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

PART I.* NON-TRANSITION-METAL IONS, LANTHANIDES, ACTINIDES, AND d^0 TRANSITION-METAL IONS

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ABBREVIATIONS

HDEHP	di(2 ethylhexyl)phosphoric acid
TBP	tri-n-butyl phosphate
TBPO	tri-n-butylphosphine oxide
TOPO	tri-n-octylphosphine oxide
TIOA	tri-iso-octylamine
TNOA	tri-n-octylamine
TTA	thenoyltrifluoroacetone

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* Part II. Transition metals. will appear in the next issue of *Coordination Chemistry Reviews*.

A. INTRODUCTION

The formation of complexes between metal ions and anionic ligands in solution has been studied by a variety of methods. The chloride anion has received special attention, and in a recent compilation[1] of stability constants, one seventh of all the pages concerned with inorganic ligands is used for the chloride ion (another seventh is used for the hydroxide ion and hydrolyzed species). Chloride ligands form strong complexes only with "type B" (Ahrland–Chatt) or "soft" (Pearson) cations, while with the majority of cations, which are of "type A" or "hard", the complexes are weak, and are formed only at high concentrations of ligand. For such concentrations, ion-exchange and solvent-extraction methods are admirably suited[2], and indeed a great deal of information on chloride complexes has been obtained using such methods.

The present review deals with information published till the end of 1965 concerning the species formed, and their relative stabilities in solution, mainly aqueous solutions. A number of authors have compiled data on the distribution of the various elements, at tracer concentration of their ions, and at different oxidation states where applicable, between ion-exchange resins or organic solvents and aqueous chloride solutions, in particular hydrochloric acid. Such compilations, presented usually in the form of a periodic table with plots of log D (the distribution coefficients) against c_{HCl} (the hydrochloric acid molar concentration) as first presented by Kraus and Nelson[3] for anion exchange, are very useful as general surveys. The data presented are, however, usually in too small a scale for making possible a detailed analysis in terms of the species formed and their relative stabilities. Such compilations have been published for a cation-exchange resin (Dowex-50X4)[4], cation-exchanging extractants (dodecylbenzenesulfonic acid[5] and bis(2-ethylhexyl)phosphoric acid)[6], neutral extractants (tributyl phosphate (TBP)[7], tributylphosphine oxide (TBPO)[8] and tri-n-octylphosphine oxide (TOPO)[9], and basic extractants (Amberlite LA-1[10], triisooctylamine[10], Primene JM-T[11]) and quaternary-ammonium[11] and -arsonium[11] ion-pair extractants. Some of these compilations are summarized in one publication[11].

In the following the various elements are discussed individually according to their groupings in the Periodic Table. For each element (and oxidiation state, where applicable) the results obtained with cation exchangers (resin and liquid), neutral extractants and anion exchangers (resin and liquid) are discussed in turn and compared.

In this first part, non-transition-metal elements are discussed, *i.e. 1)* those ions with a rare-gas electronic core: groups Ia, IIa, IIIb (including the lanthanides and the tervalent actinides), IVb (and the quadrivalent actinides), and the quinqevalent states of group Vb; and *2)* the post-transition groups: IIIa, IVa, Va and VIa. The first set contains invariably "hard" (Type A) ions, while the heavier elements of the second set are definitely "soft" (Type B). Their chloride complexes can rarely be studied by spectrophotometric methods, and only few of them have reversible electrodes for potentiometric studies. In some cases, therefere, ion exchange and solvent extraction have yielded most, and in many cases much, of the information available concerning the formation and stability of the chloride complexes.

This information, concerning the aqueous chloride solutions, can often be summarized in terms of the average ligand number $\bar{n}$, as a function of the chloride concentration, and in some cases even in terms of (effective) complex-formation constants β_n^*, which relate the experimental distribution coefficients D to the (effective) ligand activity a, to the average ligand number $\bar{n}$, and to the fractions of the metallic ion M^{m+} in the form of the various complexes MCl_n^{m-n}, α_n. It is gratifying to note that in many cases the results obtained with diverse distribution methods can be correlated with the same parameters for the aqueous phase (*i.e.* the β_n^*, α_n or $\bar{n}$), as indeed they should be, if the premises and assumptions of the distribution methods used are valid. Inductively, this gives us some confidence in using them for new systems.

B. COMPLEXES ACCORDING TO THE PERIODIC GROUPS

(i) Groups Ia and IIa

The alkali metals and alkaline earths are not, of course, expected to form any chloride complexes. Indeed, anion-exchange elution experiments of traces of these metal ions, even with concentrated HCl, gave elution peaks within what could be taken as the void column volume for a variety of resins and HCl concentrations (Dowex-1 with 7, 11 and 12 M HCl[12–13], Dowex-2 with 12 M HCl[14,15]. They can thus be assigned to the group of elements not absorbable from HCl[3,16]. Possible exceptions may be Li^I and Be^{II}, which are slightly retarded in concentrated HCl, showing D values of 0.06 and 0.09 in 12 M HCl respectively. In concentrated LiCl, however, Be^{II} shows appreciable sorption on the resin, $D = 8$ being attained in 13 M LiCl[7]. The other elements are not sorbed from aqueous LiCl.

Going to mixed solvents[18] yields appreciable sorption on anion exchangers in some cases. In solvents which were 96% organic and 0.2 M in HCl, the values of D for Ca^{II} were zero for methanol, 1 for ethanol, but as high as 20 for isopropanol, 160 for dioxane and 340 for acetone. The values decrease at increasing water content, and for ethanol, where data were given, also at very small water contents, so that a maximum is obtained ($D = 5.6$ in 90% ethanol, 0.3 M in HCl). Sorption on the resin is most probably as uncharged ion-pairs.

Neutral extractants, such as undiluted TBP[7], TBP diluted with toluene[11], or dilute trialkylphosphine oxides[8,9,11], and basic extractants, such as primary-[11], secondary-[10], tertiary-[10] or quaternary-[19,20] ammonium chlorides or tetraphenylarsonium chloride[21] in suitable diluents, do not extract these elements from HCl solutions at any concentrations.

Lithium chloride, alone of the alkali-metal and alkaline-earth chlorides, is soluble in many organic solvents to an appreciable extent. This alone does not make it extractable from aqueous solutions, but a number of solvents do indeed extract it fairly well, in spite of the great loss of hydration energy. TBP extracts the salt[22,23] yielding a species in which the lithium is hydrated by four molecules of water, and associated with the anion, $\log K_{ass} \sim 5.3$[23]. At high lithium chloride concentrations the activity of water is lowered sufficiently for TBP to substitute for it partly in the solvation shell, and at still higher concentrations aggregation seems to set in. A concentration of *ca.* 1.85 M LiCl in TBP is attained by extraction at room temperature.

Amine, although not alkylammonium-salt, solutions are also capable of extracting lithium chloride. A 40% solution of triisooctylamine (TIOA) in toluene extracts lithium chloride from concentrated solutions up to a concentration of nearly 1 M[24]. Hydrogen ions from hydrochloric acid displace the lithium very easily. The other chlorides (except beryllium) are not extracted by amines.

Acidic extractants do extract these elements from HCl, in exchange for hydrogen ions. For HDEHP the first- and second-powers dependencies on $(HX)/(H^+)$ expected for the alkali-metal and alkaline-earth ions were obtained[6]. For an unexplained reason, dodecylbenzenesulfonic acid in a 1:1 mixture of ether and ethylacetate[25], extracts Cs^I with D proportional to $(HX)^{1.6}(H^+)^{-1}$. The extraction of Be^{II} with dialkyl phosphates[26] shows some pecularities. Above 3 M HCl, chloride was found to be present in the extracted species. The chloride-concentration dependency of D points to the formation of $BeCl^+$, with $\log K_1 = -0.66$. Cation-exchange studies from concentrated $BeCl_2$ or $MgCl_2$ solutions containing high concentrations of HCl showed sorption of the cations to a higher extent than the capacity of the resin[27]. This points to the sorption of a species with lower charge than two.

(ii) Group IIIb, lanthanides and tervalent actinides

It is convenient to separate the discussion of Al^{III} and Sc^{III} from that of Y^{III}, lanthanides and tervalent actinides, since unlike the former two elements, the others show similarities, and specific group differences. Although Al^{III} is known to form the tetrachloride complex in certain non-aqueous media, its interaction with water is so strong as to preclude chloride complexing in aqueous solutions. It does therefore not sorb an anion exchanger from any concentration of HCl[12,13]. Unexpectedly, perhaps, its sorption on a cation exchanger from 0.3 M $AlCl_3$–12 M HCl points to the formation of a species with charge less than three[27].

Scandium, on the other hand, does form chloride complexes in aqueous solutions to some extent. Cation exchange in 4 M perchloric-acid medium showed that $ScCl^{2+}$, $ScCl_2^+$ and $ScCl_3$ are formed ($\log \beta_1 = -0.12$, $\log \beta_2 = -0.84$ and $\log \beta_3 = -1.40$) in the aqueous phase, but none of these is sorbed on the resin[28]. Undiluted TBP[29] gives $D = 1000$ from 12 *M* HCl, while 50% TBP in chloroform[28] extracts scandium fairly well from 4 *M* HCl (and even better from mixed 4 *M* HCl–$HClO_4$) and 25% TBP in benzene gives[29] $D = 70$, 5% TOPO in toluene gives[11] $D = 1$ and 1% TBPO gives[8,9] $D = 0.1$. The trialkylphosphine oxides show maximum *D* at 6 *M* HCl, but TBP gives *D* decreasing with lower HCl concentrations. In the range 1–8 *M* HCl, *D* varies at the third power of $a = c_{HCl}y_{\pm HCl}$, indicating that no chloride complexing occurs in the aqueous phase, but the curve levels off at the highest HCl concentrations. Writing the extraction reaction as

$$ScCl_n^{3-n} + (3-n)\,Cl^- + \overline{x\,TBP} \rightleftharpoons \overline{ScCl_3 \cdot x\,TBP} \qquad (1)$$

leads to a decrease in the slope ($\partial \log D/\partial \log a$) as *n* increases. A rough calculation, which ignores changes in TBP concentration by binding of hydrochloric acid, shows that $\bar{n} = 1$ around 9 *M* HCl, and it approaches 2 at 12 *M* HCl.

Although long-chain ammonium chlorides do not extract Sc^{III} from HCl (D 0.01)[8–11,19,20] it shows significant sorption on an anion exchanger, Dowex-1, with $D_v = 0.2$ in 7 *M* and $D_v = 1.0$ in 12 *M* HCl[12]. It shows even higher values for LiCl solutions[17] and ethanolic HCl[30], where it shows maximal *D* at 95% ethanol. This behaviour is consistent with the TBP results discussed above.

The tervalent actinides, lanthanides and Y^{III} form weak complexes in dilute chloride solutions. The extraction of Y^{III} with oxine from 3 *M* Na(Cl, ClO_4) was found[31] to depend on the chloride concentration, and it was concluded that the whole series of complexes YCl_n^{3-n}, with $n = 1, 2 \ldots 6$ is formed, $\log \beta_n = 1.02 - 0.15\,n$. From this it follows that at 2 *M* HCl the predominant species would be YCl_6^{3-}, but this is not consistent with all the other evidence. More likely is the presence of some YCl^{2+} in 1 *M* Na(Cl, ClO_4) solutions, along with Y^{3+}, as found from extraction data with dinonylnaphthalensulfonic acid[32]. This reagent was used also for the lanthanides, showing the formation of MCl^{2+} and MCl_2^+, with stability constants shown in Table 1. Constants of similar magnitude were also obtained in an extraction study with di(*p*-(1,1,3,3-tetramethylbutyl)phenyl)phosphoric acid or thenoyltrifluoroacetone, TTA(HX) from acid perchlorate media for some lanthanides and Am^{III} [33,34]. These reagents, as well as HDEHP[6] show the expected proportionality of *D* with $(HX)^3/(H^+)^3$ in dilute solutions. The cation-exchange method has also been applied for a number of elements[35–37] with results in general agreement with those discussed above (Table 1).

Cation exchangers were used to study the chloride complexes of the tervalent actinides. Grenthe[38] found that $AmCl^{2+}$ and $AmCl_2^+$ are formed in a 4 *M* $HClO_4$ medium and from the constants (Table 1) it may be estimated that in 4 *M* LiCl about two-thirds of the Am^{III} occurs as $AmCl_2^+$. Similar conclusions were reached by Ward and Welch[39], who studied Pu^{III}, Am^{III} and Cm^{III} by cation exchange, finding MCl_2^+ formation above 1 *M* HCl.

TABLE 1

STABILITY CONSTANTS OF LANTHANIDE- AND TERVALENT ACTINIDE–CHLORIDE COMPLEXES OBTAINED BY ION EXCHANGE AND SOLVENT EXTRACTION

Cation	*log* K_1	*Ref.*	*log* K_2	*Ref.*
Y^{3+}	+0.04	32		
La^{3+}	−0.05	33		
	−0.22	34	−0.42	34
Ce^{3+}	−0.05	33	−0.6	32
	−0.07	32		
	+0.10	35		
Pr^{3+}	−0.05	33		
Eu^{3+}	−0.05	33		
	−0.05	32		
	−0.02	37	−0.6	37
	−0.15	34	−0.57	34
	−0.10	36	−0.72	36
Tm^{3+}	−0.10	33		
	−0.12	32		
Yb^{3+}	−0.20	33		
Lu^{3+}	−0.40	33		
	−0.35	34	−0.22	34
Pu^{3+}	−0.23	39		
Am^{3+}	−0.05	33		
	−0.23	39		
	−0.16	38	−0.58	38
	−0.05	36		
	−0.15	34	−0.54	34
Cm^{3+}	−0.22	39		

Turning now to more concentrated solutions, it is found that chloride complexing remains rather weak. Undiluted TBP shows D increasing with Z[40] for 12 M HCl: for La $D = 0.03$, for Y[7] $D = 0.1$, for Tb $D = 0.3$ and for Yb D is as high as 30. The distribution coefficients decrease rapidly with decreasing TBP and HCl concentrations. Diluted trialkylphosphine oxides are ineffective extractants[8,9,11]. Relatively-high distribution coefficients were obtained for the tervalent actinides, and $\mathrm{Cf^{III}}$ was found to be easily separable from $\mathrm{Cm^{III}}$ in 12 M HCl using TBP[41].

Anion exchangers do not sorb $\mathrm{Y^{III}}$, the lanthanides[12] and the tervalent actinides[42], nor do various long-chain ammonium chlorides extract them[8–10,19,20], from aqueous HCl solutions, even the most concentrated. Some sorption from alcoholic HCl on anion exchangers does however occur[18,30,42]. Distribution coefficients of about 20 are obtained[18] for $\mathrm{Dy^{III}}$ and $\mathrm{La^{III}}$ in 97% ethanol, 0.3 M in HCl, and lower values at lower alcohol and HCl concentrations. This sorption need not, however, involve formation of anionic species in the resin, since $\mathrm{La^{III}}$ when eluted with solutions 2 M in HCl and above 50% in alcohol, was found[43] to be retarded on pure cellulose paper to the same extent as on a paper impregnated with an anion-exchange resin.

