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THE CHEMISTRY OF AQUEOUS SOLUTIONS OF ZIRCONIUM SALTS (DOES THE ZIRCONYL ION EXIST?)

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1. INTRODUCTION

The considerable progress made in the chemistry of zirconium in aqueous solutions in the past 10–15 years urgently demands reconsideration of some of the ideas which have prevailed in the science of zirconium for a whole century, since the time of Berzelius, Hermann, Endemann, and other 19th century chemists. This relates primarily to the assertion, which appears in all modern textbooks, that the majority of zirconium salts are derivatives of the "zirconyl", "dizirconyl", and similar radicals.

The question of the existence of the zirconyl ion is one of the fundamental and at the same time one of the most complex problems in the chemistry of zirconium. It is usually assumed that "zirconyl chloride", "zirconyl nitrate", and other basic products of the hydrolysis of the Zr^{4+} ion, containing one or two equivalents of acid per zirconium atom, are compounds whose individual nature is sufficiently well-defined and whose analytical formula has been reliably established. Nevertheless there is no direct proof for the "zirconyl" structure of these compounds.

Modern reviews of the chemistry of zirconium usually do not discuss the history of the development of the "zirconyl theory" and the "zirconyl structure" of zirconium salts is regarded as an obvious property of the element. In the present paper an attempt has been made to systematise the published data on the chemistry of zirconium in aqueous solutions. It is shown, from an examination of the properties of aqueous and acidic solutions of, for the most part, the chlorides and nitrates, that there is no justification for the zirconyl theory.

2. HISTORICAL REVIEW

When dissolved in water, zirconium tetrachloride, like most other normal zirconium salts, is readily converted to the "oxychloride", which can be isolated from solution either by concentrating solutions of the chloride or by treating these with concentrated hydrochloric acid. The fact that hydrochloric acid solutions of zirconium always give a compound containing about two chlorine atoms per atom of zirconium attracted the attention of research workers at an early date. This phenomenon was first observed by Berzelius[1], who did not, however, consider it possible to ascribe any definite formula to the basic chloride which he isolated; the Zr:Cl ratio in this compound was not always constant and often varied within the range 1:1.6–1:1.9.

Berzelius' observation — that a characteristic feature of this compound was its ready loss not only of water but also of hydrogen chloride, even at comparatively low temperatures†, so that, as he suggested, a compound of indefinite composition is formed — did not, however, prevent Hermann[2] from announcing, in 1844, the existence of zirconyl chloride.

In his first studies Hermann made no definite attempt to relate the characteristic properties of this salt to its composition, but he nevertheless put forward two ways for writing the formula of this compound: $ZrOCl_2.9H_2O$ or $Zr(OH)_2Cl_2.8H_2O$‡. In subsequent papers[3,4] Hermann finally brought into use the zirconyl formula for basic zirconium chloride, based entirely on its property of separating from acidic solutions in the form of a precipitate containing about two chlorine atoms per zirconium atom.

By analogy with zirconyl chloride, Endemann[9] attributed to the monochloride which he isolated the formula $Zr_2O_3Cl_2.xH_2O$. Subsequently workers such as Paÿkyll[10], Bailey[11], Venable[12], Ruer, Chauvenet, and others unreservedly postulated the zirconyl structure for the basic chlorides and extended it not only to chlorides of any composition but also to other basic and complex zirconium compounds.

Ruer and Chauvenet strengthened the zirconyl theory of the structure of basic zirconium compounds. In a study of the electromigration of the metal in solutions of the chlorides[6,13,14] and sulphates[14,15], Ruer found that in the latter case the zirconium migrates chiefly to the anode, whereas in the presence of hydrochloric acid, cathodic migration is observed. Ruer attributed this marked difference in the properties of the chloride and sulphate solutions of zirconium to the presence, in the sulphate solutions, of a complex ion with the zirconyl structure $[ZrO(SO_4)_2]^{2-}$. Moreover, the characteristic properties of the sulphate solutions with respect to precipitation by oxalic acid, together with the exceptional stability to heat of the monohydrate of normal zirconium sulphate, were taken by Ruer as further confirmation of the zirconyl structure of the sulphate complex. Even at the present time, Blumenthal[16–18] puts forward these hypotheses of Ruer as a decisive argument in support of the zirconyl structure for the sulphates and other compounds of zirconium.

Ruer also considered that the ions of the metal present in chloride solutions also have the zirconyl structure. Two types of ion, the zirconyl and dizirconyl ions, were said to exist.

Chauvenet[19] carried out conductimetric titration of aqueous solutions of some normal zirconium salts and found that the titration curves were not straight lines, like those usually obtained in acid–base titrations, but had an appreciable curvature. The tangents drawn at the end of the curve intersect at a point corresponding to the addition of approximately two equivalents of alkali. Chauvenet considered that these experiments provided convincing proof of the existence of the zirconyl ion.

The development of the chemistry of zirconium up to this period was reviewed by Venable[12]. On the basis of the ideas of the "zirconyl theory", he put forward the following scheme for the hydrolysis of zirconium tetrachloride:

$$ZrCl_4+H_2O \rightarrow ZrOCl_2+2HCl,$$
$$2ZrOCl_2+H_2O \rightarrow ZrO(OH)_2.ZrOCl_2+2HCl.$$

If more than two molecules of zirconyl chloride are hydrolysed, the formation of a more complex product, for example Rodd's salt $Zr_5O_8Cl_4.xH_2O$,[20] is possible.

General schemes for the hydrolysis of the chlorides, nitrates, and other compounds of zirconium were subsequently considered by many workers, but these differ little

† The liberation of free hydrogen chloride when aqueous solutions of zirconium dichloride were evaporated or during thermal dehydration of the salt $ZrOCl_2.xH_2O$ ($x \leq 10$) was subsequently shown by a number of workers[2–8].

‡ Komissarova *et al.*[8] gives a complete compilation of the hydrated forms of zirconium dichloride.

from those given above, particularly Blumenthal's schemes, and are therefore not discussed here.

Better justified views on the nature of aqueous solutions of zirconium salts were put forward by Britton[21], who repeated Chauvenet's experiments and found that the statement regarding the existence of the zirconyl ion was inaccurate. According to Britton, the mean composition of zirconium chloride in solution changes continuously during the electrometric titration; this is due to the fact that the basic chlorides do not contain zirconyl groups and the quantity of hydroxy-groups attached to the zirconium increases continuously with increase in pH. Normal zirconium tetrachloride, on dissolution in water to give a 0.1 M solution, is hydrolysed to the extent of 58%, while the basic chloride with a Zr : Cl ratio of 1 : 1.737 in 0.01 M solution is hydrolysed to the extent of 54%. One of the intermediate products of the hydrolysis is a chloride with empirical composition $[Zr(OH)_{3,5}Cl_{0.5}]$. As emphasised by Britton, the formation of this chloride is responsible for the inflection on the curve taken by Chauvenet as obvious proof of the existence of the zirconyl ion. On the basis of these data and the results of conductimetric titration of aqueous solutions of normal zirconium sulphate, Britton categorically rejected the existence of the zirconyl ion. Britton confirmed Chauvenet's observation regarding the formation, under certain conditions, of a highly hydrolysed sulphate with a $Zr : SO_4^{2-}$ ratio of 1 : 0.5. He was the first to focus attention on the colloidal nature of solutions of zirconium salts.

Unfortunately, Britton's work did not become widely known, but the correctness of his views can now be supported by a large quantity of experimental data, some of which will be examined below.

The zirconyl theory was opposed not only by Britton, but also by Kulka[22], who considered that the composition of zirconium dichloride can be expressed by a formula which does not include the zirconyl oxygen atom, and later by Schmid[23], who predicted, on the basis of structural theories, that the zirconyl ion should not exist. Schmid was the first to prepare zirconium trichloride, whose composition is close to the empirical formula $ZrOCl_2.HCl.xH_2O$ or $Zr(OH)Cl_3.xH_2O$. The existence of zirconium trichloride cannot be explained by the zirconyl theory.

Recently, Larsen[24] pointed out that 0.05 M zirconium dichloride solution has a pH of ~1. These observations are difficult to reconcile with the results of cryoscopic measurements[25,26] and electrical conductivity measurements, if it assumed, as is usually done, that the solution contains only the zirconyl ion.

3. PROPERTIES OF AQUEOUS SOLUTIONS OF ZIRCONIUM SALTS

Hydrolysis. The tetrachloride, tetranitrate, and other normal salts of zirconium cannot be recrystallised, even from strongly acidic solutions, without some hydrolysis. Dissolution in water is accompanied by extensive hydrolysis of these compounds, so that aqueous solutions of normal zirconium salts are strongly acidic. Similar properties are exhibited by solutions of basic zirconium chlorides.

Ruer[6,13] measured the electrical conductivity of 0.25 M zirconium dichloride solution at 18° and found that hydrolysis increases with time and is much more extensive at higher temperatures. Venable and Jackson[27] repeated Ruer's experiments and demonstrated the dependence of hydrolysis on the concentration of the original solution. They showed that hydrolysis increases with dilution. Similar results were obtained by Jander and Jahr[28].

