2-}$

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