Higher sorption on an anion exchanger was observed from concentrated

LiCl; for Dowex-1X8 at 87° and 10 *M* LiCl, D_v values were obtained[31], varying from 0.25 for $\mathrm{La^{III}}$ to 0.40 for $\mathrm{Ce^{III}}$, then roughly linearly to 0.90 for $\mathrm{Lu^{III}}$, with a slight dip for $\mathrm{Gd^{III}}$. Low D_v values, 0.2–1.0, were also obtained for $\mathrm{U^{III}}$, $\mathrm{Np^{III}}$ and $\mathrm{Pu^{III}}$ under similar conditions[32], but for $\mathrm{Am^{III}}$ and higher actinides, appreciable D_v values are obtained, ranging from 4 to 20 for $\mathrm{Am^{III}}$ to $\mathrm{Es^{III}}$ for the same conditions[31].

Marcus has recently discussed the anion-exchange sorption from concentrated lithium chloride solutions[46] of the lanthanide and tervalent-actinide ions. From the dependence of the anion-exchange distribution coefficients on the cross-linking of the resin and on the acidity of the solutions, it was concluded that the predominant species in the resin is $\mathrm{MCl_4}^-$, while from the dependence of the effective chloride activity in the solution, it seems that $\mathrm{MCl_2}^+$ is the major species in solution. The distribution can be described in the range 8.0–13.5 *M* LiCl by the reaction

$$\mathrm{MCl}_{3-i}{}^{i+} + i\,\mathrm{Cl}^- + p\,\overline{\mathrm{Cl}^-} \rightleftharpoons \overline{\mathrm{MCl}_{3+p}{}^{p-}} \tag{2}$$

with $p = 1$. The distribution data conform thus to the expressions[2]

$$\log D_{\mathrm{La}} = \log K_{\mathrm{La}}{}^* + p \log \bar{a} = -2.52 + \log \bar{a} \tag{3a}$$

$$\log D_{\mathrm{Lu}} = \log K_{\mathrm{Lu}}{}^* + p \log \bar{a} + \log \beta_{-1}{}^* a = -4.35 + \log \bar{a} + \log a \tag{3b}$$

$$\log D_{\mathrm{Am}} = \log K_{\mathrm{Am}}{}^* + p \log \bar{a} + \log \beta_{-1}{}^* a = -4.12 + \log \bar{a} + \log a \tag{3c}$$

$$\begin{aligned} \log D_{\mathrm{Cf}} &= \log K_{\mathrm{Cf}}{}^* + p \log \bar{a} + \log \beta_{-1}{}^* a(1 + (\beta_{-2}{}^*/\beta_{-1}{}^*)a) = \\ &= -3.25 + \log \bar{a} + \log a\,(1 + 10^{-2.6}\,a) \end{aligned} \tag{3d}$$

An examination was made[46] of the extensive data on the extraction of these elements with long-chain alkylammonium chlorides from conc. lithium chloride solutions[47–49]. For the lanthanides, extraction begins above 7 *M* LiCl, but *D* hardly exceeds unity[48], even under tbe best conditions (12 *M* LiCl, 1 *M* or 35% (w/v) TIOA in diisopropylbenzene, for $\mathrm{Eu^{III}}$. For the actinides, *D* values exceeding 100 are easily obtained. The dependence of the distribution coefficients on amine-salt concentrations (second power), and on the acidity, as well as on the chloride effective activity in the aqueous phase, lead again to $\mathrm{MCl_2}^+$ as the major species in that phase, in accord with the anion-exchange data. The finding[46] of one lithium ion extracted per americium ion, and consideration of the amine to be aggregated, makes the following reaction plausible, at least in the case of americium:

$$\mathrm{AmCl_2}^+ + 2\,\mathrm{Cl}^- + \mathrm{Li}^+ + \overline{2\,\mathrm{A^+Cl^-}} \rightleftharpoons \overline{\mathrm{A_2}^+\mathrm{Li}^+(\mathrm{AmCl_6})^{3-}} \tag{4}$$

where A^+ is an aggregate of the amine salt having dissociated one chloride ion. The distribution coefficient can be described by

$$\begin{aligned} \log D_{\mathrm{Am}} = \log K_{\mathrm{Am}}{}^* + p \log \bar{c}_{\mathrm{R_3NHCl}} - \\ - p \log (1 + K_{\mathrm{H}}{}^* c_{\mathrm{H}}{}^+ a y_{\pm\mathrm{HCl}}) + (2n - i) \log a \end{aligned} \tag{5}$$

with $p = 2$, $n = 2$ and $i = 1$, these being the indexes of the species in the organic phase $\overline{A_p^{+}Li_{n-i}^{+}[AmCl_{3+n+p-i}]^{i-n-p}}$. The constant K_H^*, pertaining to the acid dependence, is the effective equilibrium constant for the reaction $\overline{A^+Cl^-} + H^+ + Cl^- \rightleftharpoons \overline{A^+HCl_2^-}$. Although there is no direct evidence for the participation of lithium ions in the extraction of the other elements, the fact that much higher extraction is obtained from LiCl solutions than from, say, $CaCl_2$ solutions[48] of the same effective ligand activity, points to this being generally so.

Cation-exchange data for conc. HCl[50–52] or LiCl[45] point to higher complexing of the actinides than the lanthanides in the aqueous phase. Higher covalent binding for the actinides has been observed spectrophotometrically[45], and if ion pairing is the same, higher total complexing of the actinides should result. Higher D values for anion-exchange or amine extractions, as observed for the actinides, correlates often with higher complexing, and is consistent with the cation-exchange behaviour. Cation exchange results in concentrated hydrochloric acid show a value of -1.2 for $(\partial \log (D_{Am}/D_{Pm})/\partial \log a)$[50], so that 1–2 more chloride ions should be bound to Am^{III} than to Pm^{III}. The above analysis of D values for anion-exchange or amine extraction, however, indicates that approximately the same species are formed for both series in the aqueous phase (MCl_2^+ or MCl_3 in 7–12 M LiCl). This inconsistency cannot as yet be explained.

(iii) Group IVb and quadrivalent actinides

It is convenient to discuss the elements belonging to these groups together, because of the similarities of behaviour observed, for all these elements in the quadrivalent state.

Titanium(III), like its neighbour Sc^{III}, was found to be only slightly sorbed on an anion exchanger, showing $D_v = 0.5$ in 12 M HCl[12]. It can therefore be classified with the other non-absorbable tervalent elements[3,14]. Quadrivalent titanium is highly hydrolyzed in dilute HCl, and is sorbed on a cation exchanger (showing D values decreasing with increasing HCl concentrations) probably as a hydrolyzed species[53]. It has been claimed[54] that the titanyl cation, TiO^{2+}, is the species in solution below pH 1.3, and that uncharged $TiOCl_2$ is sorbed on a (weakly-basic) anion exchanger above 4 M HCl. In any case, sorption of anionic species, on (strongly-basic) anion exchangers starts above about 6–8 M HCl[13,14,53,55], with $D = 2.6$ at 9.9 M and $D = 66$ at 11.7 M HCl[1]. Parallel to this, also extraction with the secondary-ammonium chloride, Amberlite LA-1, in toluene is appreciable only above 8 M HCl[56]. Other neutral or basic extracting agents show similar behavior[1–11,19–21].

The chemistry of Zr^{IV} and H^{IV}–chloride complexes has been studied rather extensively, still, there is little agreement concerning the species formed. Hafnium was found to behave in general like Zr^{IV}, and the following discussion will be mainly in terms of Zr^{IV}. Any scheme for the species formed in, say, 1–12 M HCl will have to account for the following experimental observations, some of which being unfortunately inconsistent with each other.

Extraction with TTA from HCl solutions below 0.2 M shows[57] the aqueous species to be highly hydrolyzed, whereas in the range 0.2–2 M a less-hydrolyzed species occurs in the aqueous phase; possibly even a non-hydrolyzed species[58], as suggested also by cation exchange[59]. At higher metal concentrations, hydrolyzed polynuclear species were found to occur in the aqueous phase in cation-exchange studies[59,60]. In a more recent cation-exchange study[61], the complex formation of the species found at 2 M H^+ and 4 M constant acidity in a $H(Cl, ClO_4)$ medium was investigated. The addition of the first chloride ligand occurs readily[61] ($\log k_1 = 0.0$, compare $\log k_1 = 0.3$ found by TTA extraction[57], but the second one ($\log k_2 = -0.9$) adds with more difficulty. The suggestion of the formation of species with four ligands in the 2 M medium, and with three ligands only in the 4 M medium, with higher stability constants, seems rather unlikely.

Extraction with TBP in benzene was found[62] to yield a species with 2 TBP molecules and four chloride ligands extracted from 6–9 M HCl, most likely being $ZrCl_4 \cdot 2\,TBP$ (the species $(H \cdot x\,TBP)_2Zr(OH)_2Cl_4$ is another possibility but should have $x > 1$, the observed value). At an acidity of 6.5 M and up to 0.5 M chloride in a $H(Cl, ClO_4)$ medium the extraction results require addition of three chloride ions to produce the extracted species. The results also show depolymerization of the species as the Zr^{IV} concentration decreases. A later reinterpretation[63] of these data, in terms of species with up to four chloride ligands in the aqueous phase ($\log k_1 = 0.92$) at these low chloride-ion concentrations seems erroneous. A later TBP extraction study[64], using tracer Zr^{IV}, undiluted TBP and 4–12 M HCl, shows a fourth-power dependence of D on a in the range 4–8 M, declining to about first-power dependence in the range 9–12 M. At varying acidities, both addition of chloride ligands, and removal of hydroxide ligands must be taken into account.

The anion-exchange behavior of Zr^{IV} in HCl has been studied by a number of authors on a number of resins: Dowex-1[65,66], Dowex-2[15,67], Wofatit-SB-400[66], and although there is no detailed agreement between the distribution curves, there is agreement that $D > 1$ starts about 5–6 M, and D increases to very high values ($D > 1000$) at 12 M HCl. At relatively-high Zr^{IV} concentrations, saturation of the resin from 11.5 M HCl gave[66] a species with average negative charge of 1.7, and an average of 3.4 chloride ligands per Zr^{IV} ion, while saturation from cooled 15.3 M HCl gave a ratio Cl:Zr of 4.0. These results are consistent with species $[Zr(OH)_2Cl_3]^-$ and $[Zr(OH)_2Cl_4]^{2-}$ in the resin. At these Zr^{IV} concentrations little difference was observed for sorption from HCl and from 1 M HCl–LiCl solutions, which means that no OH^- groups are removed from the solution species to give the resin species. The results at tracer Zr^{IV} and Hf^{IV} concentrations[65] may be interpreted in terms of the reaction

$$\begin{aligned} Zr(Hf)(OH)_nCl_m{}^{4-n-m} + i\,H^+ + j\,Cl^- + p\,\overline{Cl}^- &\rightleftharpoons \\ \rightleftharpoons\ \overline{Zr(Hf)(OH)_{n-i}Cl_{m+j+p}} & \end{aligned} \qquad (6)$$

Accepting the value $p = 2$, obtained at higher $\mathrm{Zr^{IV}}$ concentrations, the results for 11–12 M HCl are consistent with $i + j = 0$, for 7–9 M HCl with $i+j = 3$, and for 9–11 M HCl with values in between. Ethanol was found[68] not to affect the sorption of $\mathrm{Zr^{IV}}$ from the solutions.

The extraction of $\mathrm{Zr^{IV}}$ (and $\mathrm{Hf^{IV}}$) with long-chain tertiary-, (*e.g.* tribenzylamine[69,70], TNOA[71] and others[71] and quaternary-ammonium[72] chlorides) has also been studied. As the reagent concentration increases, the dependency of D on it varies from second power[69] to third power[70] to fourth power[69–70]. At low $\mathrm{Zr^{IV}}$ concentrations, D was independent of metal concentration[69]. The general reaction

$$\mathrm{Zr(OH)_2Cl_n + \mathit{a}\,H^+ + (4-\mathit{n})Cl^- + \mathit{p}\,\overline{RCl} \rightleftharpoons \overline{R_pZrCl_{4+p}} + 2\,H_2O} \tag{7}$$

was proposed[70] to account for a fourth-power dependence of D on a for HCl in the range 9–10 M, zero-power dependence above 11 M HCl, second-power dependence of D on (undefined) "chloride activity" at low and fourth-power at high chloride concentration in (H, Li)Cl solutions of constant acidity 7.6 M, and a more complicated acidity dependence at constant chloride concentration. A p value of four could correspond to octaligated $\mathrm{Zr^{IV}}$ in the amine phase, unless a loose association of $\overline{\mathrm{RCl}}$ with $\overline{\mathrm{R_2ZrCl_6}}$ occurs[70].

A scheme of species more or less consistent with all these observations would be as shown in Table 2. The data for $\mathrm{Hf^{IV}}$ follow very closely those of $\mathrm{Zr^{IV}}$, showing somewhat lower D on anion exchangers and tertiary-ammonium chloride reagents, with separation factors 5–20.

TABLE 2

THE SPECIES OF $\mathrm{Zr^{IV}}$ IN HCl

The species were calculated from a reinterpretation of the data in the references cited.

HCl (M)	*Average species*	*Reactions and remarks*
<0.2	$\mathrm{[Zr(OH)_2]^{2n}}$	$n \geq 2$[44]
0.2–1	$\mathrm{[Zr(OH)_2]_n^{2n}}$	$n \sim 1$ at higher c_{Zr}[63] $n = 1$ at tracer c_{Zr}[44]
1–2	$\mathrm{[Zr(OH)_2Cl]^+}$	at tracer c_{Zr}[44, 48, 56]
3–7	$\mathrm{Zr(OH)_2Cl_2}$	$\mathrm{ZrCl_4 \cdot 2\,TBP}$ extracted[51], $D \propto a^4$ (i.e. $\mathrm{2\,H^+ + 2\,Cl^-}$)
7–8	$\mathrm{Zr(OH)Cl_3}$ $\mathrm{[Zr(OH)_2Cl_3]^-}$	$\mathrm{ZrCl_4 \cdot 2\,TBP}$ extracted[49] from anion exchange[52], $D \propto a^3$ (i.e. $\mathrm{2\,H^+ + Cl^-}$)
9–10	$\mathrm{ZrCl_4}$ $\mathrm{[Zr(OH)Cl_4]^-}$ $\mathrm{[Zr(OH)_2Cl_3]^-}$	 $D \propto a$ for TBP[51] (i.e. $\mathrm{H^+}$) species in anion exchanger[63], high c_{Zr}
11–12	$\mathrm{ZrCl_4}$ $\mathrm{[Zr(OH)Cl_5]^{2-}}$ $\mathrm{[Zr(OH)_2Cl_4]^{2-}}$	from anion exchange [52, 57], $D \propto a^0$ species in anion exchanger[63], hich c_{Zr}
Anion exchange and tertiary amine	$\mathrm{[ZrCl_6]^{2-}}$ $\mathrm{[Zr(OH)_2Cl_4]^{2-}}$	from $p = 2$[57, 58, 62]

Thorium ions, although not much larger than Zr^{IV} or Hf^{IV} ions, are appreciably less hydrolyzed, and in acid solutions occur as Th^{4+}. They associate readily with chloride ions, yielding various cationic complexes $ThCl_n^{4-n}$, $n = 0$, 1, 2, 3, and perhaps also 4. Quantitative information was obtained by TTA extraction[73,74], at various ionic strengths, and the data at 4 M $NaClO_4$ medium show good agreement; the calculated values of $\bar{n}$ increase gradually reaching just over 2 at 4 M chloride. In agreement with this the average species $ThCl_2^{2+}$ is obtained by cation exchange[75] in up to 5 N chloride solutions of H^+, Li^+, Na^+, Mg^{2+}, and Ca^{2+}. Extraction with bis(2-ethylhexyl)phosphoric acid in toluene[76,77] showed by both saturation- and acid-dependence studies that one chloride ion accompanies the Th^{IV} into the organic phase, being bound rather strongly, steric hindrance preventing the Th^{IV} to bind more than three phosphate anions. The extraction with undiluted TBP[29] conforms roughly to the presence of $ThCl_2^{2+}$ in the aqueous pbase in the range 3–9 M HCl, and $ThCl_4 \cdot x\,TBP$ in the organic phase.