According to Adolf and Pauli[29], the change in the degree of hydrolysis of zirconyl chloride with time in the concentration range 0.0022–0.125 M is irregular, and when equilibrium is reached, in ~10 days, the degree of hydrolysis amounts to 35–50%. Küntzel and Rosenbusch[30] and Tananaev and Guzeeva[31] give for similar conditions the values 48.3% and 30% respectively. Simple recalculation of the data[31] by Britton's method[21] shows, however, that the degree of hydrolysis changes with dilution from 27% in 0.25 M solution to 40% in 0.01 M solution[32]. Solovkin[32] has compiled the pH values for solutions of the dichloride of different concentrations and has pointed out that the measurements of the pH of solutions of the same concentrations by different workers often do not agree, due to the characteristic properties of zirconium salt solutions, and in particular to the slow rate of attainment of equilibrium, which may take several weeks[33], months[34], or years[35] in the case of the sulphate solutions.

Green[36] and Sandell[37] consider that the colorimetric determination of zirconium with alizarin S is possible only in 0.1–0.2 M HCl, since extensive hydrolysis takes place at lower hydrochloric acid concentrations. Mayer and Bradshaw[38] found, however, that hydrolysis of zirconium is suppressed only in 1.5 M HCl. In a study of the reaction of zirconium with alizarin S, the authors established that when solutions with an acidity less than 0.5 M with respect to HCl were allowed to stand, irreversible hydrolysis occurred, but that in 1.0–1.5 M HCl solutions of zirconium underwent no significant hydrolysis over a period of 266 h. Intensive hydrolysis of a 5×10^{-4} M solution of the dichloride was observed by Gübely and Jacoby[39]. According to their data, the reaction with alizarin S takes place only in the presence of hydrochloric acid, and the order of addition of the reagents to the aqueous dichloride solution is of considerable importance. If the alizarin S is added first, followed by HCl, the results of the determination vary considerably and are difficult to reproduce. The reversal of hydrolysis is slow. The reverse order of addition of the reagents, which also ensures that the zirconium is kept in HCl solution, makes it possible to obtain reproducible results.

Many other examples of the influence of hydrolysis on the analytical chemistry of zirconium are given by Elinson and Petrov[40].

Larsen and Gammill[41] established that zirconium solutions containing a small quantity of free hydrochloric acid contain an extensively hydrolysed ion whose mean composition can be represented by the formula $[Zr(OH)_{3,4}]_n^{0,6n+}$. This corresponds closely to Britton's data[21]. With macro-concentrations of zirconium (0.04 M), hydrolysis is observed even in 4 M HNO_3.[42] With tracer quantities of ^{95}Zr, however, according to Paramonova and Voevodskii's data[50], hydrolysis takes place only at an acidity less than 1 M with respect to HNO_3. Intensive hydrolysis of zirconium salts in aqueous and weakly-acidic solutions has been reported by a number of authors[43-48] and in some earlier papers[12,18,49]. The nature of the acid has a significant influence on the hydrolysis of zirconium. As shown by Jander and Jahr[28] and Larsen[24], hydrolysis in perchloric acid solutions is much less than that in hydrochloric or nitric acids.

Polymerisation. Sol formation in aqueous and acidic solutions of zirconium has often been observed, and this phenomenon considerably complicates the chemical behaviour of zirconium. Sol formation is directly related to hydrolysis and explains many features of the chemistry of zirconium in aqueous solutions.

When caustic alkali or ammonia is added to solutions of zirconium chlorides or nitrates, hydrolysis proceeds to completion with the precipitation of zirconium hydroxide, which has an extremely high adsorbent power[51]. Zirconium hydroxide does not form hydrates of definite composition[52-55]. The product precipitated on boiling is less soluble than that precipitated in the cold.

Boiling, or even slight heating, leads to more extensive hydrolysis. The most basic products are those obtained at high temperatures. Although zirconium can be precipitated from nitric acid solutions hydrolytically, *i.e.* merely by boiling the dilute solutions, no precipitates have been obtained hydrolytically from solutions of the chlorides. For example, Bashilov[56] reported that zirconium can be precipitated hydrolytically from hydrochloric acid solutions only if the hydrochloric acid content of the solution does not exceed several mg per litre.

Repeated evaporation of aqueous solutions of the chlorides leads to volatilisation of hydrochloric acid, and it is possible to prepare solutions in which the Zr : Cl ratio = 1 : 0.35.[7] The solutions are stable at a 5 M zirconium concentration for 6 months. Ruer[6,57,58] by repeated evaporation of a dilute aqueous solution of zirconium dichloride, obtained gelatinous precipitates of composition $(ZrO)_5(OH)_8Cl_2.xH_2O$ and $Zr_{10}O_{19}Cl_2.xH_2O$, which he believes to be derivatives of "metazirconic acid" $ZrO(OH)_2$, which is generally precipitated from boiling solutions. These compounds ("metazirconyl chlorides") are particularly stable and can be converted to zirconyl chloride only by prolonged boiling with concentrated hydrochloric acid for 30 h.

Zirconium hydroxide, particularly that prepared from boiling solutions, is readily peptised by water[59] or by solutions of zirconium nitrate or sulphate; in the latter case the peptisation product is not converted to basic nitrates or sulphates and retains the properties of a sol for prolonged periods[60,61]. The hydro-sols are stable in moderately-concentrated acid solutions[62].

Zirconium hydroxide sol has been prepared directly by precipitating with alkali and by dialysis of aqueous and acidic solutions at room temperature or above[63]. A complete review has been given by Blumenthal[18]. The sol has high adsorptive power and may have either positive or negative charges, due to adsorption of an excess of cations or anions[51,64]. The sols isolated by different methods may have zirconium : anion weight ratios of 20 : 1,[65] 7 : 1,[66] 8.1–17 : 1,[67] 40 : 1,[57] 6.6–16.2 : 1,[68] etc. The sol is sensitive to the action of electrolytes and in some cases can be precipitated quantitatively by the addition of dilute solutions of salts such as KCl, KBr, etc[45,69-72]. Increase in temperature increases the quantity of the sol, and the sol is converted to a gel[62]. Coagulation is more extensive when zirconyl chloride or zirconyl nitrate solutions are diluted[45]. Ruer[57] pointed out that addition of $AgNO_3$ to an aqueous solution of a sol prepared by dialysis of zirconium chloride does not give a precipitate of silver chloride. A precipitate can be obtained only after the sol has been boiled for a prolonged period with concentrated acid.

After aging and boiling the sol is hydrolysed with the liberation of free HCl[67]. In this case the duration of boiling has a considerable influence. The pH of the solutions remains unchanged after boiling, indicating that the process is irreversible. The pH was measured 6 h and 6 months after boiling.

According to Robinson and Ayres' data[62], the viscosity of the sol decreases with increase in temperature, and the percentage coagulation of the sol increases. Heating leads to a continuous decrease in the pH of the solutions and a decrease in the degree of hydration of the sol. Thomas and Owens[67] have shown that the decrease in pH of the solutions when the sol is aged or boiled is due to a structural rearrangement.

The nature of the polymers (colloids) obtained at low acidities or present in dilute aqueous solutions of zirconium salts differs considerably from that of the polymers observed in strongly acidic media[24]. In the latter case the reaction readily becomes reversible. Even at high hydrogen ion concentrations, however, solutions containing zirconium, when allowed to stand for a prolonged period, contain polymers whose formation is not readily reversible and which have the same properties as the polymers obtained at low acidities. For example, they are difficult to convert to compounds extractable by various organic solvents. Larsen[24] has related the difference between these two forms to their particle size.

Lister and McDonald[42] used ^{95}Zr to study spontaneous diffusion in a 0.1 M solution of zirconium in nitric acid and established that in the HNO_3 concentration range 0.02–6 M the molecular weight of the polymers decreases by a factor of approximately 6. From ion-exchange data, these authors conclude that in 6 M HNO_3 the size of the zirconium ions is not greater than 4–6 Å. The zirconium cations contain nitrate ions in addition to OH^-.

The state of zirconium in neutral and acidic aqueous solutions. The properties of freshly prepared solutions of normal and basic zirconium salts differ sharply from those of the aged or boiled solutions. The former give no precipitate when sulphuric acid or soluble sulphates are added, whereas the latter form persistent precipitates. From the freshly prepared solutions, alkali metal tartrates and oxalates precipitate zirconium salts which are readily soluble in an excess of precipitant, whereas in the case of the aged or boiled solutions the precipitates do not redissolve. The hydroxide precipitated from the boiled solution has a different composition after drying at 100° and dissolves (is peptised) in aqueous zirconium chloride solution, whereas zirconium hydroxide obtained from the freshly prepared solution is insoluble in this solvent.