Anion-exchange sorption of Zr^{IV} starts above about 7 M HCl, and of Hf^{IV} only above about 8 M HCl. It is therefore not so surprising that no significant sorption of Th^{IV} on an anion exchanger could be obtained even at 12 M HCl[65]. Neither is Th^{IV} extracted significantly with TIOA in xylene[78] or similar reagents[8–11,19–21], from HCl. With 12 M LiCl, (0.1 M in HCl to avoid hydrolysis) on the other hand, $D_v = 6$ was obtained[65] for Th^{IV} on an anion exchanger, and $D > 1$ for extraction with 20% TIOA in xylene[48]. Significant sorption on anion exchangers is also obtained from alcoholic HCl[18,30,79,80], and $D \sim 10^3$ is attained at 90% ethanol, 0.5 M in HCl. However, only a small part of the capacity can be sataurated with Th (about 7.3% from 96% isopropanol, 0.5 M in HCl). This sorption need not, however, be as an anionic complex, and partition of a neutral complex could be the main sorption reaction, as suggested by the similar paper chromatographic behavior of Th^{IV} on paper impregnated with anion-exchange resin and with plain paper[43,81].

Protactinium(IV), stabilized by a holding reductant, was found[82] to behave like Th^{IV} with respect to anion exchange from HCl solutions, showing negligible D even at 12 M HCl. Still somewhat higher complexing of Pa^{IV} than of Th^{IV} must occur, since it is extracted almost quantitatively ($D = 19$) by TNOA hydrochloride in xylene[83] above 10 M HCl, in a manner similar to that of Zr^{IV} and Hf^{IV} and contrary to that of Th^{IV}.

The quadrivalent oxidation states of U, Np, and Pu have been studied rather extensively. Extraction with TTA[84] and a cation-exchange study[85] showed cationic-complex formation for Pu^{IV} in a 4 M $H(Cl, ClO_4)$ medium of stability similar to those of Th^{IV}; $\bar{n} = 2$ is reached at about 4 M chloride. Extraction of Np^{IV} with dodecylbenzenesulfonic acid[86] and with HDEHP[87] from dilute HCl showed the aqueous species to be Np^{4+}, which is complexed at higher HCl concentrations. TBP extraction of Np^{IV} showed[88] third-power dependence on TBP concentration, and a steep increase of D with HCl concentration (for undiluted TBP), which parallels that of $\mathrm{Th^{IV}}$ and $\mathrm{Hf^{IV}}$, except that it shows a maximum at 8 M HCl. The curve for the extraction of $\mathrm{Np^{IV}}$ with 10% TNOA in xylene[89] is superimposable on that for TBP up to 6.5 M HCl and the same is observed for $\mathrm{Pu^{IV}}$, with $K_{\mathrm{TIOA}}/K_{\mathrm{TBP}} = 170$, K being the equilibrium constant for the extraction[90]. At higher HCl concentration the different invasion properties of the two extractants as regards HCl causes some difference. A rough calculation, disregarding this complication, shows $\bar{n} = 1$ being attained not before 5 M HCl, and $\bar{n} \sim 2$ around 7 M HCl, at much higher concentrations than for $\mathrm{Pu^{IV}}$. The extraction curve for $\mathrm{Pu^{IV}}$ with TOPO[91] also shows a maximum around 8 M HCl. The maxima for $\mathrm{Np^{IV}}$ and $\mathrm{Pu^{IV}}$ for the neutral extractants are due to competition with HCl for the extractant, and not to the formation of anionic species. These are hardly formed at all in 12 M HCl for $\mathrm{U^{IV}}$ and $\mathrm{Np^{IV}}$, and only to about 75% for $\mathrm{Pu^{IV}}$, the species being identified spectrophotometrically[92] as $\mathrm{PuCl_6^{2-}}$. The species extracted into the amine hydrochloride phase was identified for all three elements as $\overline{\mathrm{R_2MCl_6}}$, from the dependence of D on the amine concentration, and from the comparison of the spectra with those of known compounds[89]. Uranium(IV) showed extraction behavior with TNOA from HCl like[89] $\mathrm{Np^{IV}}$. The extraction of $\mathrm{Pu^{IV}}$ with amine hydrochloride leads to the values[78,89] $\bar{n} = 1$ at 3–4 M HCl, $\bar{n} = 2$ at 4–7 M HCl (in agreement with the cation-exchange results[85]) and $\bar{n} = 3$ at 8–10 M HCl. Qualitative anion-exchange data show sorption of $\mathrm{Pu^{IV}}$ above 2.5 M HCl[93], although it is easily eluted below 4 M HCl and strongly held only above 8 M HCl[94], while[94] $\mathrm{Np^{IV}}$ and[65,94] $\mathrm{U^{IV}}$ are eluted below 6 M and held above 8 M HCl[94]. A more detailed study, in which the oxidation states were controlled spectrophotometrically[95] showed somewhat stronger sorption of $\mathrm{Np^{IV}}$ than of $\mathrm{U^{IV}}$, with $D_v = 1$ at 6, and 5 at 5 M HCl for $\mathrm{U^{IV}}$, $\mathrm{Np^{IV}}$ and $\mathrm{Pu^{IV}}$ respectively, and $D_v = 10$ about 1 M HCl higher. The species in the resin were identified spectrophotometrically[92] as $\mathrm{MCl_6^{2-}}$, the same $\mathrm{U^{IV}}$ species being sorbed from conc. HCl or LiCl. That the spectrum differs from that of $\mathrm{MCl_6^{2-}}$ in solid compounds, but resembles that of $\mathrm{MCl_6^{2-}}$ extracted by tertiary-ammonium chlorides, is explained[96] by hydrogen bonding to $\mathrm{H_3O^+ \ldots Cl}$ in the resin (and $\mathrm{R_3NH^+ \ldots Cl}$ in the amine) even for resins equilibrated with LiCl solutions containing small amounts of HCl.

The species of $\mathrm{Th^{IV}}$, $\mathrm{U^{IV}}$, $\mathrm{Np^{IV}}$ and $\mathrm{Pu^{IV}}$, believed to predominate in HCl solutions of various concentrations, as obtained from an analysis of anion-exchange[65,82,92,96], amine-hydrochloride[78,83,89,90] and neutral phosphorus-ester[29,88,91] extraction data, are shown in Table 3.

(iv) Group Vb

Vanadium(III) and -(IV) are only very slightly complexed in HCl solutions, as evidenced by the small sorption on anion exchangers even in concentrated

TABLE 3

SPECIES OF QUADRIVALENT ACTINIDES IN HCl

HCl (M)	*Th*^{IV}	*U*^{IV}	*Np*^{IV}	*Pu*^{IV}
1	Th^{4+}	U^{4+}	Np^{4+}	Pu^{4+}
2	$ThCl^{3+}$	UCl^{3+}		
3			Np^{4+}	$PuCl^{3+}$
4	$ThCl_2^{2+}$			$PuCl_2^{2-}$
5			$NpCl^{3+}$	
6		UCl^{3+}		
7			$NpCl_2^{2+}$	
8		UCl_2^{2+}		$PuCl_3^{+}$
9				
10				$PuCl_3^{+}$
11				
12				$PuCl_6^{2-}$
Amine · HCl		R_2UCl_6	R_2NpCl_6	R_2PuCl_6
M HCl above which $D_v > 1$ (20% TIOA)	>12	5.5	4.5	3.8
Anion exchanger		R_2UCl_6	R_2NpCl_6	R_2PuCl_6
M HCl above which $D_v > 1$	>12	6	5	5

HCl[12–14] ($D \lesssim 1$ at 12 *M* HCl[12]). Vanadium(III) resembles in this respect its neighbor Cr^{III}. Neither is V^{IV} extracted with a secondary-ammonium chloride from HCl[97] although from alcoholic HCl, V^{IV} does show appreciable sorption on an anion-exchange resin[18,98] ($D = 5.6$ in 97% ethanol, 0.3 *M* in HCl and $D = 4.5$ for 55% isopropanol, 4.5 *M* in HCl[18]).

Vanadium(V), on the other hand, shows considerably stronger chloride complexation, as judged by its anion-exchange and extraction behavior. It was found to be sorbed as a brown band on an anion-exchange column[12], with $D = 100$ at 9 *M* HCl and $D = 400$ at 12 *M* HCl. It is, however, readily reduced on the column, because of the high affinity of chlorine, and the low affinity of V^{IV} for the resin, and may be eluted with 9 *M* HCl[14]. In alcoholic HCl too V^V shows[98] higher *D* than V^{IV}, increasing with chain length of the alcohol and with its branching, but independent of the acidity. Tributyl phosphate was found to extract V^V, *D* depending on the second power of the concentration of TBP in chloroform (in the range 30–100% TBP), and it was suggested that the extracted species is $VOCl_3 \cdot 2\,TBP$ (with no conclusive evidence)[99].

Niobium and tantalum are highly hydrolyzed in HCl solutions, much more so even than Zr^{IV}, and the species interconvert slowly. It is questionable whether any mononuclear cations are formed and the evidence concerning anionic complexes is not at all conclusive. These elements have been studied rather extensively, especially Nb^V, in connection with the separation of fission products, but there is little agreement among various authors on the details of their behavior. There is, however, some agreement on the general features of extraction with diverse reagents (TBP[64], ethers and ketones[64,100,101], amine hydrochlorides[20,72,78,102–104] or of anion exchange[15,67,105,106]). There are a decrease in D at increasing HCl concentrations up to 3–4 M, a minimum in D at 3–5 M HCl, a steep increase in D above 5 M up to 9 M HCl, and in some cases a maximum in D, and in all cases a slower increase, above 10 M HCl. At acidities below *ca.* 4 M irreproducible depolymerization reactions probably occur, and it is difficult to interpret the observed results. The decrease of D for anion exchangers or for amine hydrochlorides is possibly due to a decrease of the charge of the polymeric oxyanions of Nb^V and Ta^V, as the hydrogen-ion concentration increases. At high HCl concentrations, the extraction of HCl by the various solvents and the invasion of exchangers makes direct comparison difficult. In the range 5–7 M HCl, however, many reagents show for Nb^V a uniform fifth-power dependence of D on a. The significance of this observation is difficult to judge, because both the removal of hydroxide groups and the addition of chloride ions are involved in the extraction with oxygenated solvents, in addition to the co-extraction of hydrogen ions accompanying the Nb^V complex. At a higher acidity range (7–11 M HCl), Omori and Suzuki[104] concluded from an extraction study with tribenzylammonium chloride in chloroform that the main aqueous species is $[Nb(OH_2)Cl_4]^-$, in agreement with spectrophotometric results[107], while the main organic species is $R_2Nb(OH)_2Cl_5$. The same organic species was also proposed by Ellenburg[97]. With most reagents, Nb^V is extracted beter than Ta^V, and in general the curves for Ta^V parallel those for Nb^V. Unexpectedly, Ta^V was found to extract much better than Nb^V in some cases (*e.g.* with quaternary-ammonium chlorides)[20].

Protactinium(V), the heaviest member of the Va group, is expected to undergo less hydrolysis than the other members. Still, even in 6 M HCl, Pa^V is metastable, forming at a certain time after the preparation of the solution some inextractable, polymeric species, along with a part that remains in dynamic equilibrium among various species[108]. It is therefore necessary to assure oneself that the Pa^V one works with is indeed in dynamic equilibrium. Much of the older work was not controlled in this manner, and this led to irreproducible results. The work carried out on Pa^V in HCl solutions includes studies on the anion exchange[15,105,106,108–111] and the extraction with oxygenated solvents (ketones and carbinols[103,112–114], ether[115], neutral phosphorus esters[64,116–118], amine hydrochlorides[101,102,119], etc.). The most definitive studies, which attempted to derive the species predominant in the aqueous-, the resin- and various organic phases, are due to Casey and Maddock[101] and to Schärf and Herrman[120].

Protactinium, at tracer level, extracted from HCl into oxygenated solvents with $\varepsilon > 10$, was found[101] to be dissociated to $(HS_x{}^+)_p\ PaX_{5+p}{}^{p-}$, where $X = Cl^-$, OH^- or $\frac{1}{2}\,O^{2-}$. This result was obtained from the metal-concentration dependence and the perchloric-acid effect. Electromigration experiments[118] show the Pa^V to be largely cationic below 3 M HCl and largely anionic above 6 M HCl. Anion-exchange sorption starts above about 6 M HCl, although extraction is efficient already in the range 3–5 M HCl.This is taken[101] as evidence for the sorption of doubly-negatively charged species (*e.g.* $PaCl_7^{2-}$) on the anion exchangers, and the extraction of singly-charged species (*e.g.* $PaCl_6^-$). Other views on the species sorbed on anion exchangers have been advanced, in particular that a singly-charged anion[109] (*e.g.* $[Pa(OH)_2Cl_4]^-$) is sorbed[98]. Neutral species exist in the range 3–6 M HCl, as confirmed by electrical migration[118]. Anhydrous $PaCl_5$ is soluble in carbon tetrachloride, but this reagent cannot extract Pa^V from aqueous solutions, even at HCl concentrations where neutral species predominate. These may then be the hydrated pentachloride (*e.g.* $Pa(H_2O)_2Cl_5$)[109] or hydrolyzed species (*e.g.* $Pa(OH)Cl_4$)[101]. The dependence of D on amine-hydrochloride concentration was found[101] to be 1.6 power at low amine concentrations, decreasing to zero and negative powers as the amine concentration increases. Little may be learned from these observations concerning the species extracted. Various oxygenated extractants show a 3.5-power dependence of D on a, and about 1.5-power dependence on hydrogen-ion concentration at constant chloride concentration. Other solvents give different slopes (ketones higher, TBP lower). The differences in slope at the same HCl concentrations are difficult to explain, and require the extraction of different species. Over the range $10^{-14} < c_{Pa} < 10^{-5}$ M, $(\partial \log D/\partial \log c_{Pa})_a = 0$, so that the species in both phases are most probably mononuclear[120] (except the non-extractable portion)[108]. The species extracted into 2,6-dimethylheptanol-4 were found to be undissociated, and to contain two solvent molecules per Pa^V extracted, and may contain hydroxyl- or oxide anions (*e.g.* $HPa(OH)_2Cl_4$)[120]. The uncertainty of the species in the organic phase, however[101,120], precludes a definite statement concerning the species in the aqueous HCl phase. Two proposed schemes are shown in Table 4, showing disagreement in many respects.

TABLE 4

SPECIES OF Pa^V IN AQUEOUS HCl SOLUTIONS

HCl	*Predominant species*		*Minor species*	
(M)	*Ref. 101*	*Ref. 120*	*Ref. 101*	*Ref. 120*
<2		$[Pa(OH)_3]^{2+}$		
3–4	$[Pa(OH)Cl_3]^+$	$[Pa(OH)_3]^{2+}$	$Pa(OH)_2Cl_3$, $[Pa(OH)_2Cl_4]^-$	$Pa(OH)_3Cl_n^{2-n}$
5–6	$[Pa(OH)_2Cl_4]^-$	$[Pa(OH)_2Cl_5]^{2-}$	$[Pa(OH)Cl_5]^-$, $[PaCl_6]^-$	$[Pa(OH)Cl_6]^{2-}$, $[Pa(OH)_2Cl_n]^{3-n}$
7–8	$[PaCl_6]^-$	$[PaCl_6]^-$		$[PaCl_7]^{2-}$
>9	$[PaCl_7]^{2-}$	$[PaCl_7]^{2-}$		
DIBC	(H^+) $[Pa(OH)Cl_5]^-$	$HPa(OH)_{2n}Cl_{6-2n}$	(H^+) $[PaCl_6]^-$	

(v) Group IIIa

As a tervalent ion, gallium(III) is sorbed strongly on a cation exchanger from dilute hydrochloric acid, and since it is not complexed appreciably by chloride ions up to a few molar chloride, D is indeed inversely proportional to the cube of the hydrogen-ion concentration in HCl $< 3\ M$. Gallium(III) however, is similar to iron(III) in the dramatic increase of D at chloride concentrations above 3–4 M, both in hydrochloric acid[121–123] and in lithium-[122] or sodium-chloride[121] solutions. Although at these high concentrations gallium(III) is certainly in the form of $GaCl_4^-$, it shows $D = 10^5$ at 12 M LiCl on Dowex-50X12. No good explanation of this high sorbability of negatively-charged species on the cation exchanger has as yet been offered.

It is conceivable that as, *e.g.* hydrochloric acid invades the cation exchanger at high concentrations, $GaCl_4^-$ ions can replace chloride ions in the inner solution of the resin-phase forming ion-pairs with the hydrogen ions. Such ion-pairs are the form in which gallium(III) is found in extracts with oxygenated organic solvents. Swift[124] found good extractability of gallium(III) from concentrated hydrochloric acid with diethyl ether, D increasing with increasing gallium(III) concentrations. He did not, however, investigate very low concentrations, the range 10^{-12} to $10^{-3}\ M$ gallium(III), in which Grahame and Seaborg[125] found D to remain independent of the gallium(III) concentration. The extraction into diisopropyl ether was studied by Nachtrieb and Fryxell[126], who confirmed the dependence of D on the gallium(III) concentration above $10^{-3}\ M$. The organic phase had the composition $H_{1.0}GaCl_{4.0}$ after correction for the hydrochloric acid extracted by the ether in the absence of gallium, and provided that the hydrochloric acid concentration was below 6 M. Above that concentration the gallium carries along with it more hydrochloric acid than corresponds to the species $HGaCl_4$, and eventually, above 8 M HCl, two organic phases of variable concentrations are formed. Two such phases are also formed when ammonium tetrachlorogallate(III) is dissolved in ether[127]. The species extracted from concentrated hydrochloric acid into diethyl- and diisopropyl ethers (and also that in the aqueous phase) has been definitely shown, by Raman-spectroscopic studies, to be tetrahedral $GaCl_4^-$, ion-paired to solvated hydrogen ions[128, 129]. From lithium chloride solutions the distribution coefficients are lower, but the species of gallium(III) is the same[128]. However, when an inextractable chloride is present (*e.g.* sodium chloride) or when the ratio of total chloride to gallium in the system is less than four (as for extraction from chloride-containing perchlorate solutions), the species $GaCl_3 \cdot H_2O$, which is also tetrahedral, becomes important. When gallium(III) chloride is dissolved in diisopropyl ether, $GaCl_3 \cdot (i\text{-}C_3H_7)_2O$ is the main species[128].

The dependence of D on c_M has been shown to be a function of the dielectric constant of the solvent[130]. For solvents of low dielectric constant there is association of the H^+(solvated) and $GaCl_4^-$ as c_M decreases again causing D to increase[130, 131]. The dependence of D on the hydrochloric acid concentration[130] suggests that $GaCl_2^+$ and $GaCl_3$ have a very narrow existence range in the aqueous phase, since the curve rises very steeply. The fraction α_4 of $GaCl_4^-$ has been calculated, and was found to reach essentially unity at 8 M HCl, the results from nitrobenzene- and bis(β-chloroethyl)-ether extraction agreeing well. A single

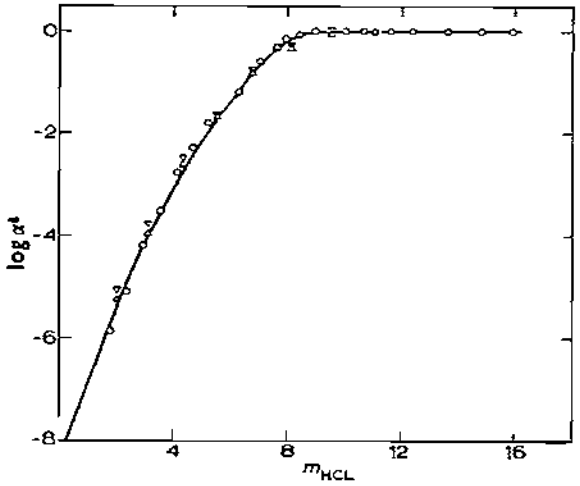

Fig. 1. Fraction of gallium(III) as $GaCl_4^-$ in hydrochloric acid solutions. (○) anion exchange[132]; (△) bis(β-chloroethyl) ether[130]; (▽) nitrobenzene extraction[130]; (——) calculated with $\log \beta_4^* = -6.50$.

parameter, $\log \beta_4^* = -6.50$ accounts for these extraction results, assuming that only Ga^{3+} and $GaCl_4^-$ exist in the aqueous phase (Fig. 1).

The anion-exchange behavior of gallium(III) has been studied by Kraus and his coworkers[12, 17, 132–134] and others[121]. For hydrochloric acid, D increases steeply from negligible values near 1 M to a maximum of $\log D = 5.3$ at 7 M HCl, then decreases somewhat to $\log D = 4.5$ at 12 M HCl[12, 134]. Considerable sorption of gallium(III) occurs from sodium chloride solutions[121], and from conc. lithium chloride solutions, D is even higher[17]. The linear variation of $\log D$ with m_{HCl} above *ca.* 8 M HCl was ascribed to changes in the activity-coefficient quotient G, and it was assumed that this behavior can also be extrapolated to lower concentrations. Deviations from this extrapolated line were ascribed to incomplete formation in the aqueous phase of the species $GaCl_4^-$ as the hydrochloric acid becomes diluted. Thus the fraction α_4 can be calculated from the anion-exchange data according to[132, 133]

$$\begin{aligned}\log \alpha_4 &= \log D + \log (m_{Cl}/\overline{m}_{Cl}) - \log K/G \\ &= \log D + \log (m_{Cl}/\overline{m}_{Cl}) - (A + B m_{Cl})\end{aligned} \tag{8}$$

where $A = \log K/G$ at 8 M HCl and $B = 0.1$, as found empirically, and A is normalized so as to yield $\alpha_4 = 1$ at $m_{HCl} \geq 8\ M$. The values of α_4 so obtained agree very well with the values obtained by similar considerations from the extraction data discussed above, and the single parameter, $\log \beta_4^* = -6.50$, together with the empirical relationship found for K/G, describe the anion-exchange distribution curve (Fig. 1). A large negative enthalpy was found for the ion-exchange equilibrium $\underline{GaCl_4^-} + \overline{Cl^-} \rightleftarrows \overline{GaCl_4^-} + Cl^-$ from measurements at several temperatures between 25° and 150°, suggesting a chemical reaction rather than simple exchange: this is in line with the very high distribution coefficients[133]. The fraction α_4 increases rapidly with increasing temperature, but the single-step transition from Ga^{3+} to $GaCl_4^-$ observed at 25° seems not to persist at higher temperatures, the more gradual increase of D with m_{HCl} pointing to a possible existence of the species $GaCl^{2+}$, $GaCl_2^+$ or $GaCl_3$ over a certain concentration range at the higher temperatures.

Long-chain ammonium chlorides are very effective for extraction of gallium(III), the distribution curves being similar to those obtained for anion-exchange resins. The secondary amine Amberlite LA-1, 10% in xylene, shows appreciable extraction above 2 *M* HCl[135], while 5% TIOA in the same solvent[10] extracts at even lower concentrations. At low hydrochloric acid concentrations D increases in the order primary < secondary < tertiary < quaternary-ammonium extractants[136], but at higher concentrations only the primary extractants show much lower D values than the others. The distribution coefficient decreases somewhat above 8 *M* HCl, but it does not show a decrease in lithium chloride solutions at high concentrations. In loading experiments with tri-n-octyl- and tri-iso-octyl-ammonium chlorides and with methyltricaprylammonium chloride, 0.1 *M* in toluene, the limiting ratio of one mole extractant per one mole gallium(III) was found. Thus the species in the organic phase is most likely[136] $\overline{(R_3NH)^+GaCl_4^-}$ or $\overline{R_4N^+GaCl_4^-}$. However, the dependence of D on extractant concentration (R_4NCl, R = heptyl) shows non-integral slopes in the log–log plot (1.6 to 1.9 over two orders of magnitude)[137], which are incompatible with the conventional interpretation of these plots in terms of the composition of the extracted species. Extraction with trilaurylammonium chloride shows a slope of two at low, and of one at high amine concentrations. No conclusions can be drawn from this concentration dependence. The overall extraction reaction was found from measurements at 5–40° to have a large positive enthalpy. Since, however, the complex formation in the aqueous phase has an even larger enthalpy change, the exchange step $GaCl_4^- + \overline{R_3NHCl} \leftrightarrows \overline{R_3NHGaCl_4} + Cl^-$ has a negative enthalpy change.

Indium(III) forms relatively-stable chloride complexes even in dilute solutions. Thus, it is possible to study the formation of the species $InCl^{2+}$, $InCl_2^+$ and even $InCl_3$ at ionic strengths of one or less, using the cation-exchange method. Shufle and Eiland[138] applied this method in a 1 *M* sodium perchlorate ionic medium, with a sodium-form cation exchanger at pH 3.8. Although they realized that hydrolysis of the In^{3+} cation is an important complication, and that their constants should be modified by a certain factor to take this into account, they underestimated this factor considerably. Sundèn[139] tried to correct this by working at a lower pH (~2.5), at the same ionic strength. He, however, encountered the complication that the distribution coefficients, instead of decreasing continuously as the ligand concentration increased, tended to level off. It was, therefore, possible to calculate only the first stability constant. Sundèn ascribed the difficulty to the presence of small amounts of strongly-coordinating groups in the resin. Sorption of $InCl^{2+}$ on the resin can lead to the same result. The most definitive work in this area is that of Carleson and Irving[140], who used an ionic medium of 0.69 *M* $HClO_4$, thus completely obviating the hydrolysis problem. They used Fronaeus' method, and with up to 0.43 *M* chloride, substituted for perchlorate, obtained the following values for the stability constants: $\log \beta_1 = 2.35$, $\log \beta_2 = 3.63$ and $\log \beta_3 = 3.9$. The values of the exchange constants of In^{3+}, $InCl^{2+}$ and $InCl_2{}^+$ with sodium ions on the resin, recalculated from the data, are reasonable, there being a decrease by a factor of about ten per unity decrease in the charge of the species. The validity of the constants found by Carleson and Irving[140] may still suffer from the fact that the medium was permitted to vary considerably, more than 60% of the perchlorate ions being exchanged for chloride ions at the limit, so that activity coefficients would have changed considerably. This mainly affects β_3, the value of which is therefore open to revision. Busev and Kanaev[141] confirmed the constants found by Carleson and Irving, applying a modified calculation method to the data of these authors, and to their own data, obtained with a different resin.

Indium(III) shares with gallium(III) and a few other metal cations the property of showing a minimum in the distribution curve on cation exchangers, though to a much smaller extent. Although some workers did not find any increase in *D* at high hydrochloric-acid[122, 123] or lithium-chloride[122, 142] concentrations (whereas a pronounced effect was observed in bromide and iodide solutions[142]), Tsintsevich and coworkers[143] found a minimum in *D* at 3 *M* HCl, with some increase at higher concentrations, using the Russian resin KU-2.

A liquid cation exchanger has been used by Sundèn[144]: α-oxynaphtoic acid, 0.2 *M* in diisopropyl ether, to extract indium from a 1 *M* sodium perchlorate ionic medium, with up to 0.12 *M* chloride substitution at pH 2.7–3.0. Assuming that only the species $In(\alpha\text{-oxynaphtoate})_3$ occurs in the organic solvent, he obtained $\log \beta_1 = 2.20$ and $\log \beta_2 = 3.56$, in good agreement with his resinous-cation-exchange results[139]. With dinonylnaphthalenesulfonic acid, White, Kelly and Li[145] determined only the stability of the first complex finding a somewhat higher value than the other workers. No account was taken of the aggregated nature of the liquid cation exchanger by these workers.

The extraction of indium(III) with solvating solvents was studied more extensively. Although diethyl ether is a poor extractant[146, 147], other solvents permit appreciable extraction of indium. Irving and Rossotti[146, 148] were the first authors to give a comprehensive treatment of the extraction of indium(III) from chloride solutions, and later Diamond[151, 152] and others[128, 131, 148, 153, 154] contributed to our knowledge on this system. Irving and Rossotti found by analysis that $HInCl_4$ is the predominant species extracted from hydrochloric acid into methyl isobutyl ketone[148]. The tetrahedral grouping of $InCl_4{}^-$ has been established in diethyl-ether extracts by Raman spectroscopy[129], although, of course, no information on ion-pairing with solvated hydrogen ions or aggregation to larger, loosely-bound species, could be obtained. Irving and Rossotti[148] predicted a maximal initial slope of +5 for the log D *vs.* log c_{HCl} curve, provided that "ideal" behavior is exhibited *i.e.* that no miscibility changes occur as c_{HCl} increases, and that concentrations can replace activities in the mass-action law expression. In some cases where appreciable extraction occurs only from relatively concentrated ($>4\ M$) hydrochloric acid, slopes d log D/d log $c_{HCl} > 5$ have been observed, showing that with these solvents (diethyl-, diisopropyl- and bis(β-chloroetyl) ethers, isopentanol and isopentyl acetate) "non-ideal" behavior occurs. With other solvents (*e.g.* furfuraldehyde and methyl propyl-, methyl isopropyl- and methyl isobutyl ketones), which extract from more dilute hydrochloric acid solutions, slopes in line with known degrees of formation $\bar{n}$ of indium(III)–chloride complexes in the aqueous phase were obtained according to the equation

$$\log D = \text{const.} + (5 - \bar{n}) \log c_{HCl} \tag{9}$$

valid if associated $HInCl_4$ is the organic species. Diamond[150,151] pointed out that this behavior is expected only with solvents of such a dielectric constant that neither aggregation to ion-multiplets, nor dissociation of the ion-pairs, occur. With the solvent bis(β-chloroethyl) ether, where miscibility is minimal even at high hydrochloric acid concentrations, and where the organic species is the dissociated ion pair H^+ and $InCl_4^-$ (due to the high dielectric constant), the distribution data of Mendez[152] and Dietz[128] yielded values of $\log K_3 = -0.4$ and $\log K_4 = -1.2$, for the formation of $InCl_3$ and $InCl_4^-$ from their precursors.