It is possible to distinguish arbitrarily three states of zirconium in neutral and weakly acidic aqueous solutions of its salts, depending on the temperature and time (for macroconcentrations). Solutions freshly prepared in the cold show many reactions characteristic of the relatively weakly hydrolysed and polymerised ionised zirconium, which is present predominantly, as will be shown below, in the cationic form (nitrates, halides, perchlorates). Solutions which have been allowed to stand for a short time, or solutions which have been extensively diluted, are characterised by a greater degree of hydrolysis and polymerisation, and this leads to the separation of such strongly basic products as Rodd's salt. Aqueous solutions of Rodd's salt differ from freshly prepared solutions in that they give precipitates when sulphate ions are added.

Boiling for a short period with hydrochloric acid converts it almost completely to basic zirconium chloride, indicating that the hydrolysis and polymerisation processes taking place during its formation are reversible. In solutions which have been allowed to stand for a prolonged period, or which have been boiled, irreversible rearrangement of the colloidal zirconium structure takes place, leading to the appearance of such stable compounds as Ruer's salt. The processes taking place in this case will be examined below. The unhydrolysed monomer can exist only in strongly acidic media.

The conversion of zirconium from one state to another is accompanied by the following phenomena: a change in the pH of the solution, with time, a change in viscosity, an increase in the degree of hydrolysis and polymerisation, conversion of the sol to a gel, the formation of non-extractable forms, etc.

The very marked influence of the conditions of preparation and storage of solutions of zirconium salts on their properties necessitates special methods for the preparation of solutions of monomolecular zirconium, particularly in work with radioactive isotopes.

Ayres[73] has shown by an ion-exchange method that 0.1 M zirconium nitrate solution is colloidal and has no clearly defined ionic character. In 1.5 M HNO_3, however, the cationic character of zirconium is retained for one month[75]. Contrary to the data of Benedict and Schumb[75], it has been reported, on the basis of a study of the adsorption of zirconium on cation-exchange resins[71,72,74], that solutions of tracer quantities of zirconium in 1 M HNO_3 and HCl are partly colloidal. In accordance with this, Schubert and coworkers[71,72,74] and Steinberg[76] recommend that zirconium be kept in 10 M HCl. They consider that only under these conditions does zirconium remain in the form of a monomeric cation. The storage of zirconium in concentrated acids to prevent hydrolysis and polymerisation is recommended by a number of authors[38,39,77].

Starik[78], however, suggests that the data of Schubert and coworkers can be explained by the formation, in moderately acidic media, of neutral molecules of the type $[Zr(OH)_x(NO_3)_{4-x}]^0$ whose existence has been established for the case of macroquantities of zirconium[42].

The cationic nature of zirconium in dilute hydrochloric, perchloric, and nitric acids, which have a weak complexing action on zirconium, is now generally accepted. The cathodic migration of zirconium in hydrochloric acid solutions was first observed by Becquerel[79], who electrolysed zirconium and ferric chlorides and isolated a film of zirconium crystals on the cathode. Ruer[6] studied the electromigration of zirconium in 0.5 M HCl and found 0.028 g of the metal on the cathode but only 0.0005 g on the anode. The existence of a singly-charged zirconium cation in weakly acidic solutions has been demonstrated by Hildebrand[80], Britton[21], and the Kurbatovs[45]. Laubengayer and Eaton[43] tried to reduce zirconium in hydrochloric acid solutions to the tri- and di-valent states. According to their data, aqueous solutions of the chlorides are complex in character, and in weakly acidic solutions the chief form of zirconium is a cation with Zr : Cl = 1. The cationic nature of zirconium in the range of at least moderate concentrations of acids and the presence of cationic forms in aqueous solutions of the normal sulphate have been shown by ion exchange[81,82], electrolysis[83-86], and other methods[46,87]. The existence of the hydrated cation $[ZrO(H_2O)_4]^{2+}$ has been reported by Hevesy and Wagner[88].

Repeated assertions in the literature that anionic forms of zirconium exist in aqueous solutions of the chlorides and nitrates, or in weakly acidic (HCl, HNO_3) solutions, have not subsequently been confirmed experimentally. Adolf and Pauli[29] tried to establish the composition of the equilibrium solutions of basic zirconium chloride. According to their data, measurements of the pH of the solutions and study of electromigration indicate the presence of ions of two types: the cations $[2Zr(OH)_4.ZrOCl_2.ZrO]^{2+}$, $[Zr(OH)_4.ZrO]^{2+}$, $[2Zr(OH)_4.ZrO]^{2+}$, etc., and the anions $[Zr(OH)_2Cl_4]^{2-}$, $[Zr(OH)_4Cl_2]^{2-}$, etc. An interesting feature is that in these formulae the authors introduce hydroxyls as well as zirconyl groups; none of the anionic forms assume the zirconyl structure.

Sidgwick[64] and Weiser[51] consider, however that Adolf and Pauli's conclusions[29] regarding the existence of anionic forms of zirconium under the conditions described are contradictory to other data, particularly the data of Ruer[6,13,14] and Britton[21], and that the source of their errors is sol formation and the extremely high adsorptive power of the sols.

In this respect Blumenthal's work is significant. In 1949 Blumenthal[16] detected the existence of the $[ZrO_2Cl_2]^{2-}$ ion during the conductimetric measurement of the pH of boiling aqueous solutions of zirconium chloride, and assumed that the zirconyl chloride is present almost entirely in the form of this complex. Nevertheless, no indications of the formation of such an acido-complex were found in subsequent papers[17,18].

The existence of negatively charged zirconium ions is possible only in strongly acidic media or in the presence of powerful complex-forming reagents. The anionic nature of zirconium, particularly in concentrated hydrochloric acid and nitric acid solutions, has been shown by ion exchange[89], extraction[32], and preparative methods[34]. In the presence of complex-forming reagents such as HF,[90,91] salicylate, citrate, tartrate, H_3PO_4,[92] and H_2SO_4,[93] zirconium for the most part forms negatively charged complexes.

Considerable anodic migration of zirconium in perchloric acid solutions at $HClO_4$ concentrations greater than 1 M was established by Lister and McDonald[42]. These authors noted that, in sulphuric acid solutions, zirconium migrates chiefly to the anode, but that in 0.5 *N* H_2SO_4 anodic migration takes place to a much smaller extent than was observed by Ruer[13] and decreases in the H_2SO_4 concentration range 1.5–3 *N*. Lister and McDonald pointed out that the rate of hydrolysis and polymerisation processes in zirconium salt solution is low, so that equilibrium in systems such as the perchloric, hydrochloric, nitric, and sulphuric acid solutions is established slowly over a period of many days or weeks, depending on the nature of the anion of the acid. For concentrations of the order of 0.1 M the authors give the following possible formulae for the state of zirconium in solution.

1. In perchloric acid solutions, with increase in acidity, colloidal $Zr(OH)_4$ is first converted to highly polymerised, positively charged ions and then to the dizirconyl ion $Zr_3O_3^{2+}$, which in turn is converted to the monomer $Zr(OH)_2^{2+}$ and to acido-complexes whose nature has not been established.

2. In nitric and hydrochloric acid solutions Lister and McDonald[42] identified a large number of ionic and molecular forms of zirconium containing nitrate or chloride ions: $Zr_3O_5^{2+}$ (or $Zr_4O_7^{2+}$) $\xrightarrow{HNO_3}$ $Zr_2O(OH)_4^{2+}$ $\xrightarrow{HNO_3}$ $\xrightarrow{HNO_3}$ $Zr(OH)_3^+$ $\xrightarrow{HNO_3}$ (at low zirconium concentrations) $Zr(OH)_2(NO_3)^+$ $\xrightarrow{HNO_3}$ $Zr(OH)_2(NO_3)_2$ and $Zr(NO_3)_2^{2+}$ $\xrightarrow{HNO_3}$ $\xrightarrow{HNO_3}$ $Zr(OH)_2(NO_3)_4^{2-}$ or $Zr(NO_3)_6^{2-}$.

3. In sulphuric acid solutions, in the H_2SO_4 concentration range $< 0.5\ N$, zirconium exists in both cationic and anionic forms, but in the H_2SO_4 concentration range $> 1.5\ N$ only neutral and negatively charged forms are assumed to be present. Similar results have been obtained by other workers[94,95].

On the basis of their studies, Lister and McDonald concluded that the Zr^{4+} ion does not exist, but Larsen and Wang[96] pointed out that this conclusion is erroneous. Subsequently, the Zr^{4+} ion was identified by a number of workers by extraction, ion exchange, and other methods (see below).

Contrary to the data of Lister and McDonald[42], Nabivanets[97] in a study of the electromigration of zirconium ions at a zirconium concentration 0.05 M, observed no significant migration of zirconium to the anode in perchloric acid solutions. He found that Lister and McDonald's error in the design of their experiment lay in the use of zirconium nitrate as starting material; this could lead to the formation in solution of mixed nitratoperchlorato anionic species. Nabivanets[97] established that in perchloric, hydrochloric, and nitric acids at $[H^+] \leq 0.5$ M, zirconium is present only in cationic forms. Increase in the perchloric acid concentration above 1 M leads to the appearance of anionic complexes, but the cationic species still predominate; the quantity of neutral complexes increases with increase in the $HClO_4$ concentration. The formation of anionic and neutral complexes is observed in hydrochloric and nitric acid solutions at $[H^+] > 0.5$ M. The quantities of cationic and anionic species become equal at HCl and HNO_3 concentrations 8–9 M and ≥ 4 M respectively.