In a study of the extraction of indium(III) tracer from solutions of hydrochloric acid with another mineral acid at constant acidity, Diamond[150] showed that d log D/d log c_{Cl} is a complicated function, depending on: a) the increase of $\bar{n}$ in the aqueous phase; b) the variation of $\bar{c}_{H^+}$ in high-dielectric-constant solvents, due to varying dissociation of hydrochloric and the other mineral acid, causing a common-ion effect; c) on mixed aggregate formation (*e.g.* $H^+ClO_4^-H^+InCl_4^-$) in preference to species such as $H^+Cl^-H^+InCl_4^-$ in low-dielectric-constant solvents; and d) the different salting power of the various acids, *e.g.* through their effect on water activities in the aqueous phase. Thus the actual behavior found depends on the nature of the solvent and on the nature of the mineral acid added. If, on the other hand, the chloride ion concentration is kept constant, and the hydrochloric acid is mixed with an alkali-metal or tetraalkylammonium chloride. Diamond[151] found other factors to affect the distribution curve. The slope d log D/d log c_{H^+} now depends on: a) the much higher extractability of hydrochloric acid compared to the chloride salt, leading to a variation of the common-ion effect and to "consumption" of the solvent; b) the basicity and steric availability of the donor atom in the solvent; c) the increasing extractivity into high-dielectric-constant solvents of ion-pairs $C^+InCl_4^-$ with increasing size of the cation C^+; and d) the salting ability and ligand activity provided by salts, compared with the acid.

For both studies, slopes were found to be positive, negative or of changing sign, depending on which factor predominates.

The dependence of the distribution coefficient on total indium(III) concentration has been studied by Poskanzer, Mendez and others[128,131,152], and effects similar to those discussed in the case of gallium(III) extraction were observed. The extraction of macro quantities of indium has received only little attention. Extraction from 0.85–4 *M* $InCl_3$, containing hydrochloric acid at high concentration, into diethyl ether has been described by Woodward and Taylor[129], who did not give data on the concentrations obtained in the equilibrium organic phase. Knox and Spinks[155] reported the extraction from concentrated indium(III) chloride in 6 *M* HCl into a variety of organic solvents.

The anion-exchange behavior of indium(III) in chloride solutions has been reported first by Sundèn[139], Kraus[12] and Jentzsch[157], who noted moderate absorbability only. Subsequently more data have been reported[156,143], which were summarized in a detailed study which also included the effects of varying crosslinking and secondary cations[158–160]. It has been demonstrated that differences in crosslinking and secondary cation effects can be taken into account by the use of parameters and functions obtained independently of the indium(III) distribution measurements, and that all the anion-exchange data (including those of Chu[156], obtained with a similar resin) can be described by the expression

$$\log D = \log K_{x=8} + \Delta + p \log \bar{a} - \log \sum_{-3}^{1} \beta_i'^{*} a^i \qquad (10)$$

In this expression $\log K_{x=8} = 1.00$ is the constant for the 8% crosslinked resin, Δ is a normalizing factor for other crosslinkings, $p = 1$, for $InCl_4^-$ being the resin species, as found from loading experiments, and $\log \beta_{-2}'^{*} = -0.50$, $\log \beta_{-1}'^{*} = -0.45$ and $\log \beta_1'^{*} = -1.6$, being the values for the formation constants of $InCl^{2+}$, $InCl_2^+$ and $InCl_4^-$ from $InCl_3$, in sodium- or lithium-chloride solutions. The low value of *K* for indium(III), compared with tervalent gold, iron or gallium, is probably due to the tendency of indium to form octahedral, hydrated species, $InCl_4(H_2O)_2^-$, which interact strongly with water, and prefer the (aqueous) phase with the higher water activity.

The sorption of trace indium(III) on anion exchangers with different crosslinkings from 0.5 or 1.0 *M* lithium chloride in absolute methanol or ethanol was studied by Maydan[160]. While in aqueous solutions *D* is somewhat dependent on crosslinking, it is hardly at all dependent in the organic solvents, and is about the same at the two salt concentrations. Compared with $D = 4$ to $D = 16$ in the aqueous solutions, $D = 600$ in methanol and $D = 2500$ in ethanol. The direction of variation of *D* with solvent and the decreasing sensitivity to crosslinking are in line with the changes in dielectric constant in both phases as the solvent is varied.

The extraction of indium(III) with long-chain amines has received a considerable amount of attention. Nakagawa[135] observed moderate extractability of indium(III) from hydrochloric acid solutions with the secondary amine Amberlite LA-1, 10% in xylene. The distribution curve has a maximum at 6.7 *M* HCl. The extraction from dilute hydrochloric acid solutions has been studied by White, Kelly and Li[145]. They found log D to depend linearly on log c_{HCl} (in the range 0.3–1.3 *M* HCl), with a slope of 1.35. They compared their data with values calculated on the premise that $InCl^{2+}$ and $InCl_2{}^+$ are present in the solution (disregarding $InCl_3$ which should be predominant, considering the magnitude of the constants they use), and stated that they agree, although the latter values show a slope of 1.0. Thus the results do not substantiate the supposed presence of $InCl^{2+}$. At the same chloride concentrations D for HCl–NaCl mixtures was found to be lower than for pure HCl solutions. At a constant hydrochloric acid concentration of 1.3 *M*, log D was shown to depend linearly on log $\bar{c}_{R_3NHCl}$ (R = n-octyl; diluent, benzene) in the range 0.06–0.11 *M* (with only four experimental points), with a slope of 1.87. The authors concluded from this that the species in the organic phase is $(R_3NH)_2InCl_5$. Subsequent studies were not in complete agreement with this. The curve of log D vs. log $\bar{c}_{R_3NHCl}$ was found to curve upwards at high amine hydrochloride concentrations for extraction from 0.1–4.0 *M* NaCl[160], 0.075–1.86 *M* HCl[159] and 3.66 *M* LiCl[137], being straight (with a slope near two) only at or above 3 *M* HCl[159]. As the triisooctylammonium chloride concentration in xylene decreases and approaches 0.02 *M*, the slope tends to one, while as the concentration approached 0.3 *M* the slope tends to three[159], or at least to some value between 2.4 and 3.1. There are certainly systematic deviations at both ends when it is attempted to fit the data to a straight line of slope two. There is not, however, complete agreement on the slope (not to say on its interpretation), even for a given amine type and solvent. Thus Good and Holland[136] find a slope of 0.89 for 0.005–0.25 *M* tricaprylmonomethyl(quaternary)ammonium chloride, and 1.9 for the same range of tri-n-hexyl(tertiary)ammonium chloride, both in toluene, extracting indium(III) tracer from 1 *M* HCl with no indication of upward curvature. For nitrobenzene diluent, slopes of 0.79 are obtained[161] for extraction with 10^{-5}–0.1 *M* tri-n-octyl(tertiary)ammonium chloride from 1 or 4 *M* HCl. The low value is explainable in terms of dissociation in the high-dielectric-constant solvent. A further complication is the disagreement of loading data, not only with the slopes, but also among the various authors. For 0.1 *M* solutions in toluene, extraction isotherms[136] show a loading of one indium(III) ion per one quaternary-ammonium ion, but per two tertiary-ammonium ions (for extraction from 6 *M* HCl or LiCl), while for 0.01 or 0.1 *M* solutions in nitrobenzene, isotherms[161] show a loading of one indium(III) ion per three tertiary-ammonium ions (for extraction from 8 *M* HCl).

Infrared-absorption data[162] indicate that whatever the limiting loading or the slope, the indium(III) species is tetrahedral $InCl_4{}^-$, ion-paired with a long-chain ammonium cation, and associated further with long-chain ammonium chloride ion-pairs in certain cases. These association reactions in the organic phase

$$\overline{(R_3R'N)^+InCl_4^-} + n\,\overline{(R_3R'N)^+Cl^-} \rightleftarrows \overline{(R_3R'N)^+InCl_4\cdot\bar{n}(R_3R'N)Cl} \quad (11)$$

with $R' = H$ or CH_3 and $n = 1$ or 2 have still to be correlated with the nature of the diluent, the group R′, and the concentration. The equilibrium constant for this reaction was found[159] to be 120 ± 20 for $n = 2$ in xylene diluent and triisooctylammonium chloride extractant. The failure of increasing c_{In} in loading experiments to shift the equilibrium to the left, as free $R_3NH^+Cl^-$ is consumed, is attributed[160] to the generally-low tendency of indium(III) to form the tetrahedral species, as has already been pointed out earlier[159].

Focusing the attention back to the aqueous phase, it was found[159] that at a definite amine hydrochloride concentration (thus without regard to uncertainties as to the nature of the organic species) the extraction data agree very well with the anion-exchange data for sodium-chloride and hydrochloric-acid solutions, confirming the presence of $InCl^{2+}$, $InCl_2^+$, $InCl_3$ and $InCl_4^-$ (all probably hydrated to octahedral coordination) in the concentration range studied (0.1–5 *M*). The constants $\log K_3 = 0.45$ and $\log K_4 = -1.6$ are in fair agreement with those calculated from extraction data using oxygenated solvents.

The ion-exchange and solvent-extraction properties of thallium(I), as well as those of thallium(III), received relatively little attention. The former ion is known to be absorbed on cation exchangers with a relatively high affinity, but no information is available on the decrease in absorbability with chloride ion concentration, due to complex formation. Thallium(I) is also not known to be extractable by oxygenated solvents, coordinating either to the metal ion, or to hydrogen ions extracting anionic chlorothallium(I) species. That such species do form seems to be established by other kinds of evidence, such as solubility or potentiometric data. Anion-exchange experiments under controlled conditions, such as a nitrogen atmosphere or the presence of sulfur dioxide as a holding reductant, showed that tracer thallium(I) is not sorbed on anion exchangers[163]. This confirms the observations of Nelson, Rush and Kraus[134], that thallium(I) at the millimolar concentration level is not sorbed on an anion exchanger from 0.1 to 12 *M* HCl. Air oxidation was found[163] to convert thallium(I) tracer to an absorbable species presumably of thallium(III), which is strongly sorbed on the exchanger. The presence of a reductant (sulfur dioxide in 1 *M* HCl, but apparently not iron(II) or titanium(III)) brings about easy elution[163]. These findings contradict those of Horne[164], who found *D* values exceeding 1000, with a maximum near 2 *M* HCl in uncontrolled experiments. Horne himself, however, claimed his results to be upper limits for *D* only, and it is now apparent that oxidation has made his results for thallium(I) completely useless, and the constants calculated from them not valid.

In conclusion, there seems to be no reliable information obtained from ion-exchange and solvent-extraction data concerning chloride-complex formation of thallium(I).

Thallium(III) is sorbed on a cation exchanger (4% crosslinked) from 1 *M* $HClO_4$ with $D = 10$, while from 1 *M* HCl *D* is much lower (about 1.2)[123]. From very dilute hydrochloric acid appreciable sorption on a cation exchanger occurs, but it decreases as the hydrochloric acid concentration is raised above *ca.* 0.001 M[164]. This reflects the strong complex formation, which leads to $TlCl_3$ and $TlCl_4^-$ even at very low chloride concentrations. Thallium(III) shows an increase in D at high chloride concentrations, similar to the behavior of iron(III), gallium(III) and gold(III), only to a much smaller extent. With a 12% crosslinked resin, $D = 3$ at 12 M HCl[124], whereas it is 10 at this concentration for a 4% crosslinked resin[123]. For 8 M LiCl $D = 42$, on a 12% crosslinked resin, following the trend of the other ions mentioned.

The extractability of thallium(III) from hydrochloric acid solutions by ether has been known for a long time, and has been made use of in separation schemes by Noyes, Bray and Spear[165]. Irving[147] showed that 90–95% of the thallium(III) present at 6 M HCl is extracted by an equal volume of ether. Harbottle and Dodson[166] analyzed the yellow solution resulting when thallium(III) is extracted into ether from about 6 M HCl ($d = 1.12$), and found a composition $H_{1.0}TlCl_{4.0}$, with maximal deviations of the indices of ±0.05. A more detailed study has been published by Horrocks and Voigt[167], who studied the extraction of tracer thallium(III) into diisopropyl ether from (H,Li)(Cl,ClO$_4$) solutions. They confirmed the species $HTlCl_4$ in the organic phase (within a wider margin of error), and noted the formation of a second organic phase above 5 M ionic strength though independently of the presence or absence of thallium(III), at the millimolar level. The thallium concentrates (90–96%) in the heavier of the two ether phases. The distribution results at ionic strengths of 2 and of 3 conform nicely to the expression

$$\log D = \log K_{Tl} + \log c_{H^+} + 4 \log c_{Cl^-} - \log \sum_{n=0}^{5} \beta_n^{(*)} c_{Cl^-}{}^{n} \tag{12}$$

provided the parameters K_{Tl} and $\beta_n^{(*)}$ are assumed to be constant, at the constant ionic strengths of 2 or 3 M. The parameter K_{Tl} includes the thermodynamic constant for the equilibrium $H^+ + TlCl_4^- \leftrightarrows \overline{HTlCl_4}$, the thermodynamic formation constant of $TlCl_4^-$, the inverse of the activity coefficient of $HTlCl_4$ in the organic phase, and the second power of the mean ionic-activity coefficient of hydrochloric acid (assumed constant at the constant ionic strength). The parameters $\beta_n^{(*)}$ include the thermodynamic overall formation constants of the species $TlCl_n^{(3-n)+}$, and the inverse of the activity coefficient of this species and the $(n-3)$ power of the activity coefficient of chloride ions (again assumed constant at the constant ionic strength). The terms with $n = 0$, $n = 1$ and $n = 2$ are negligible and can be ignored, the terms with $n = 3$ and $n = 4$ can use Benoit's constants[168], provided certain assumptions are made concerning the activity coefficients ($\log K_3 \simeq \log K_4 \simeq 2.2$), and with the same assumptions $\log K_5 = -0.53$ results. This constant pertains to the formation of $TlCl_5^{2-}$ in the aqueous phase and not to $HTlCl_4$, since the last term in eq. (12) is explicit in the chloride ion concentration, and not in that of hydrochloric acid.

There exists some controversy concerning the formation of species $TlCl_n^{(3-n)+}$ with $n > 4$ in aqueous chloride solutions. The concensus of recent opinion is that such species are not important below 0.1 *M* chloride[169]. This does not exclude the possibility of their formation at higher concentrations, and the magnitude of the constant proposed by Horrocks and Voigt[167] has $TlCl_5^{2-}$ exceeding 10% of the total thallium(III) only above 0.4 *M* chloride, which is not in contradiction with the known facts. Assuming that $TlCl_3$ is the species extracted into diisopropyl ether from (neutral) sodium chloride solutions, Nord and Ulstrup[169] obtain $\log K_3 = 3.02$ and $\log K_4 = 1.22$ for the thermodynamic constants in aqueous sodium chloride up to 0.1 *M*.