Lister and McDonald's data[42], obtained for macroconcentrations, cannot be extended to solutions containing tracer quantities of zirconium. In the first place, at microconcentrations, no polymerisation takes place over a wide range of hydrogen ion concentrations[78], which simplifies considerably the identification of the ionic state of zirconium in solutions of perchloric, hydrochloric, and nitric acids.

The state of tracer quantities of zirconium in solution was studied by ion exchange and electrophoresis by Belyavskaya and Mu Ping-Wên[98], who found that hydrochloric acid solutions contain the $Zr(OH)_3^+$ ion at an HCl concentration $\sim 0.1\ N$, the $Zr(OH)_2^{2+}$ ion in the range 0.5–1.5 N HCl, and the $Zr(OH)^{3+}$ ion in 2 N HCl. In the case of nitric acid solutions in the HNO_3 concentration range 0.03–2 N these authors assume that positively charged zirconium ions predominate, and that neutral species are also formed. In sulphuric acid solutions, they observed considerable cationic absorption at an H_2SO_4 concentration 0.076 N, but in $\sim 4\ N$ solution the cationic absorption decreases sharply to zero and anionic absorption becomes fairly high. More acidic solutions apparently contain only negatively charged ions and neutral molecules. These assumptions were confirmed by electrophoretic data.

In agreement with Belyavskaya and Mu Ping-Wên, Yatsimirskii and Raizman[99] assume that the $Zr(OH)_3^+$ ion predominates at pH 1 in dilute solutions of the dichloride.

Starik[78] made a detailed examination of the state of radiozirconium ^{95}Zr in solutions. Comparison of the data of Starik[78] and coworkers with published data obtained in the study of the state of zirconium by different methods showed that in aqueous solutions at a concentration $\sim 10^{-11}$ M, depending on the conditions, zirconium may exist as simple and complex ions, neutral molecules, adsorption colloids (pseudocolloids) (pH 1.6–4), and true colloids (pH 4–12) of zirconium hydroxide.

4. COMPLEX FORMATION BY ZIRCONIUM IN AQUEOUS AND ACIDIC SOLUTIONS OF ITS SALTS

Complex formation with OH^- ions and polymerisation. Zirconium is a typical transition element with valence-electron configuration $4d^25s^2$, and its properties in aqueous solutions are determined by the electrostatic characteristics of the Zr^{4+} ion. The high charge, small radius, and comparatively low ionisation potential make it possible to classify Zr^{4+} among the electrostatic complex-forming ions[100].

In an examination of complex ions in solution it is necessary to take into consideration the fact that water molecules may also act as ligands, forming complex aquo-ions. In the formation of aquo-complexes a decisive part is played by ion–dipole interaction. For the formation of a stable complex with ionic bonding, it is necessary not only that the central ion have a high charge and small radius, but also that the ligand be able to satisfy conditions for ion–dipole interaction to a sufficient extent. Water has a considerable dipole moment and high electron affinity, and forms stable aquo-ions with Zr^{4+} characterised by ionic bonding[100].

The first task in the study of aquo-complexes should be the determination of the pH range in which they exist in the presence of anions which are not complex-forming agents.

Qualitative predictions of the hydrolytic behaviour of hydrated ions can be made on the basis of energetic characteristics. If the type of bonding is the same, in all cases the relative tendency of quadruply-charged ions to undergo hydrolysis should increase in the order

$$Th^{4+} < U^{4+} < Np^{4+} < Pu^{4+} \simeq Ce^{4+} < Hf^{4+} < Zr^{4+},$$

i.e. in the order of increasing ionic potential, f. The Zr^{4+} ion, which has the highest ionic potential ($f = 5$, $z = 4$, $r = 0.8$)[100,101] in this series, shows a clearly defined tendency to undergo complex formation with hydroxide ions. Theoretical calculations show that the equilibrium constant for the reaction

$$M(H_2O)_x^{4+} + H_2O \rightleftharpoons M(OH)(H_2O)_{x-1}^{3+} + H_3O^+,$$

should vary[101] from approximately 2×10^{-4} for Th^{4+} to 2.5×10^{-1} for Zr^{4+}, so that hydrolysed hydrated ions, particularly the Zr^{4+} ion, should be stable in solutions of dilute acid.

Recent experimental studies not only give qualitative data on the state of zirconium in solution over a wide range of hydrogen ion concentrations, but also make possible a quantitative characterisation of the hydrolytic and polymerisation processes.

Using different physicochemical methods, Starik and Skul'skii[102] studied the state of ^{95}Zr ($\sim 10^{-9}$ M) in nitric acid solutions. According to their data, zirconium exists in the following forms, depending on the pH of the medium: the monomers Zr^{4+} and $Zr(OH)^{3+}$ at pH < 0; the monomers $Zr(OH)^{3+}$, $Zr(OH)_2^{2+}$, $Zr(OH)_3^+$, and $Zr(OH)_4$ at pH 0–1; the monomer $Zr(OH)_4$ and polymers $[Zr(OH)_x^{4-x}]_n$ at pH 1.5–4; polymers $[Zr(OH)_4]_n$, colloidal, at pH 4–12; zirconates at pH > 12. Similar results were obtained for hydrochloric acid solutions in the hydrogen ion concentration range 0.1–2 M.[97]

Connick and coworkers[103,104] studied the hydrolysis and polymerisation of zirconium perchlorate at 25° by extracting ^{95}Zr with thenoyltrifluoroacetone and found that, at tracer concentrations in 2 M $HClO_4$, zirconium exists chiefly in the form of the monomer Zr^{4+}. In the range 0.2–2 M $HClO_4$ the mean composition of zirconium ions corresponds to the formula $Zr(OH)^{3+}$, and at $HClO_4$ concentrations less than 0.2 M to the formula $Zr(OH)_2^{2+}$. The equilibrium constant for the reaction[24]

$$Zr(OH)^{3+} + H_2O \rightleftharpoons Zr(OH)_2^{2+} + H^+,$$

is 0.187. Increase in the zirconium concentration leads to the formation of polymers. The concentration threshold for polymerisation is $\sim 2 \times 10^{-3}$ M in 2 M $HClO_4$ and decreases to 2×10^{-4} M at $[H^+] = 1$ M.

According to Paramonova and Sergeev's data[105], hydrolysis in solutions containing tracer quantities of zirconium begins at $HClO_4$ concentrations less than 1–1.2 M. Larsen and Wang[96] report that, at concentrations of the order of 10^{-4} M in 2 M $HClO_4$, zirconium exists chiefly as the Zr^{4+} ion[96].

Solovkin[32] used Connick and McVey's experimental data[103] to calculate the equilibrium constants for the successive reactions involved in the hydrolysis of the Zr^{4+} ion in $HClO_4 + LiClO_4$ solutions at an ionic strength of 2:

$$Zr^{4+} + H_2O \rightleftharpoons Zr(OH)^{3+} + H^+; \quad K_1 = 0.6 \pm 0.05,$$

$$Zr(OH)^{3+} + H_2O \rightleftharpoons Zr(OH)_2^{2+} + H^+; \quad K_2 = 0.24 \pm 0.03,$$

$$Zr(OH)_2^{2+} + H_2O \rightleftharpoons Zr(OH)_3^+ + H^+; \quad K_3 = 0.09 \pm 0.01,$$

$$Zr(OH)_3^+ + H_2O \rightleftharpoons Zr(OH)_4 + H^+; \quad K_4 = 0.068 \pm 0.006.$$

The values of the first and second constants agree satisfactorily with other published data[24,101].

Peshkova *et al.*[106] give the following values for the hydrolysis constants of the Zr^{4+} ion at tracer concentrations at an ionic strength of 1, maintained by $HClO_4 + NaClO_4$: $K_1 = 2 \times 10$; $K_2 = 0.87$; $K_3 = 0.45$; and $K_4 = 0.23$.

The constant for the hydrolysis of the Zr^{4+} ion according to the equation

$$Zr^{4+} + H_2O \rightleftharpoons ZrO^{2+} + 2H^+,$$

was estimated approximately ($K \simeq 2$)[107] on the basis of a study of the solubility of zirconium mandelate in $HClO_4$ solution. Pyatnitskii and Pilipyuk[107] postulated the existence of the ZrO^{2+} ion.

Quantitative data characterising the polymerisation process, which, according to Schultz and Larsen[108], takes place according to the equation

$$Zr_n(OH)_{nx}^{n(4-x)+} \rightleftharpoons nZr(OH)_x^{(4-x)+},$$

and the most probable forms of the polymers in dilute perchloric and hydrochloric acids have been given by Zielen and Connick[109] and Kraus and Johnson[110,111]. The latter[110] studied 0.05 M solutions of zirconium in the systems 1 M MCl + 1 M HCl, where M = Li, Na, and Cs, by means of an ultracentrifuge and detected only one form of zirconium, with an apparent degree of polymerisation equal to 3 and charge < 3. In solutions of 0.1 M HCl + + 1.9 M NaCl the degree of polymerisation varied in the range 4–5.4. Similar observations were made for $HClO_4 + NaClO_4$ solutions but in this case the charge on the polymers was higher.

Later[111] it was found that in 1 M HCl or $HClO_4$ the most stable species are trimers and tetramers, with a charge of ~ 1 per monomeric unit in the case of the solutions in HCl. Decrease in temperature from 25° to 5° leads to a considerable decrease in the degree of polymerisation of zirconium in 0.08 M HCl. Aging or heating increases the degree of polymerisation. In 5 M HCl the degree of polymerisation is < 2.

These results were confirmed by Zielen and Connick[109], who established that in 1 M and 2 M $HClO_4$ at 25°, in the zirconium concentration range $0.02–10^{-4}$ M, the chief forms are the trimer $Zr_3(OH)_4^{8+}$ and the tetramer $Zr_4(OH)_8^{8+}$. These authors[109], in agreement with Johnson and Kraus' data[111], found no evidence of the existence of dimers (the dizirconyl ion). This contradicts the results of Lister and McDonald[42] and imposes some limitations on their conclusions. The formation constants at 25° for the trimer and tetramer

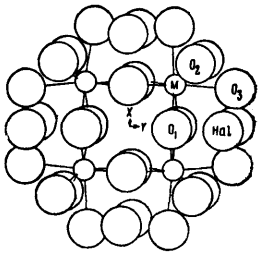
$$nZr^{4+} + xH_2O \rightleftharpoons Zr_n(OH)_x^{(4n-x)+} + xH^+,$$

at an ionic strength of 2 and hydrogen ion concentrations 1 M and 2 M were found to be $(2.4 \pm 0.3) \times 10^5$ and $(2.5 \pm \pm 0.4) \times 10^5$ for the trimer and $(2.0 \pm 0.2) \times 10^8$ and $(1.5 \pm \pm 0.2) \times 10^8$ for the tetramer, respectively.

This work[102–104,109–111] provides an experimental basis for a critical examination of existing views on the chemistry of zirconium in aqueous medium, particularly with regard to the statements that zirconyl and dizirconyl ions are the chief forms in which zirconium exists in aqueous solution. The incorrectness of these views is proved not only by the work cited, but also by X-ray diffraction studies of crystalline basic zirconium chloride and bromide[112] and their aqueous solutions[113], and by data on the dehydration of the basic chloride, whose composition, according to various workers[114], is represented by the empirical formula $ZrOCl_2 . 9(10)H_2O$.

There is no need to deal in detail with Clearfield and Vaughan's demonstration[112] that the structure of basic zirconium chloride is described by a formula including the tetramer $[Zr_4(OH)_8 . 16H_2O]^{8+}$, although this is of considerable interest from the viewpoint of the structural and preparative chemistry of zirconium. For an understanding of the phenomena taking place in aqueous solutions of zirconium salts, an X-ray diffraction study[113] of aqueous solutions of basic zirconium chloride and bromide is more important.

Aqueous solutions (2 M) of these salts were studied. The experimental data clearly indicate the existence, under these conditions, of $[Zr_4(OH)_8(H_2O)_{16}]X_8$, where $X = Cl^-$ or Br^-. The dichloride is more stable than the dibromide. Similar observations were made for hafnium halides. On the basis of these results, a structural formula is suggested (see Figure) for the "oxyhalides" of zirconium and hafnium in solution (for the latter, in the salt concentration range 0.5–2 M).



Structure of zirconyl chloride and hafnyl chloride in aqueous solutions[113]. [Here M = metal, O = oxygen, and Hal = halogen atom. Muha and Vaughan[113] comment that this structure for the hafnyl halides gives good agreement with X-ray scattering data but the agreement is not as good for zirconyl halide solutions and there may be more highly polymerised species in the latter (Ed. of Translation).]

An extremely unusual feature is that the chloride ions in the structure of the tetramer are not directly bound to the zirconium ion.

In the light of this work, the ideas of Larsen[24] and Connick and McVey[108] regarding the continuous polymerisation of zirconium in aqueous solutions§ in the range of concentrations of zirconium and hydrogen ions studied[109-111,113] are incorrect. It follows from the above that, depending on the metal concentration and acidity of the aqueous solution, zirconium may exist either in the form of monomers of general formula $Zr(OH)_x^{4-x}$, where $x = 0, 1, 2, 3$, and 4 (at a zirconium concentration of the order of 10^{-9} M and pH < 1.0) or in the form of the trimer and tetramer (at high acidities up to a zirconium concentration 2 M). The existence of an extended concentration plateau corresponding to polymer formation was noted by Lister and McDonald[42], but these authors did not determine the composition of the polymers and merely drew attention to their small dimensions. The average charges on the trimer and tetramer depend on the acidity, zirconium concentration, and nature of the anion of the acid. In perchloric acid solutions (1 M and 2 M) the average charges on one monomeric unit are 2.66 and 2.0 respectively (the degree of hydrolysis and polymerisation increases), but in 1 M HCl the charge is approximately equal to unity, and this is apparently due both to an increase in the degree of hydrolysis and to complex formation by the Zr^{4+} and Cl^- ions. In aqueous 2 M solutions of basic zirconium halides, the zirconium is present in the form of a neutral hydrated complex (tetramer). The trimer and tetramer (together with the monomer) are evidently the most stable forms of zirconium in aqueous solutions. Ions and molecules with a higher degree of polymerisation are observed only in the range of low hydrogen ion concentrations, or, what is essentially the same thing, in dilute solutions of zirconium salts. The latter feature, although it appears to contradict the ideas regarding the increase in the degree of polymerisation with increase in the zirconium concentration, is fairly simply explained: dilution of solutions of, for example, zirconium dichloride, leads to a decrease in the total concentration of hydrogen ions (despite the increase in the degree of hydrolysis), and this facilitates polymerisation (the concentration threshold of polymerisation is displaced towards much lower concentrations in the range of high pH values). This can be seen particularly clearly from a paper by Solovkin[7], who showed that, whereas 5 M solutions of the chloride with a Zr : Cl ratio = 1 : 0.35 are transparent and stable over a fairly prolonged period, the 0.5 M solutions show a marked opalescence and a tendency to deposit a gel. The retarding influence of hydrogen ion on polymerisation was observed by Britton[21]. The question of whether the polymerisation process under these conditions is stepwise or continuous has not been clarified.

The foregoing relates to solutions which have not been heated or aged. As already noted, heating or aging changes the properties of aqueous solutions of zirconium salts, and this has a significant influence on much of the work with zirconium.

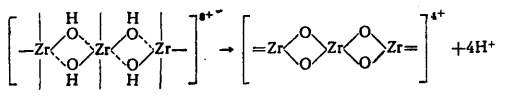
A theoretical explanation of the processes taking place when zirconium salt solutions are aged or heated has been given by Thomas[116,117], who found that zirconium salts in solution are condensed systems in which the metal atoms are joined by hydroxyl and (or) oxygen bridges to form polyatomic ions or molecules. The first stage in the condensation involves hydrolysis and the formation of hydroxyl bridges, accompanied by the liberation of the appropriate number of protons (olation). Here it is assumed that the formation of hydroxyl bridges involves the water molecules present in the first coordination sphere of the hydrated ion, for example according to the reaction (for the formation of the trimer)

$$3[Zr(H_2O)_x]^{4+} + 4H_2O \rightleftharpoons [Zr_3(H_2O)_{3x-4}(OH)_4]^{8+} + 4H_3O^+.$$

Increase in temperature or the duration of the aging process leads to further dissociation with the liberation of protons (oxolation):

$$[Zr_3(H_2O)_{3x-4}(OH)_4]^{8+} + 4H_2O \rightleftharpoons [Zr_3O_4(H_2O)_{3x-4}]^{4+} + 4H_3O^+.$$

When the hydrogen ion concentration in the solution is low, the rates of the olation and oxolation reactions increase. The first of the reactions is reversible (although the reactivity of the coordinated OH^- ions decreases in the olation process), whereas the second is difficult to reverse, particularly in the case of the zirconium oxide hydrosols. The condensed ions or molecules often contain the anions of the acid present in the solution. If the coordination sphere of the hydroxo- or oxo-compounds contains a sufficient number of anions, the complex acquires a negative charge (when an excess of soluble salts is added). The structural formulae of the condensed ions can be represented as follows:



The removal of two protons from the water molecule at the zirconium explains the appearance, under suitable

§ It has recently been found by dialysis[115] that the degree of polymerisation of zirconium in 2 M, 1 M, and 0.1 M solutions of $HClO_4$ increases continuously with change in the metal concentration from 1×10^{-3} M to 1×10^{-1} M, but these results, according to the authors are approximate, since the degree of hydration of the simple and, particularly, the polymeric forms of zirconium is unknown. Moreover, the retarding action of the membrane may be different for particles whose dimensions differ considerably.

conditions, of small but extremely stable species in strongly acidic media (probably the trimer or tetramer with oxygen bridges), whose formation cannot easily be reversed[24]. At high pH values further hydrolysis of the polymers takes place by the above mechanism, leading finally to an increase in the degree of polymerisation and dehydration (the mechanism of dehydration of basic zirconium chloride has been examined by Castor and Basolo[114]). The formation of Rodd's salt is apparently the first step in this direction. The properties of Rodd's salt show that the bond between the zirconium atoms in this case is formed chiefly by hydroxyl-bridges.