The extraction of thallium(III) with TBP has been studied briefly[170]. The slope of the $\log D$ *vs.* $\log c_{HCl}$ curve has been found to be 2.7 in the range 2–5 *M* HCl for 5% TBP in benzene. This is rather surprising, since in this range it is expected that the extractable species $H^+TlCl_4^-$ is completely formed, and that extraction of hydrochloric acid, which binds part of the TBP to make it unavailable, should cause a decrease in D with increasing c_{HCl}. The data are rather few and incomplete and not too much weight should be put on this observation. The dependence of D on the TBP concentration in the range 2–20% for 1.6 and 6.3 *M* HCl is third power, a reasonable number if solvation of the hydrogen ion of the extracted ion-pair is assumed. With undiluted TBP a very shallow maximum in D is observed at 2–6 *M* HCl[7], which is in contradiction with the data quoted above, which show a steep increase in D in this range.

The anion-exchange sorption behavior of thallium(III) has been reported by Kraus, Nelson and Smith[12], who found $\log D$ to decrease from 5.2 at 2 *M* HCl to 2.8 at 11.5 *M* HCl at loadings of less than 1% in the presence of chlorine to prevent reduction. Later work[134,163,164] confirmed the results and shows that D decreases slightly as the hydrochloric acid concentration is decreased from 1.0 to 0.1 *M*. Perchloric acid exhibits its usual depressing action on D: in 1 *M* HCl, thallium(III) shows $\log D = 5.7$[164], addition of 0.001 *M* $HClO_4$ decreases D by a factor of 4, addition of 0.10 *M* $HClO_4$ by a factor of 80 and addition of 1.0 *M* $HClO_4$ by a factor of 500. Addition of 1.0 *M* HCl, on the other hand, decreases D only by a factor of 2.5. The dilute region has been explored by Horne[164], who has found a maximum in the distribution curve near 0.1 *M* HCl. The results conform to the expression

$$\log D = \log K_{Tl^{III}} + p \log \bar{a} - \log \sum_{i=-1}^{2} \beta_i'^{*} a^i \qquad (13)$$

with $\log K_{Tl^{III}} = 6.80$, $p = 1$ for $TlCl_4^-$ being the predominant resin species, and $\log \beta_{-1}'^{*} = -3.0$, $\log \beta_1'^{*} = 1.5$ and $\log \beta_2'^{*} = 1.2$ (equivalent to $\log K_3^{*} = 3.0$, $\log K_4^{*} = 1.5$ and $\log K_5^{*} = -0.3$). These constants are in agreement with those obtained by Nord[169] and Horrocks[167] but not with those calculated by Horne[164] from the data by apparently similar methods. The term involving K_5 may be interpreted either in terms of $TlCl_5^{2-}$ or in terms of $HTlCl_4$ (undissociated in the aqueous phase). There is no evidence supporting a supposition that $HTlCl_4$ is a weak acid, not dissociated at 1 M H^+, so that $TlCl_5^{2-}$ is preferred, in agreement with Horrocks and Voigt. A supposition of $TlCl_5^{2-}$ or $TlCl_6^{3-}$ as the predominant species in the resin with $p = 2$ or 3 in eq. (13) is, however, not completely excluded, since this leads to the presence of $TlCl_3 \ldots TlCl_6^{3-}$ or $TlCl_4^- \ldots HTlCl_6^{2-}$ (or $TlCl_7^{4-}$) in the range 3×10^{-4}–12 M HCl. The former of which is not completely excluded by the known stability constants. Thus without more definite information on the species sorbed on the anion exchanger there is some doubt concerning the interpretation of the data.

Little has been published concerning the extraction of thallium(III) with long-chain ammonium chloride solutions. The results obtained[10] for 10% Amberlite LA-1 (a secondary amine) and 5% triisooctylammonium chlorides in xylene pertain to an indefinite oxidation state of thallium, hence are worthless. The data for extraction with 0.1 M Hyamine 1622 (quaternary-ammonium chloride) in 1,2-dichloroethane from 0.1–10 M HCl show[72] a maximum at 5.0 M HCl for thallium(III), which is unexpected, compared with the anion-exchange data, or as discussed above, for extraction with TBP. Extraction from 0.11 M HCl or 2.25 M HCl–1.00 M $NaClO_4$ with 0.006–0.2% (?) trinonylammonium chloride in benzene shows[170] a first-power dependence of D on $\bar{c}_{R_3NHCl}$, as expected for the species $R_3NH^+TlCl_4^-$ predominating in the organic phase. Sodium perchlorate has been added in order to depress the extractability of the thallium, so as to bring it into convenient range for measurement. The effect of perchlorate here is similar to that observed with anion-exchange resins.

(vi) Group IVa

Germanium dioxide is soluble in hydrochloric acid, the solubility being most appreciable in the range 6–9 M. Germanium tetrachloride is strongly hydrolized below 6 M hydrochloric acid, and germanium dioxide slowly precipitates from the solutions. Germanium tetrachloride is volatile, on the other hand, and serious losses can occur from >9 M HCl. These facts must be taken into account in discussing the chemistry of Ge^{IV} in hydrochloric acid solutions.

The hydrolyzed species formed by germanium(IV) in dilute hydrochloric acid, *e.g.* $GeCl_i(OH)_j(H_2O)_k^{4-i-j}$, seem to be absorbable (reversibly?) on a cation exchanger to some extent[171]. The absorbability decreases rapidly as the hydrochloric acid concentration is increased[171] probably because i increases faster than j decreases, so that the net positive charge decreases. In any case absorbability of germanium(IV) from 9 M HCl on 4% crosslinked Dowex-50 is negligible[123].

Germanium(IV) is one of the few elements which can be extracted from aqueous chloride solutions by the so called "inert" solvents. The extractability of germanium(IV) by carbon tetrachloride has been suggested by Sandell[172] as an isolation method, and Newcombe *et al.*[173] reported distribution data for the extraction of germanium(IV), which however, could not be confirmed later[174, 175], possibly because of the loss of volatile germanium tetrachloride in the earlier work. The most comprehensive study of the species formed in the aqueous phase (consisting of mixtures of $(H^+, Li^+)(Cl^-, ClO_4^-)$ using extraction into carbon tetrachloride is that of Benoit and Clerc[176], while comparisons of the extraction into several solvents were published by Brink *et al.*[174] and by Siekierski and Olszer[178]. Most of the data[171, 174–177] are in good mutual agreement, and for 5–12 *M* HCl, solutions may be interpreted in terms of the following reactions:

$$GeO_2(aq)+4\,H^+ +4\,Cl^- \rightleftarrows GeCl_4(aq)+2\,H_2O;\; K \tag{14a}$$

$$GeO_2(aq) \rightleftarrows \overline{GeO_2}; \qquad p_1 \tag{14b}$$

$$GeCl_4(aq) \rightleftarrows \overline{GeCl_4}; \qquad p_2 \tag{14c}$$

According to this scheme, hydrated GeO_2 (possibly $Ge(OH)_4$) is the major species in hydrochloric acid below about 7 *M*, above which $GeCl_4$ becomes important. In the carbon-tetrachloride phase, GeO_2 is important only at very low hydrochloric acid solutions. From the solubilities of germanium dioxide in carbon tetrachloride ($3.3\times 10^{-7}\,m$)[176] and in dilute hydrochloric acid ($2\times 10^{-2}\,m$)[179], a value $\log p_1 = -4.8$ can be calculated. From the distribution data at high hydrochloric acid concentrations, a value $\log p_2 = 3.0$ is obtained. The distribution results, according to the reaction scheme (14a–c) should conform to the following expression

$$\log D = \log(p_1 + p_2 K a^8) - \log(1 + K a^8) \tag{15}$$

which they do, with $\log K = -16.4$, as seen in Fig. 2. The fourth-power dependence of the distribution coefficient on the hydrochloric acid activity (eight-power dependence on the mean ionic activity, a) has already been noted by Benoit and Clerc[176], who concluded that (14a) is the main reaction in hydrochloric acid solutions, although it probably does not occur in one step. A series of species $GeCl_i(OH)_j(H_2O)_k$ with i increasing from zero to four and j decreasing from four to zero is consistant with the data. From data in $H(Cl, ClO_4)$ and $(H, Li)Cl$ solutions Benoit and Clerc[176] concluded that in 9 *M* HCl, $i = 4.2$ and $j = 0.7$, but admitted that non-constancy of activity coefficients could cause some differences. Some migration of germanium(IV) to the anode in concentrated hydrochloric acid solutions has been observed, so that $[GeCl_4(OH)(H_2O)]^-$ is a possible species. The scatter of the distribution data at high hydrochloric acid concentrations admits the possibility that this, rather than $GeCl_4(aq)$ is the predominant species, but volatility and solubility data favor $GeCl_4(aq)$.

Analysis of the carbon tetrachloride solutions has shown[176] the species in this phase to be $GeCl_4$, and the ideal behavior of the solutions, and the independence of the distribution coefficient from variations in the germanium(IV) concentrations indicate the species to be monomeric and tetrahedral. Similar species seem

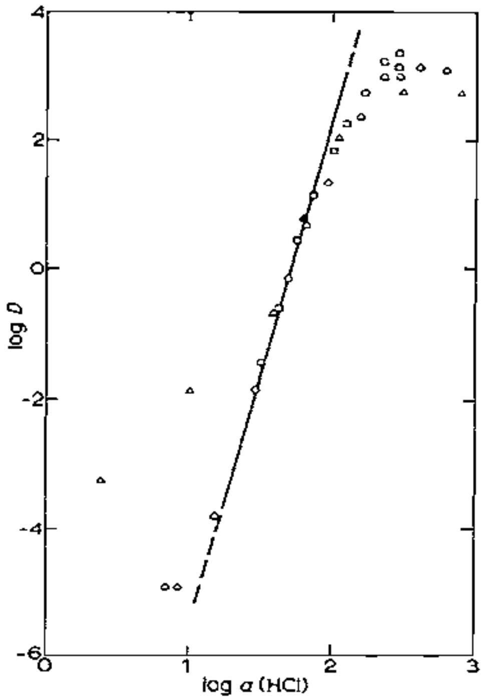

Fig. 2. Distribution data for germanium(IV). (○) from ref. 176, (□) from ref. 173, (△) from ref. 174, (●) ref. 178; (——) straight line with slope = 8.00.

to be extracted into the other "inert" solvents, since the distribution curves[180] are quite similar. With oxygenated solvents, however, such as β,β'-dichlorodiethyl ether or TBP, different curves are obtained, and this could be due to the extraction of other species, such as $[H(solvated)^+]_2GeCl_6$. Distribution coefficients are somewhat higher with the oxygenated solvents (for 6 *M* HCl, $D = 0.6$ for β,β'-dichlorodiethyl ether, 1.0 for diethyl ether[147] and 17 for TBP, compared with 0.05 for carbon tetrachloride or benzene).

The sorption of germanium(IV) tracer on an anion exchanger from hydrochloric acid solutions has been studied by Nelson and Kraus[180,181] and by Yoshino[182]. Germanium(IV) is absorbable not only from aqueous hydrochloric acid, but also from gas streams, into which $GeCl_4$ is swept from concentrated hydrochloric acid solutions[181]. For interpreting the anion-exchange data[180], it is again assumed that (14a) is the main reaction in the aqueous phase, while in the resin, $[Ge(OH)_4Cl_2]^{2-}$ and $GeCl_6{}^{2-}$ predominate at low (6–9 *M* HCl) and high (9–12 *M* HCl) hydrochloric acid concentrations, respectively, formed according to

$$GeO_2(aq) + \overline{2\,Cl^-} \rightleftarrows \overline{[Ge(OH)_4Cl_2]^{2-}}; \qquad p_1 \qquad (16a)$$

$$GeCl_4(aq) + \overline{2\,Cl^-} \rightleftarrows \overline{GeCl_6{}^{2-}}; \qquad p_2 \qquad (16b)$$

The former species conforms to the findings of Everest and Harrison[179], with macro germanium(IV) concentrations, that the ratio Cl : Ge in the resin (equilibrated with 6–9 *M* HCl solutions) is 2, and that there are about 0.5 moles germanium per equivalent at maximal loading. The latter species is consistent with the precipitation of Cs_2GeCl_6 from concentrated hydrochloric acid[177, 179]. Accordingly, the anion-exchange distribution should follow the expression

$$\log D = \log (p_1 + p_2 K a^8) + 2 \log \bar{a} - \log (1 + K a^8) \tag{17}$$

The agreement of the curve, calculated with the same value of K as used above, and with $\log p_1 = -2.3$ and $\log p_2 = -2.7$, with the data is good as shown in Fig. 2.

Very little information is available concerning the extraction of germanium(IV) with long-chain ammonium chlorides. Nakagawa[182] used Amberlite LA-1 and tribenzylamine in xylene solutions. His results are surprising since he found lower distribution coefficients for these extractant for 8–12 *M* HCl, than bas been found for benzene alone[174]. The general trend he observed is, however, reasonable; the distribution coefficients increasing from negligible values at hydrochloric acid concentrations below 6 *M* to a flat maximum near 10 *M* HCl.

Tin(II) has been accorded little attention from workers in the ion-exchange and solvent-extraction field. It is extractable from hydrochloric acid by diethyl ether (at 6 *M* HCl, $D \simeq 0.3$)[147], where it probably exists as the ion-pair $[H(\text{solvated})]^+SnCl_3^-$, the pyramidal $SnCl_3^-$ ion having been identified by Raman spectroscopy[183]. Diisoamyl phosphate, 20% in benzene, has also been used[153] to extract tin(II), the distrubiton coefficients falling from 10^4 to 10^{-2}, as the hydrochloric acid concentration is increased from zero to 10 *M*. It appears that the extractant acts as a liquid cation exchanger rather than as a neutral extractant, since the acid seems to compete with the tin(II) for the exchanger very successfully.

The anion-exchange behavior of tin(II) has been studied by Jentzsch and Pawlik[257], and a few data have also been reported by Nelson, Rush and Kraus[134]. The elution data obtained by the former authors are similar to those they obtained for zinc(II) but pertain to a resin, Wofatit L-150, for which no invasion data are available. Since they are very different from those of the other group ($D_{max} = 18$ at 2–7 *M* HCl, against $D_{max} = 1000$ near 1 *M* HCl), they cannot be analyzed even approximately in terms of the species formed. New and comprehensive data would be welcome particularly in view of the possibility that $SnCl_3^-$, rather than $SnCl_4^{2-}$ is the saturated complex.

Somewhat more extensive data are available for tin(IV). It bas been described as absorbable on a cation exchanger from dilute hydrochloric acid[171], probably as a hydrolysis product. From 9 *M* hydrochloric acid sorption is negligible[123]. Diisoamyl phosphate shows[153] low extractive power for dilute hydrochloric acid solutions ($D = 0.1$ at 1.5 *M* HCl), but somewhat better extraction from more concentrated solutions, with a maximal distribution coefficient of about 3. In this case, contrary to that of tin(II) discussed above, the ester seems to act as a neutral extractant. Diethyl ether is a rather poor extractant ($D = 0.2$ at 6 *M* HCl[147], maximal *D* near 4 *M* HCl). The species extracted has been stated to be $SnCl_4$, at least up to 4 *M* HCl, not the corresponding acid $[H(solvated)^+]_2SnCl_6$, but no definite proof has been given[184].

The decrease in extractability at high hydrochloric acid concentration has been attributed by Smith to the formation of $SnCl_6^{2-}$, which is non-extractable. A more plausible explanation is the general phenomenon of decreasing extractability into diethyl ether, observed for all systems, due to the increasing mutual solubility of the two phases. Anhydrous tin tetrachloride reacts with ether to form a solvate insoluble in the ether[185]. Addition of five moles of water per mole of tin(IV) causes complete dissolution. However, the Mössbauer effect (chemical shift) observed for $SnCl_4 \cdot 5\,H_2O$ (crystals, at liquid nitrogen temperatures)[186] is different from that observed in ketone extracts of tin(IV) from 10 *M* HCl, which in turn is similar to that of tin(IV) in ammonium hexachlorostannate(IV) or in concentrated hydrochloric acid (frozen at liquid nitrogen temperatures). The data are interpreted as extraction of $[H(solvated)]_{i-4}^+\ [SnCl_i\,(H_2O)_{6-i}]^{4-i}$ ion pairs, *i*, as well as *D*, increasing with increasing hydrochloric acid concentrations in the range 1–11 *M* HCl. 4-Methylpentanone-2 (hexone) proves to be a fairly good extractant showing $D = 10$ for 7 *M* LiCl, and $D = 13$ for 7 *M* HCl[187]. A continuous variation study shows $SnCl_4$ to be the organic-phase species (without presenting the data or naming the extractant). Extraction with TBP shows two moles of extractant to be associated with one mole of extracted tin(IV) species, from the slope of the extraction curve, $\log D$ *vs.* $\log \bar{c}_{TBP}$, the species postulated being $SnCl_4 \cdot 2\,TBP$[187].

The anion-exchange behavior of tin(IV) has been studied by Jentzsch[151], by Nelson and Kraus[65,134] and by Everest[188] and their co-workers. Macro quantities of tin(IV) can be loaded on an anion exchanger to a ratio somewhat higher than one mole tin(IV) per two equivalents of exchanger[188]. The not quite-definite stoichiometry found, and the equivalent-accounting method used, actually cannot differentiate between several possible species such as $SnCl_6^{2-}$, $SnCl_5^- + Cl^-$ or $SnCl_4 + 2\,Cl^-$, and is not very helpful. The distribution coefficients obtained with the German resin Wofatit L-150[157] are much lower than those obtained with Dowex-1, and show a gradual increase over the whole concentration range 0.5–12 *M* HCl. The distribution curve for Dowex-1 shows a flat maximum at 4–9 *M* HCl, with a rapid decrease of *D* towards lower concentrations, and a more gradual one towards higher ones[65,134]. At low hydrochloric acid concentrations, tin(IV) is extensively hydrolyzed, and a species $[SnCl_5(OH)]^-$ will show the same effect on $d \log D / d \log a$ (for hydrochloric acid) as a species $SnCl_4$. However, assuming $SnCl_6^{2-}$ to be the species sorbed on the resin, permits fitting of the data above 2 *M* HCl with the expression

$$\log D = \log K_{\mathrm{Sn^{IV}}} + 2\log \bar{a} - \log(1+\beta_1^{*\prime}a+\beta_2^{*\prime}a^2) \tag{18}$$

with $\log K_{\mathrm{Sn^{IV}}} = 2.43$, $\log \beta_1^{*\prime} = -0.4$ and $\log \beta_2^{*\prime} = -1.5$, indicating the presence of $SnCl_5^-$ and $SnCl_6^{2-}$ in concentrated hydrochloric acid solutions. This is by no means to be taken too seriously, because of the uncertainties connected with the species in the resin, and with hydrolysis effects. Still, the formation of $SnCl_6^{2-}$ in both the resin and concentrated hydrochloric acid (>7 *M*) is reasonable.

The extraction of tin(IV) by long-chain amines has been studied by Nakagawa[182], who found a maximal $D = 30$ at 4.5–6 *M* HCl with 10% Amberlite LA-1 in xylene. The distribution coefficients decrease to about unity in both 1 *M* and 12 *M* HCl. No detailed study of the species formed in the organic phase, or in the aqueous phase, has been reported.

Surprisingly little has been published concerning the ion-exchange and solvent-extraction behavior of lead(II)–chloride complexes, although such complexes are well known from studies using other methods. The distribution coefficients of lead(II) from hydrochloric acid onto a cation exchanger decrease very rapidly with increasing ligand concentration, from $D \sim 500$ in the absence of ligand to $D = 4$ at 1 *M* HCl and values below unity at still higher concentrations[123]. In a study not published in detail, Karlson[189] used a cation exchanger with a 1 *M* $NaClO_4$ ionic medium to find $\log \beta_1 = 0.81$, which is somewhat low, compared with other published values.

Lead(II) does not seem to be particulary well extractable from chloride media with polar solvents. Neither undiluted TBP[7], nor 5% TOPO in toluene[190], give distribution coefficients exceeding unity over the whole hydrochloric acid concentration range.

The anion-exchange behavior of lead(II) has been studied by Jentzsch[157], Liska[71] and Yoshimura[13] and their coworkers, who gave very little information except reporting the possibility to sorb lead(II) at low hydrochloric acid concentrations (*e.g.* 2 *M*) and elute it at higher ones (*e.g.* 7 *M*). Lead is also sorbable from sodium- and calcium-chloride solutions[69]. More detailed information has been given by Nelson and Kraus[191], and by Barbieri, Guada and Rizzardi[192]. The former authors used a batch technique with Dowex-1X10 and hydrochloric acid, the latter used column elution with Amberlite IR-400 and chromatography with anion-exchange-resin-impregnated paper SB-2 and lithium chloride solutions. The results from all three methods with the different exchangers and bulk electrolytes agree very well, considering differences in invasion functions. Indeed all these results conform to the expression

$$\log D = \log K_{\mathrm{Pb}} + p\log \bar{a} - \log(\beta_{-2}{}'^{*}a^{-2}+\beta_{-1}{}'^{*}a^{-1}+1+\beta_1{}'^{*}a+\beta_2{}'^{*}a^2) \tag{19}$$

where D stands for the weight: volume distribution coefficient in the batch method, for the volume-distribution coefficient D_v in the elution method, and for the parameter $R_M = (R_F^{-1}-1)$ in the paper-chromatographic method, R_F having its usual meaning. The value $p = 1$ has been selected as giving a reasonable limiting slope

$$\lim_{a\to\infty} \mathrm{d}\log D/\mathrm{d}\log a = \bar{i} = 2 - \bar{n} \simeq -2. \tag{19}$$

This means that $PbCl_3^-$ is the predominating species in the resin, while $PbCl_4^{2-}$ predominates in concentrated chloride solutions. The values of the constants are $\log \beta_{-2}'^* = -1.8$, $\log \beta_{-1}'^* = -0.40$, $\log \beta_1'^* = -0.12$ and $\log \beta_2'^* = -0.8$ in both hydrochloric-acid and lithium-chloride solutions. For Dowex-1 and hydrochloric acid, $\log K_{Pb} = 1.30$ approximately. Nelson and Kraus[191] have suggested $PbCl_5^{3-}$ as the predominant species in the exchanger to explain the low value of K_{Pb}, realizing that the penta-coordination is unusual. Since they based the suggestion on analogy with presumed $IrCl_6^{3-}$ and $InCl_6^{3-}$ ions, which are, however, not the species sorbed for these elements with low K_M, there is no reason for accepting $PbCl_5^{3-}$ either.

Again, rather scant information has been published concerning the extraction of lead(II) from chloride solutions with long-chain ammonium chlorides. Petrov[193] studied the extraction of lead(II) from dilute hydrochloric acid with a 30% solution of Aliquat 336 in benzene, while Nakagawa[182] studied its extraction with Amberlite LA-1 and tribenzylammonium chlorides in benzene. The distribution curve is similar to that for anion-exchange resins, exhibiting a maximum around 1.5 *M* HCl. These measurements are not sufficiently detailed to permit an analysis in terms of the species formed.

Lead(IV) is not stable in hydrochloric acid in the absence of chlorine, and no studies on its behavior towards ion exchangers and solvents have been reported. On the other hand, alkylplumbate(IV) species are stable in aqueous chloride solutions, and form chloride complexes. Diethyllead and triethyllead have been found to sorb on an anion exchanger as the hexacoordinated anions, $[(C_2H_5)_2PbCl_4]^{2-}$ and $[(C_2H_5)_3PbCl_3]^-$ respectively[194], and cationic, neutral and anionic species are present in lithium chloride solutions, as found from an analysis of the distribution curve, corrected for invasion[195].

(vii) Group Va

There is no clear evidence for the presence of cations containing arsenic(III) in aqueous solutions, although basic dissociation of arsenious acid, H_3AsO_3, to $As(OH)_2^+$ has been assumed[197]. Arsenic(III) is extracted into a variety of solvents from hydrochloric acid above *ca.* 4 *M*. Both "inert" solvents, such as benzene, 1,2-dichloroethane, chloroform and carbon tetrachloride[174,198,199], and polar, oxygenated solvents such as diethyl ether[147,196], isopropyl ether, β,β'-dichlorodiethyl ether[174,197] and 4-methylpentanone-2[187] are capable of extracting arsenic(III). The arsenic(III) entity is extracted at least from the more concentrated hydrochloric acid solutions, into both kinds of solvent as the species $AsCl_3$, as found by direct analysis, correcting for the free hydrochloric acid co-extracted. At the lower hydrochloric acid concentrations the ratios Cl : As are somewhat below three[174, 197], and this is ascribed to coextraction of $As(OH)Cl_2$. There is no evidence for the extraction of $HAsCl_4$, in analogy with other tervalent metals. As to the aqueous phase, a gradual transition from H_3AsO_3 (= $As(OH)_3$), through $As(OH)_2^+$, $As(OH)_2Cl$, $As(OH)Cl_2$ to $AsCl_3$ is consistent with the extraction data[197]. The general equilibrium may be written as

$$As(OH)_{3-i}Cl_i + H^+ + Cl^- \rightleftarrows As(OH)_{2-i}Cl_{i+1} + H_2O \qquad (20)$$

with $\log K_i = [As(OH)_{2-i}Cl_{i+1}]\, a_{H_2O}/[As(OH)_{3-i}Cl_i]a^2$ being -1.08 for $i = 0$, -3.47 for $i = 1$, and -4.20 for $i = 2$[197]. The distribution coefficients do not vary with the arsenic(III) concentration over the wide range from carrier-free As^{74} to 0.1 M[174, 197, 199], signifying the presence of monomeric species only. The extraction from lithium chloride solutions is much higher than from a hydrochloric acid solution of equal concentration (with 4-methylpentanone-2, $D = 7$, respectively 0.5 for 7 M solutions)[187]. No detailed study has been made to explain this observation.

Arsenic(III) is sorbed on anion exchangers, D reaching a shallow maximum of 25 at 10 M HCl[180]. This value is more than can reasonably be expected from a mechanism not involving sorption of an anionic species, and it seems reasonable to assume that the arsenic(III) is sorbed as $AsCl_4^-$. The data are compatible with the assumptions of the presence of $As(OH)Cl_2$, $AsCl_3$ and $AsCl_4^-$ in hydrochloric acid of increasing concentration, but not with the detailed stability constants given by Arcand[197]. At 10 M HCl $AsCl_3$ seems to predominate in any case, but the presence of $AsCl_4^-$ at higher concentrations is by no means certain.

Whereas the distribution coefficient with the anion exchanger varied only from *ca.* 0.8 at 0.1 M HCl to 25 M at 10 M HCl, that with the long-chain ammonium chloride Amberlite LA-1, 5% in xylene varied much more, from *ca.* 0.01 at 0.1 M HCl to 16 at 10 M, and the maximum is more pronounced[200]. The data are not sufficiently detailed to merit analysis in terms of species.

Arsenic(V) is not appreciably extractable from hydrochloric acid solutions (to which chlorine is added to keep the arsenic oxidized) into inert solvents, such as benzene ($D \simeq 0.003$)[174] even in the presence of a long-chain ammonium chloride[200]. Its sorption on an anion exchanger is also slight, a maximal $D = 4$ being attained in concentrated hydrochloric acid solutions[180]. The species sorbed seems to be the arsenic(V) acid, H_3AsO_4.

Antimony(III) is extractable into various solvating solvents from aqueous hydrochloric acid. Diethyl ether shows appreciable extraction from 1–6 M HCl, with a maximal $D = 0.3$ at 3 M HCl[196]. Diisopropyl ether shows much less extraction over the range 3–11 M HCl, maximal $D = 0.017$ being observed[201]. This observation is surprising and might be explained by the hydrolysis of the relatively-concentrated antimony(III) solutions (0.06–0.3 *M*) used. A higher ether, diisopentyl ether, has been found to be more effective in the extraction of antimony(III) from lithium–hydrogen chloride solutions, again hydrolysis decreasing the distribution coefficients drastically[202]. Various other solvents such as alcohols, ketones[187], esters and TBP have also been studied[203,204]. In every case maximal *D* has been found near 3–4 *M* HCl. This maximum is not the same as that observed *e.g.* at 7 *M* HCl for diethyl ether and many metals, which is due to the sharply-increasing mutual solubility of the two phases above that limit. In the present case the maximum is probably due to a chemical effect in the aqueous phase, the formation of a non-extractable complex. Iofa and Daker[204] interpreted their distribution data in terms of the formation of $[(H, Li)(H_2O)_mS_n]^+SbCl_4^-$ in the organic phase. From the concentration dependence in benzene-diluted hexanol, it has been found that $n = 1.4$. Electrical measurements, however, show that there is no migration of antimony(III) in hexanol extracts. Fomin[205] has criticized the conclusions of Iofa and Daker, as not being based on a valid interpretation of the data. Indeed, if the formation of a non-extractable species at high hydrochloric acid concentration, the non-migration of antimony(III) in the extract, and analogy with arsenic(III) which is extracted as solvated $AsCl_3$, are considered, it is reasonable to assume that the extracted species is $SbCl_3$, while in solution $SbCl_4^-$ is formed. There is, however, no proof for this hypothesis, and further investigation is clearly warranted.

Antimony(III) is sorbed strongly on anion exchangers[134,206]. A maximum in the distribution curve is shown at 2 *M* HCl ($D = 2000$)[134]. Too few data are given to permit a detailed analysis in terms of the species formed, particularly in view of the strong hydrolysis in dilute solutions. The data are generally compatible with the assumption of $SbCl_4^-$ being formed in the external solution at the higher concentrations but do not exclude other possibilities. The amine extraction behavior is similar to the anion-exchange behavior, however, the maximum is shifted to 4 *M* HCl[200]. Again, the data are insufficient for a detailed analysis.

Antimony(V) undergoes slow hydrolytic reactions in dilute and moderately concentrated hydrochloric acid so that its behavior at <6 *M* HCl tends to be erratic. A further complication is the possibility of reduction to antimony(III) which is usually less extractable by solvents, or sorbable on resins. An early estimate that antimony(V) shows $D = 10$ for 16 *M* HCl or 10 *M* LiCl on the cation exchanger Dowex-50X12[122], has been subsequently corrected to give much higher distribution coefficients, $D = 2000$ for 9–12 *M* HCl on Dowex-50X4[123].