The theory devoloped by Thomas explains many of the properties of boiled or aged solutions of zirconium salts, described in detail above. In particular, it explains the formation and exceptional stability of Ruer's metazirconyl chloride and metazirconic acid, and also the chief properties of boiled or aged solutions, compared with freshly prepared solutions or solutions which have been allowed to stand for a short period.

Complex formation with other inorganic and organic ligands. It has been established[118] that the tendency to form complexes with zirconium, shown by the ligands normally used in chemistry, decreases in the following order: $OH^- > F^- > PO_4^{3-} > > C_2O_4^{2-} > SO_4^{2-} > NO_3^- > Cl^-$. It has also been noted[72] that HF has a much more powerful complexing action on zirconium than H_3PO_4 and, more particularly, H_2SO_4. The formation of complexes by zirconium with HF[31,38,71,115,119] and H_2SO_4[38,39,50,120-126] has been described.

Thomas and Owens[67] studied the influence of the addition of neutral potassium salts of various organic and inorganic acids on the pH of a zirconium hydrosol and showed that the ligands which they studied can be arranged in the following order: citrate > oxalate > malate > > tartrate > glycolate > succinate ~ malonate ~ maleate ~ ~ propionate ~ acetate ~ fumarate > formate > sulphate > chloride ~ nitrate.

Complex formation by zirconium with sulphuric, hydrofluoric, oxalic, malonic, succinic, glutaric, fumaric, maleic, orthophosphoric, orthoboric, metasilicic, acetic, and trifluoroacetic acids, and with hydrogen peroxide, was studied by Connick and McVey[103], who established that of these the most powerful complex-forming reagents are HF, $H_2C_2O_4$, and H_2SO_4. Acetic, orthoboric, succinic, and malonic acids have almost no complexing action on zirconium.

Connick and coworkers[103,104] made a detailed study of complex formation by zirconium with sulphate and fluoride ions in 2 M $HClO_4$ and showed that the complexes formed by zirconium with F^- ions are more stable than those formed with HSO_4^- ions. They obtained the following values for the successive reactions involved in the formation of complexes with F^- and HSO_4^- ions:

$$Zr^{4+} + HF \rightleftharpoons ZrF^{3+} + H^+; \quad K_1 = 63 \times 10^5,$$
$$ZrF^{3+} + HF \rightleftharpoons ZrF_2^{2+} + H^+; \quad K_2 = 2.1 \times 10^4,$$
$$ZrF_2^{2+} + HF \rightleftharpoons ZrF_3^+ + H^+; \quad K_3 = 6.7 \times 10^2,$$
$$Zr^{4+} + HSO_4^- \rightleftharpoons ZrSO_4^{2+} + H^+; \quad K_1 = 4.6 \times 10^2,$$
$$ZrSO_4^{2+} + HSO_4^- \rightleftharpoons Zr(SO_4)_2 + H^+; \quad K_2 = 53,$$
$$Zr(SO_4)_2 + HSO_4^- \rightleftharpoons Zr(SO_4)_3^{2-} + H^+; \quad K_3 = 1.$$

As can be seen from these equations, the authors did not assume the zirconyl structure for the complexes which they identified.

Complex formation by zirconium with sulphate ions was studied by Marov[127] by an ion-exchange method at an ionic strength of 2.33; he obtained for the equilibrium constants of the reaction

$$Zr^{4+} + i\ HSO_4^- \rightleftharpoons Zr(SO_4)_i^{4-2i} + iH^+ \quad (i \leqslant 3),$$

the values $K_1 = 466$, $K_2 = 3.48 \times 10^3$, and $K_3 = 3.92 \times 10^5$.

Nitrate and chloride ions have a weak complexing action on zirconium. The above data show that the tendency to form complex ions with Zr^{4+} is much less for Cl^- and NO_3^- ions than for sulphate and fluoride ions and many organic acids. According to Adamskii *et al.*[128], increase in the nitric acid concentration leads first to a decrease and then to an increase in the activity coefficients of zirconium. The nature of the change in the activity coefficients indicates that processes leading to an increase in the effective zirconium concentration (particularly as a result of extensive hydration) have a greater influence than ion association. All the quantitative calculations on complex formation in nitric and hydrochloric acid solutions refer to tracer quantities, *i.e.* to conditions under which polymerisation does not take place.

Connick and McVey[103] studied the extraction of zirconium nitrate and chloride by thenoyltrifluoroacetone at an ionic strength of 2 and found that the equilibrium constant K_1 for the reaction

$$Zr^{4+} + A^- \rightleftharpoons ZrA^{3+},$$

where A = Cl or NO_3, is equal to 2 in both cases. They pointed out that the values may be high, due to the presence of impurities. Later McKay[129] studied complex formation by Zr^{4+} with thenoyltrifluoroacetone in aqueous solution and obtained $K_1 = 0.59$ and $K_2 = 0.090$ (at an ionic strength of 4).

The values $K_1 = 2.2$, $K_2 = 1.3$ ($K_2 = 1.7$ is given by Paramonova and Sergeev[105]), $K_3 = 0.55$, and $K_4 = 0.15$ were obtained by Solovkin[32] from data on the extraction of ^{95}Zr by tri-n-butyl phosphate in $HNO_3 + HClO_4$ mixtures at a total hydrogen ion concentration 4 M. It was shown that the curve giving the dependence of the logarithm of the zirconium partition coefficient on the nitrate ion concentration in the hydrogen ion concentration range 3–4 M can be explained if it is assumed that under these conditions negatively charged $Zr(NO_3)_5^-$ and $Zr(NO_3)_6^{2-}$ ions, with formation constants $K_5 \simeq 0.03$ and $K_6 \simeq 0.02$, are formed. The existence of these complexes in the HNO_3 concentration range above 2.5 M was pointed out by Trofimov and Stepanova[130].

Marov[127], using an ion-exchange method, found for the stability constants of the nitrato-complexes of the Zr^{4+} ion the values $K_1 = 0.92$, $K_2 = 0.46$, at an ionic strength of 2, and $K_1 = 0.88$, $K_2 = 0.14$, at an ionic strength of 4.

Solovkin[32] used the data of Levitt and Freund[131], obtained at an ionic strength of 6.54, to calculate the constants for complex formation by the Zr^{4+} ion with chloride ions and obtained $K_1 = 8.4$, $K_2 = 21$, $K_3 = 32$, and $K_4 = 15$. He did not consider the possibility of the formation of acido-complexes under these conditions, although Alimarin *et al.*[132] and earlier workers (see above) proved the existence of negatively charged zirconium complexes by ion exchange, electrophoresis, and other methods. According

to Marov's data[127], the stability constants of the chloro--complexes of the Zr^{4+} ion are $K_1 = 0.95$, $K_2 = 0.12$, $K_3 = 0.07$, and $K_4 = 0.08$ at an ionic strength of 2, and $K_1 = 1.1$, $K_2 = 0.21$, and $K_3 = 0.05$ at an ionic strength of 4.

There are no quantitative data on complex formation by zirconium, at macroconcentrations with hydrochloric and nitric acids. Qualitative observations show that the formation of polynuclear ions and hydrosols containing the anions of the acid present in the solution are exceptionally widespread in the case of zirconium.

Perchloric acid is often used to maintain a constant ionic strength in the study of complex formation by zirconium in solution by various physicochemical methods, and it is usually assumed that the perchlorate ion does not react with Zr^{4+} ions. Lister and McDonald[42], Nabivanets[97], and others have shown, however, that zirconium forms acido-complexes with perchlorate ions even at fairly moderate $HClO_4$ concentrations. On the other hand, data on the extraction of zirconium from perchloric acid by tri-n-butyl phosphate show that reaction between zirconium and $HClO_4$ is also possible at low acidities[133,134]. In particular, Siekierski[134] pointed out that the tendency of the Zr^{4+} ion to form complexes with the ClO_4^- ion is greater than that of the rare-earth elements. Quantitative data on complex formation in perchloric acid solutions have been given by Rama Murthy and Patel[135], who studied the adsorption spectra of zirconium perchlorate and found that the instability constant of zirconyl perchlorate is 1.856×10^{-3}. The adsorption maximum for zirconium in perchloric acid solution was found to be close to 205 mμ, with $\log \epsilon = 1.05 \times 10^2$.