The extraction of antimony(V) by diethyl[147,196] or diisopropyl[201] ethers, has been found to be very high. Again, the results seem to suffer from irreproducibility at HCl <6 *M* because of hydrolysis and reduction. A decrease in *D* at higher concentrations can be ascribed to increased miscibility of the two phases. In the absence of water, antimony pentachloride is solvated by diethyl ether, but the product is insoluble, unless 6 moles of water are added per mole of antimony[188].

Other solvents such as ethyl acetate[207] or diisopentyl ether and isopentanol[202] are also effective extractants.

Anion exchangers sorb antimony(V) very strongly, a maximal $D = 2.5 \times 10^5$ is obtained with Dowex-1X10 around 10 *M* HCl. Sorption starts ($D = 1$) at 1 *M* HCl and increases rapidly at higher acidities[134,206]. The nearly constant D values above 8 *M* HCl are compatible with the species $SbCl_6^-$ occuring in both the resin and the external-solution phases. The published results have not been presented accurately enough to warrant a more detailed analysis. The amine extraction behavior is, again, similar to the anion-exchange behavior[200]. Nearly-constant distribution coefficients are obtained above 8 *M* HCl.

Bismuth(III) is known to form strong chloride complexes, and although hydrolyzed at low acidities, complex formation is reversible and rapid above *ca.* 0.1 *M* acid. Even from 0.1 *M* HCl bismuth(III) is much less absorbed on a cation exchanger ($D \sim 20$) than from a corresponding perchloric acid solution (extrapolated $D \sim 10^4$) and the distribution coefficient decreases to values below unity above 0.5 *M* HCl[123]. Although the distribution coefficients increase to very high values in concentrated perchloric acid there is no increase in concentrated hydrochloric acid solutions[122,123].

Bismuth(III) seems to be only poorly extractable from chloride solutions into solvating solvents, such as diethyl ether[147], TBP[7], 4-methylpentanone-2[187], etc. This may be connected with the pronounced tendency of bismuth(III) to form anionic complexes with a charge more negative than -1 (such as $BiCl_5^{2-}$, or $[Bi(H_2O)Cl_5]^{2-}$, and $BiCl_6^{3-}$), which have such a high affinity towards water that they cannot be efficiently extracted.

Anion exchangers, on the other hand, sorb bismuth(III) very efficiently, from both concentrated and dilute chloride solutions, so that it is difficult to elute[13,191,208] and non-chloride solutions such as sulfuric or nitric acid must be used[191]. The distribution coefficients with Dowex-1X10 decrease from 2×10^5 at 0.25 *M* HCl to 57 at 12 *M* HCl. An analysis of the distribution curve shows that the data[191] conform nicely to the expression

$$\log D = \log K_{Bi} + 2 \log \bar{a} + \log (1 + 10^{-1.7} \bar{a}) - 2 \log a - \log (1 + 10^{-0.1} a) \tag{21}$$

with $\log K_{Bi} = 3.45$. This behavior indicates the formation of $BiCl_5^{2-}$ at low, and of $BiCl_6^{3-}$ at high hydrochloric acid concentrations, both in the resin phase and in solution. The magnitude of the constants is so that $BiCl_6^{3-}$ is formed in the solution at lower hydrochloric acid concentrations than required for its formation in the resin, where, as observed for other systems, species of lower charges are favored. The species indicated for the aqueous phase agree with results from other methods, and also the constant, $\log \beta_6^*/\beta_5^* = -0.10$, is reasonable. More information, as possibly obtainable from resin loading, crosslinking variation and secondary cation variation, as well as spectral studies, would be helpful in establishing the validity of the above interpretation, or in providing an alternative one.

The extraction of bismuth(III) with long-chain ammonium chlorides has received little attention, in spite of the expected good extractability. Nakagawa used the secondary amine, Amberlite LA-1 in xylene[200], and found a curve generally resembling that for the resin anion exchanger. Sheppard and Warnock[209], in a more detailed study, found a second-power dependence of D on $\bar{c}_{\mathrm{R_3NHCl}}$, using 0.002–0.3 M trilaurylammonium chloride in xylene. At the lowest amine concentration it seems to be monomeric, while it may aggregate at higher concentrations. It is, therefore, surprising in this case, as it is also for many other cases, that the slope of the curve remains 2.0 ± 0.1, while changing $\bar{c}_{\mathrm{R_3NHCl}}$ over more than two orders of magnitude. This same slope has been obtained for several hydrochloric acid concentrations, in the range 0.1–8.0 M HCl. The absorption spectrum of the organic phase shows a peak centered at 332 nm, compared with a peak at 327 nm attributed to $\mathrm{BiCl_5}^{2-}$. This evidence taken together indicates the formation of $\overline{(\mathrm{R_3NH})_2\mathrm{BiCl_5}}$ in the organic phase. However, the decrease of the distribution coefficient with increasing hydrochloric acid concentrations (from a maximum of about $D = 90$ at 0.6 M HCl to $D = 0.11$ at 8 M HCl, with 0.038 M trilaurylammonium chloride in xylene) is too small compared with an inverse second-power turning into an inverse third-power dependence on a, expected from the reaction

$$\mathrm{BiCl}_{3+x}^{\,x-} + 2\,\overline{\mathrm{R_3NHCl}} \rightleftarrows \overline{(\mathrm{R_3NH})_2\mathrm{BiCl_5}} + x\,\mathrm{Cl}^- \quad (x = 2 \text{ or } 3) \qquad (22)$$

More information such as the behavior with lithium chloride solutions, is desirable in order to permit a decision between alternative interpretations of the data.

(viii) Group VIa

Selenium is classified as a non-metal, still some of its ions in solution are capable of serving as central ions, coordinating chloride ions around them. Thus selenium(IV) in hydrochloric acid seems to form chloride complexes, which can be extracted with TBP[210] or TOPO[190] with distribution coefficients exceeding 100 at 12 M HCl. Selenium(IV) is also sorbed on an anion exchanger from hydrochloric acid solutions[3, 211], D increasing rapidly above 6 M HCl. The species involved in this sorption have not been elucidated; however it has been suggested[3] that some of them (*e.g.* $\mathrm{SeCl_4}$ or $\mathrm{SeOCl_2}$) are not in rapid equilibrium with each other, a fact which causes difficulties in the elution. The extraction of selenium(IV) in Amberlite LA-1 and tribenzylamine from hydrochloric acid has also been studied[212], the distribution curve resembling that for anion-exchange resins.

This seems to be all the published information concerning ion exchange and solvent extraction of selenium(IV), or selenium altogether. More detailed work capable of identifying the species formed is clearly desirable.

The information available concerning chloride complexes of tellurium ions is more extensive. Tellurium(IV) is extracted from hydrochloric acid solutions by a variety of solvents. Thus from 6 *M* HCl, diethyl ether shows $D = 0.5$[147], TBP shows $D = 200$[7], and good extraction is also observed with diisopropyl ether and bis(β-chloroethyl) ether[213]. The distribution coefficients show a maximum at 8.5 *M* HCl with the ethers. Analysis of the organic phase has shown it to contain $TeCl_4$, when extraction occurs from dilute hydrochloric acid solutions, and H_2TeCl_6, when extraction is performed from concentrated solutions. For the reaction $\overline{TeCl_4}+\overline{2\,HCl} \leftrightarrows \overline{H_2TeCl_6}$ in bis(β-chloroethyl) ether, it was found that $\log K = 4.0$. No information has been given concerning the species in the aqueous phase. The data indicate that H_2TeCl_6 is extensively dissociated in the ether to give hydrogen ions and hexachlorotellurate(IV) anions, the acid being much stronger than hydrochloric acid[213].

Anion-exchange data for tellurium(IV) in chloride solutions have been given by Schindewolf[214], Sasaki[211,215], Kleemann[216], Mizumachi[217] and Gaibakyan[218]. It has been suggested that anionic chloride complexes of tellurium(IV) are formed above 3 *M* HCl[214]; in any case, appreciable sorption starts above 1 *M* HCl, and *D* reaches high values, and a shallow maximum, at 7–8 *M* HCl ($D \sim 10^4$)[214,216,218]. It is reasonable to assume that tellurium(IV) is sorbed from very dilute hydrochloric acid as TeO_3^{2-}, and as the hydrochloric acid concentration increases, a species such as TeO^{2+} is formed, causing the low distribution coefficients observed at 0.5–1 *M* HCl[218]. At still higher concentrations species such as $TeOCl_4^{2-}$ or $TeCl_{4+n}^{n-}$ are formed, with a high affinity towards the exchanger[217,218]. It has been observed that in mixtures of hydrochloric acid and lithium chloride, at constant chloride concentration, *D* increases as the acid concentration increases[214,217]. Indeed, *D* is very low for pure lithium chloride solutions, except when very concentrated (>10 *M* LiCl)[214]. This behavior is contrary to the usually depressant effect of acid, and must be attributed to the transition from species such as $Te(OH_m)^{4-m}$ (*e.g.* TeO^{2+}) to more highly-sorbed species such as $TeCl_{4+n}^{n-}$, as the hydrochloric acid component in the mixture increases. As with selenium(IV), slow equilibria cause difficulties in the elution of tellurium(IV)[217], but when sorbed from concentrated hydrochloric acid, tellurium(IV) is easily eluted with 1 *M* HCl[216].

The amine extraction behavior of tellurium(IV) is again similar to that with anion-exchange resins. Above 6 *M* HCl, there is good extraction ($D > 100$) with Amberlite LA-1 and with tribenzylammonium chlorides[212,219].

Tellurium(VI) is sorbed on anion exchangers, is extracted into amine hydrochloride solutions only at high hydrochloric acid concentrations, and shows generally much lower distribution coefficients than tellurium(IV).

Polonium, although posing difficulties because of strong radiolysis and also hydrolysis in solution, has received a considerable amount of attention, in particular in the form of the most-stable valency state, polonium(IV). Polonium(IV) can be sorbed on a cation-exchange resin, such as Dowex-50, from dilute hydrochloric acid ($<0.1\ M$) and eluted with more concentrated hydrochloric acid ($>2\ M$)[220,221]. Although hydrolysis is extensive below 1 M HCl, equilibration is complete within a few hours, and apparently reversible[221]. The presence of polonium as a cationic hydrolyzed species (such as PoO^{2+}, $[Po(OH)_mCl_n]^{4-m-n}$ with $m+n<4$, etc.) has been suggested, but polymeric species cannot be excluded.

Polonium(IV) can be extracted from hydrochloric acid solutions by a variety of solvents. Diethyl ether is a poor extractant for polonium(IV), at 6 M HCl, D is only 0.03[221,223], but mesityl oxide[222] and various ketones (diisopropyl ketone, acetylacetone[222] and 4-methylpentanone-2[224]) or carbinols[225] are practical extractants. The history of the polonium sample before the extraction has been found to be of importance, and near 2 M HCl a minimum in the extraction curve with 4-methylpentanone-2 is observed[224]. The results indicate the occurence of a slow equilibrium between two extractable species: $[Po(OH)_2Cl_4]^{2-}$ and $PoCl_6{}^{2-}$, predominating at low and high hydrochloric acid concentrations, respectively[224]. The former species is not compatible with the sorbability on cation exchangers, observed in this range of acidity.

TBP is a useful solvent for extracting polonium(IV) from hydrochloric acid solutions, as first suggested by Karracker and Templeton, who used a solution of this extractant in dibutyl ether diluent[226]. Subsequent studies by Bagnal[222,227], showed that at high loadings, *i.e.* saturated solutions of polonium(IV) in TBP diluted with decalin, the species $\overline{PoCl_4 \cdot 2\,TBP}$ is formed, with the constant for the reaction $PoCl_4 + \overline{2\,TBP} \rightleftharpoons \overline{PoCl_4 \cdot 2\,TBP}$ being $\log K = -1.4$ at 22°. This result does not exclude the formation of species richer in TBP at lower polonium concentrations, and a slope of 3 has been found in the logarithmic plot of D against $\bar{c}_{TBP}$. The distribution curve shows a minimum near 2 M HCl and a maximum near 7 M HCl. It is difficult to explain the minimum but the maximum is probably due to binding of TBP by the hydrochloric acid extracted at high concentrations[227].

The anion-exchange behavior of polonium(IV) has been studied by Sasaki[211] and by Danon and Zamith[221]. The latter authors have found very high distribution coefficients ($D = 2\times10^5$ at 0.5 M HCl and $D = 3\times10^4$ at 12 M HCl), and although equilibrium is attained rather slowly, the sorption is completely reversible[221]. The distribution curve follows the expression:

$$\log D = \log K_{Po} + 2\log \bar{a} - \log(1+10^{0.1}\,a^2) \tag{23}$$

with $\log K_{Po} = 4.77$. The data thus indicate that $PoCl_6{}^{2-}$ is the species sorbed on the resin, and $PoCl_4$ (or $[Po(OH)Cl_5]^{2-}$) and $PoCl_6{}^{2-}$ being the species predominating in the solution, the latter taking over above ca. 1 M HCl.

The extraction of polonium(IV) with long-chain amines is also very easy. Thus methyldi-n-octylammonium[228] or trilaurylammonium[209] chlorides give very high distribution coefficients, varying with the second power of the amine concentration. At high hydrochloric acid concentrations, the distribution curve conforms to the extraction of $(R_3NH)_2PoCl_6$ from a solution in which $PoCl_6^{2-}$ predominates, but at concentrations below *ca.* 6 *M* HCl, *D* does not increase as expected, when the acid is diluted, and an irregularity in the curve occurs near 1 *M* HCl. It is thus possible that another species besides $PoCl_6^{2-}$ is extracted into the organic phase, possibly $[Po(OH)Cl_5]^{2-}$. Such a suggestion[209] may explain the apparent discrepancy between the anion-exchange and the amine-extraction results.

SYMBOLS

The following symbols are used throughout this review; some other symbols, used only once for a specific purpose, are defined where they are used.

a	effective ligand activity ($a = m\gamma_{\pm}$ or $a = cy_{\pm}$ for 1:1 electrolytes)
c_X	molar concentration of X
D	distribution coefficient, the ratio of the concentration of the distribuent in the organic phase (*M*) or resin phase (moles/kg air-dried resin) to its concentration in the aqueous phase (*M*)
D_v	volume-distribution coefficient, obtained from resin-column elution, moles distribuent per liter of resin bed to moles per liter aqueous solution
E	elution constant ($E = 1/(D)_v +$ interstitial volume fraction)
k_n	stepwise complex-formation constant for species MCl_n^{m-n}
K_X	general symbol for equiblibrium constant, for reaction specified by X
m_X	molal concentration of X
n	average ligand number
y	molar activity coefficient
α_n	fraction of metal in form of species MCl_n^{m-n}
β_n	overall complex-formation constant for species MCl_n^{m-n}
γ	molal activity coefficient
ε	dielectric constant
(X)	concentration of species X
$\overline{X}$	species or symbol (such as concentration, etc.) pertaining to the resin or the organic solvent phase
X^*	effective complex-formation constant, used in mass-action law expressions involving the effective ligand activity, a ($X = \beta$ or K)

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* The part below 70% alcohol in Fig. 4 is obviously wrong, *cf.* ref. 80, Fig. 1b.

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