With oxalic acid and soluble oxalates, zirconium forms soluble complexes[76,76a], which do not contain zirconyl groups[136]: $Zr(C_2O_4)^{2+}$, $Zr(C_2O_4)_4^{4-}$, $Zr(C_2O_4)_5^{6-}$ (these complexes have been briefly described by Grinberg and Astapovich[137]). Complex formation with quinic, maleic, and sulphosalicylic acids[138] has been studied; it has been shown that complexes are formed with 2-nitroso-1-naphthol[139], chloranilic[140], citric[141,142], tartaric, malic, trihydroxyglutaric[127,142], ascorbic[40], diethylenetriaminepentaacetic[142a,143], and nitrilotriacetic acids and other polydentate ligands, and with ammonium carbonate[132]. Extremely stable complexes are formed in the reaction with ethylenediaminetetraacetic acid[144,145]. Many data on the use of complex-forming reagents in the analytical chemistry of zirconium have been given by Elinson and Petrov[40]. Grdenic[146] has shown by X-ray diffraction that the characteristic coordination number for zirconium complexes is 8.

The data given here on the ability of zirconium to form complexes with inorganic and organic ligands are not exhaustive, and the number of complexes which have been studied is fairly high. The chemistry of zirconium, including that in aqueous medium, is essentially the chemistry of complex ions and molecules. This is due to the high electrostatic field of the Zr^{4+} ion. The question of the chemistry of zirconium complexes, however, has not yet been specially dealt with in the literature.

5. PREPARATIVE CHEMISTRY OF ZIRCONIUM COMPOUNDS AND ITS RELATION TO THE CHEMICAL STATE OF ZIRCONIUM IN SOLUTIONS

Venable[12] has divided zirconium compounds into three main classes: the first consists of normal tetravalent zirconium salts, which are very few in number, the second consists of the zirconates, and the third and largest group consists of the so-called zirconyl salts and other basic products of hydrolysis of the normal salts. It would be no great exaggeration to say that if we exclude complexes isolated under conditions preventing hydrolysis, the chemistry of zirconium is the chemistry of complex hydrolysis products, which is undoubtedly related to its chemistry in aqueous solutions.

The complexity of the state of zirconium compounds in aqueous and acidic solutions and the variety of forms produced, depending on the concentration of metal and hydrogen ions, the presence of complex ligands, or change in temperature, method of solution preparation, order of addition of reagents to the solution, etc., all leave their mark on the preparative chemistry of zirconium. Descriptions have been given of a number of zirconium compounds which are surprising in their unusual composition, for example the ferrocyanides[147], or variety, or both, for example the sulphates[12,18]. In the chemistry of zirconium, many examples are known of non-reproducibility of individual experiments, and contradictory results have been obtained in experiments carried out under similar conditions. Many basic zirconium compounds, to which a definite composition has been attributed, are isolated in the solid state only when the conditions of acidity, temperature, time, etc., are strictly observed. All this makes it necessary to proceed with caution when dealing with the identification, as individual compounds, of the majority of basic products of hydrolysis of the normal salts, described in the literature, particularly for the sulphates, fluorides, etc.

Recent data on the composition of the iodates[7,93,148] and ferrocyanides[149] emphasise convincingly the decisive part played by the ionic state of zirconium in aqueous solutions in the precipitation of sparingly soluble salts, whose mechanism of formation involves chiefly interaction of the ions of the precipitant with all forms of the zirconyl ion present in the solution, and this for the most part leads to the formation of precipitates of indefinite composition, which depends on the concentration of hydrogen ions (*i.e.* on the degree of hydrolysis of the Zr^{4+} ion), the metal concentration (*i.e.* on the degree of polymerisation of the zirconium), the temperature, and the "age" of the solutions (*i.e.* on the structure of the zirconium ions). A characteristic feature of zirconium is thus the formation of precipitates of indefinite composition. This is shown not only in the case of sparingly soluble salts, but also, for example, by the readily soluble nitrates[59] and chlorides (Endemann[9], in particular, isolated compounds of the following empirical compositions: $Zr_3O_4Cl_4.xH_2O$ and $8ZrO_2.7HCl.xH_2O$, and Britton[21] obtained a basic chloride with a Zr : Cl ratio = = 1 : 1.73 by evaporating an aqueous $ZrCl_4$ solution).

In the case of the iodates and ferrocyanides there is no preferential formation of salts containing two equivalents of precipitant per zirconium atom. Moreover, it is found that aqueous solutions of zirconium dichloride or dinitrate, at concentrations < 0.01 M, generally give precipitates containing ~ 1.3 equivalents of precipitant per zirconium atom[148,150], and this suggests the existence, under these conditions, of polymers, possibly the trimer or tetramer, which are hydrolysed to a much greater extent than the trimer or tetramer identified by Zielen and Connick. Under the conditions of maximum hydrolysis[7] the usual products are precipitates with extremely varied values of the Zr : Cl ratio (in the range < 1). From acid solutions, potassium iodate gives precipitates in which the Zr : IO_3 ratio is close to 1 : 3 when a large excess of precipitant is present, and

precipitates containing 1–3 iodate groups per zirconium atom when the iodate concentrations are not too high. At a constant concentration of precipitant the number of hydroxyls in the precipitate is greater the lower the hydrogen ion concentration. With suitable control of the excess amount of precipitant, it is possible to obtain a solid phase of so-called definite composition. Precipitates of indefinite composition have been obtained by the reaction of zirconium with H_3AsO_4,[48] 8-hydroxyquinoline[47], etc. Zirconium hydroxyquinolinates of definite composition can be isolated only by precipitation from a medium containing a powerful complex-forming reagent, for example an oxalic acid medium[136].

An extremely interesting feature is that the existence of the trimer is confirmed by the data of Schmid[23], who attributed to the compound which he isolated the empirical formula $ZrOCl_2.HCl.xH_2O$ and in actual fact usually obtained a precipitate with Zr : Cl ratio $\simeq 1:2.7$. The formation of these precipitates at high acidity (concentrated hydrochloric acid saturated with gaseous HCl) and at high concentrations of metal in the solution can be explained only if it is assumed that the trimer is present¶.

In the absence of HCl the chief form of zirconium is the tetramer, and this explains the separation, in the solid phase, of compounds containing approximately two equivalents of precipitant per zirconium atom. Since the tetramer forms less soluble salts than the trimer (the solubility of zirconium salts usually decreases with increase in the basic character), the precipitates correspond to the composition of zirconyl chloride, if they do not undergo hydrolysis during washing with water or drying. Indeed, the fact that the tetramer predominates in acidic solutions of zirconium chloride explains the identification of the zirconyl ion. If alcohol or acetone, which decrease considerably the solubility of the chloride, are added to the solutions, precipitates of indefinite composition, like the iodate and ferrocyanide precipitates, are formed if the hydrogen ion concentration is sufficiently low. Similar results may be obtained at higher hydrochloric acid concentrations (in the presence of large quantities of acetone). In this case the precipitates contain more than two chlorine atoms per zirconium atom.

One of the reasons for the formation of precipitates of indefinite composition, particularly the double potassium zirconium iodates[148] or sulphates[153] is the slow rate of attainment of equilibrium in systems containing the liquid and solid phases. As a result of this, analysis of non-equilibrium precipitates, which are mixtures of indefinite composition, usually leads to the identification of a wide variety of compounds of unusual formulae. Moreover, since zirconium salts are readily hydrolysed when washed with water or weakly acidic wash liquid, it is easy to obtain low results for the concentration of precipitant ion present. The question of the influence of the acidity of the wash liquid on the composition of precipitates has been examined in detail for the case of the iodates[148].

It can thus be stated that the iodates and ferrocyanides are not exceptions to the general rule, and merely emphasise the main feature of the chemical behaviour of zirconium. The low solubility of these compounds, even in strongly acidic media, makes it possible to reveal more clearly the regular features of the chemical properties of zirconium. These are apparently common to all the known classes of compound, although they are not taken into account in the discussion of the results of preparative work on zirconium, as can be clearly seen for the case of the sulphates.

¶ The existence of the tetramer is also proved by data on the thermal analysis of zirconium and hafnium fluorides[151] and the existence of the trimer by data on the influence of excess precipitant on the composition of zirconium phosphates[152].

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Zirconium is an element with complex chemical properties, but despite some contradictory data the following general remarks may be made regarding the state of the element in aqueous and acidic solutions.

In the case of microconcentrations (10^{-9}–10^{-11} M ^{95}Zr) in solutions of hydrochloric, nitric, and perchloric acids considerable hydrolysis of the Zr^{4+} ion is observed at hydrogen ion concentrations less than ~ 2 M. Hydrolysis takes place in stages with the formation of hydroxo-cations of general formula $[Zr(OH)_x]^{4-x} (x \leqslant 3)$, the monomolecular hydroxide $Zr(OH)_4$, and mixed complex cations and neutral molecules of the type $[Zr(OH)_xA_i]^{4-(x+i)}$, where $(x+i) \leqslant 4$ and A = Cl, NO_3, and, apparently, ClO_4. In the hydrogen ion concentration range > 2 M, hydrolysis of zirconium is almost suppressed. Under these conditions, the products formed include not only complex cations and neutral molecules ZrA_i^{4-i} $(i \leqslant 4)$, but also negatively charged ions, the quantity of which increases in the $[H^+]$ range > 5–6 M. The analytical formulae of the acido-complexes of zirconium in solutions of strong acids have not been established, but preparative data indicate that, in the presence of weak complex-forming reagents such as HCl, HNO_3, and $HClO_4$, the formation of ions of only one type, $[ZrA_6]^{2-}$ is most probable. From the high value of the ionic potential of Zr^{4+}, it is obvious that the quadruply-charged zirconium ion and its complex ions are hydrated to a considerable extent in aqueous solutions. There are no quantitative data characterising the hydration. Colloidal zirconium (radiozirconium) has been detected at high pH values: adsorption colloids (pseudocolloids) in the pH range 1.6–4 and true colloids of zirconium hydroxide in the pH range 4–12.

In solutions containing macroquantities the chemical behaviour of zirconium is complicated by a number of reactions whose nature has been reliably established only recently. In aqueous solutions of normal or basic zirconium salts, hydrolysis increases with time and becomes much more intense with increase in temperature or on going from more concentrated to less concentrated solutions. In contrast to this, at constant hydrogen ion concentration in acidic solutions the degree of hydrolysis increases with increase in the zirconium concentration: for macroconcentrations 0.04–0.1 M, hydrolysed species are detected even in 4 M nitric acid.

These and other facts can be explained if allowance is made for the possibility of a number of hydrolytic reactions and olation and oxolation reactions.

The aquo-complexes and hydroxoaquo-complexes of zirconium, at suitable metal concentrations, react to form polymers. The first stage in this process, the removal of a proton from a water molecule of the aquo-complex (hydrolysis), is completed with the formation of OH bridging groups, each of which reacts with two zirconium atoms (unlike the bridging or olating groups, coordinated OH groups are joined to only one metal atom). The olation reaction takes place fairly slowly. It is favoured by increase in the metal concentration and temperature and, more particularly, by increase in the concentration of

alkali. Dilution (without significant decrease in the hydrogen ion concentration) or cooling of solutions of the bridged hydroxo-compounds reverses the process very slowly, *i.e.* the olation process decreases the reactivity of the coordinated OH groups. Dilution leading to a decrease in the hydrogen ion concentration, particularly at high pH values, facilitates the olation reaction. The hydroxo-groups readily form aquo-groups under the influence of hydrogen ions. The bridging hydroxo-groups react with hydrogen ions or are replaced by anions less readily, but nevertheless they do react slowly, so that the polymers of low molecular weight formed in quite strongly acidic media can be converted fairly rapidly, under suitable conditions, to simple hydroxoaquo-complexes or to aquo-complexes. The property of more or less ready reversibility is shown by zirconium salt solutions which have been allowed to stand in the cold for a short period, by very dilute solutions, or aged solutions which have been allowed to stand in the cold in acidic media.

The bridging hydroxo-groups give up a proton and are converted to oxo-groups rapidly on heating but extremely slowly in the cold. The compounds formed as a result of the oxolation reactions are extremely stable. The reversal of the oxolation process is extremely slow. In general, compounds with hydroxo-bridges are depolymerised more readily than oxo-compounds, since the protons react more readily with bridging hydroxo-groups than with oxo-groups. The extent to which oxolation proceeds is greatest in dilute solutions of zirconium salts at high pH values with heating, or in concentrated solutions.

In perchloric acid solutions containing 1–2 M $HClO_4$ and $\sim 10^{-4}$–0.02 M zirconium at 25° the olation process takes place in stages and is completed with the formation of the trimer $[Zr_3(OH)_4]^{8+}$ and the tetramer $[Zr_4(OH)_8]^{8+}$. There is no published proof of the existence of the dimer (the dizirconyl ion).

In hydrochloric and nitric acid solutions the compounds containing hydroxo-bridges are present in equilibrium with the ions in the solution, so that in systems containing even relatively weak complex-forming reagents, the charges on the trimer and tetramer are lower than those in perchloric acid solutions. The tetramer is the chief form in which zirconium exists in aqueous solutions of its dichloride at a salt concentration 2 M (and possibly at lower concentrations). In the absence of strong complex-forming reagents the trimer and tetramer containing hydroxo–bridges are converted to the oxo-forms, the conversion being rapid with heating and gradual in the cold. Anions which can enter the coordination sphere and replace hydroxo-groups prevent the formation of hydroxo-bridges, so that in solutions of powerful complex-forming reagents, zirconium appears to be present only in the monomolecular form, for example in oxalic acid media. The extent of the replacement of hydroxo-bridges by anions is determined by the relative concentrations of the reagents, the relative tendency of the anion to enter the coordination sphere, and the duration of aging of the solutions.

In weakly acidic media the olation and oxolation processes are not terminated with the formation of the trimer and tetramer, and proceed without interruption with the final formation of polymers of high molecular weight. In hydrochloric and nitric acid solutions, or when neutral salts with the same anion are added, a change in the charge of the complex ions may take place as the anion penetrates into the coordination sphere of the complex, or as the result of the adsorption of an excess of anions or cations by the large surface of the highly polymerised aggregate. Reversal in the sign of the charge is widely encountered in the case of zirconium oxide hydrosols, and is responsible for the "identification" of a number of non-existent zirconium compounds.

The olation and oxolation processes can take place not only in solution but also in the solid phase. Zirconium hydroxide freshly precipitated in the cold appears to be a complex of relatively low molecular weight, in which the ratio of the number of bridging hydroxo-groups to the number of oxo-groups may be fairly high. This hydroxide dissolves readily in acids. When the hydroxide is precipitated in the cold and allowed to stand for a prolonged period, or when the hydroxide is precipitated from hot solutions, the bridging hydroxo-groups are converted to oxo-groups. The oxides, in which the bridging hydroxo--groups are completely converted to the oxo-form, are quite inert.

The processes taking place in the solutions have a definite influence on the preparative chemistry of zirconium compounds. Published data show convincingly the decisive part played by the ionic state of zirconium in aqueous solutions in the precipitation of sparingly soluble salts, the mechanism of whose formation involves chiefly the reaction of the ions of the precipitant with all the ionic zirconium species present in the solution, and this leads for the most part to the formation of precipitates of indefinite composition, which varies according to the degree of hydrolysis and polymerisation of the zirconium ions and also their structure. Moreover, since washing of the precipitates with a hydrolysing wash liquid leads to replacement of the anions by hydroxo-groups, low results can easily be obtained for the quantity of precipitant anion present. A further reason for the formation of precipitates of indefinite composition is the slow rate of attainment of equilibrium in systems containing liquid and solid phases. The formation of precipitates of indefinite composition is observed not only in the case of sparingly soluble salts, but also in the case of the readily soluble chlorides and nitrates.

The above features of the chemical behaviour of zirconium explain the "identification" of a large number of zirconium compounds of unusual composition, particularly in the case of the sulphates, and the reliability of the analytical formulae for these compounds requires careful confirmation.

SUPPLEMENT

Work reported since the present review was written supplements the data in the main sections.

Zaitsev and Bochkarev[154], using a method involving the displacement of OH^- by fluoride ions, concluded that the zirconyl ion does not exist in aqueous solutions of zirconium salts. They consider that the zirconyl ion, ZrO^{2+} [together with $Zr(OH)_2^{2+}$], can exist only in solids.

Kharitonov and Buslaev[155] and Kharitonov and Rozanov[156] showed, from a study of the infra-red spectra of crystalline salts, that the Zr=O bond is not present in the following compounds: $ZrOCl_2.8H_2O$, $Zr_4F_{10}(OH)_6.3H_2O$, $ZrF_4.3H_2O$, $ZrF_4.H_2O$ (obtained by dehydrating $ZrF_4.3H_2O$), and $Zr_4F_{14}O$. According to their data, the following compounds contain the Zr=O bond: $Zr_4F_{10}O_3$, $ZrF_4.H_2O$ (obtained by dehydrating $HZrF_5.4H_2O$), $ZrOF_2$, $KZrOF_3.2H_2O$,

and $ZrO(NCS)_2.MNCS.2H_2O$ (where M = NH_4, K, Rb, Cs, or pyridine).

Singh and Banerjee [157] studied the precipitation of basic zirconium salts and hydroxide from solutions of the sulphate, chloride, and nitrate. Their data for the most part confirm Britton's conclusions[21]. Conductimetric and potentiometric (pH) titration of aqueous solutions of the salts with barium and sodium hydroxides gave basic salts of the following empirical compositions $Zr(OH)_{3.72}(SO_4)_{0.14}$, $Zr(OH)_{3.92}Cl_{0.08}$, and $Zr(OH)_{3.94}(NO_3)_{0.06}$.

The relationship between the chemistry of aqueous solutions of zirconium salts and the preparative chemistry of the element has been pointed out in a number of papers. Ionova and Tananaev[158] noted the influence of hydrogen ion concentration on the composition of zirconium ferrocyanides and confirmed that normal zirconium ferrocyanide can be precipitated only from acid media. Karlysheva and Sheka[159] isolated zirconium cupferronates of variable composition, depending on the concentration of acid in the zirconium salt solutions, the method of preparation, and the time for which the solutions were kept.

Babko and Gridchina[160] studied the influence of the state of zirconium in different media on the rate and extent of the reaction of zirconium with xylenol orange.

New data on the values of the successive instability constants of fluoro-complexes of zirconium have been given by Buslaev[161].

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