ELSEVIER

Coordination Chemistry Reviews
149 (1996) 33–57

COORDINATION
CHEMISTRY
REVIEWS

The experimental determination of thermodynamic properties for aqueous aluminium complexes

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Received 23 January 1995

Contents

Abstract

Based on the use of thermodynamic data, chemical modelling offers a unique technique to predict and understand the behaviour of aluminium in aquatic systems. In this paper we describe the necessary precautions that must be taken to evaluate these thermodynamic data with the highest accuracy possible. The review is mainly concerned with the practical side of equilibrium studies and it puts a certain emphasis on the need for an unbroken chain from accurate solution preparation, via high quality measurements, to an unbiased data evaluation.

SSDI 0010-8545(95)01153-6

In the paper we also discuss how these thermodynamic data change with changes in ionic strength and temperature.

Keywords: Al complexes; Aquatic chemistry; Thermodynamic data; Potentiometry; ^{27}Al NMR; Equilibrium analysis; Chemical modelling; Medium effects; Temperature effects

1. Introduction

The present great interest in the aquatic chemistry of aluminium(III) originates to a large extent in the extensive use of acidifying fossil fuels. Through this use, soil and water pH values have decreased in large areas with poorly buffering (aluminosilicate) bedrocks, and as a consequence a dramatically increased mobility of aluminium has resulted [1].

Although aluminium was previously regarded as a relatively innocuous element, it has recently been found that certain aquatic forms appear to be a very serious threat to aquatic life [2]. However, it has also been found that although the Al^{3+} ion and hydrolytic complexes thereof predominantly cause fish death [3] and root damage [4] at low concentrations, the toxic effects greatly diminish if the metal ion is bound to an organic ligand or to an inorganic ligand other than the hydroxide ion [3–5].

Through the increased mobility of aluminium in natural waters, its exposure to man has also increased during recent decades, and today it is believed that aluminium plays a toxic role in several human diseases and disorders [6]. Here also the chemical form in which aluminium is administered seems to be of utmost importance for its bioavailability [7,8]. However, in contrast to the observation made in aquifers, the chemical forms most susceptible to biouptake seem to be certain soluble, net-neutral organic complexes that are able to cross cell membranes via a passive diffusion mechanism [9].

These two examples can serve as clear illustrations that, to understand the specific toxicity of aluminium in a given application, a knowledge of its chemical speciation is a prerequisite. The characterisation of an aquatic trace metal system in terms of its chemical speciation can in principle be executed in either of two significantly different ways.

The first approach, which is experimental, involves the application of a physicochemical separation procedure before analysis. By designing this procedure so that significantly different fractions of aluminium (e.g. “quickly reacting” [10] or “non-labile monomeric”, “labile monomeric” and “acid soluble” [11]) are analysed stepwise or by difference, estimates of the chemical forms of occurrence can be reached. There are three main drawbacks with this approach. First of all, most separation schemes in use today are purely operational, implying that no fundamental connection exist between the amount found in a given fraction and the actual chemical species which are accounted for. Secondly, because of reaction kinetics, time-dependent transfers between the fractions will inevitably take place unless the separation procedure is more or less instant. This poses a special problem to most manual separation schemes, since differences due to variations between the persons carrying out the determinations will occur. Finally, a third major drawback with this approach is that it lacks predictive capability. This implies that each determination will give a view of the actual situation but that nothing can be said about the consequences of a change in chemical conditions.

The second approach, which is more theoretical, involves the use of thermodynamic data, together with measured free or total concentrations of reacting components, to compute the equilibrium concentrations (or activities) of the various species. This approach is commonly named chemical modelling and is regularly performed through the use of a suitable computer program. In a review by Nordstrom and Ball [12], more than 50 computer programs capable of making chemical equilibrium calculations are described. Perhaps the most appealing features with this approach are (i) that few input data are needed and (ii) that the model has in it a predictive ability, i.e. the consequences of a change in input composition can be foreseen. There are, however, also major drawbacks with this approach. One of these concerns the assumption of chemical equilibrium and is likely to pose a problem if conditions are such that extensive dissolution or precipitation of a solid will occur. Another major problem concerns the validity and completeness of the thermodynamic data base (i.e. equilibrium model and/or equilibrium constants) on which the calculational result fully depends. It can thus be stated that there is a direct dependence between the validity of the results obtained from thermodynamic modelling and the quality of the underlying thermodynamic data base.

We have been working within the field of aluminium complexation for more than a decade (e.g. Ref. [13]), and the objective of the present paper is to share our experience and to present some guidelines on how to determine thermodynamic data experimentally for aqueous aluminium complexes. The review is mainly concerned with the practical side of equilibrium studies and it puts a certain emphasis on the need for an unbroken chain from accurate solution preparation via high quality measurements to an unbiased data evaluation.

2. Preparation of solutions

The evaluation of thermodynamic properties for an aqueous proton–metal–ligand system is generally based on a large number of experimental determinations of one or several measurable characteristics, occurring as a function of proton, metal and ligand concentration and proton to metal to ligand ratio. To prepare this series of solutions, the use of accurately standardised stock solutions is highly recommended. This use implies that individual weighing errors vanish, that analytical determinations of analyte and "dirt" can be made once and for all and that post-corrections of these quantities may be performed.

The proton source consist of two different solutions; a dilute strong mineral acid (i.e. H_3O^+) and a dilute strong base (i.e. OH^-). Of these, the latter solution must be stored in thick-walled plastic containers to avoid silicate contamination. It must also be protected from air to avoid contamination of carbon dioxide. Even with these precautions, longer storage times than approximately two weeks cannot be recommended. The preparation of the dilute mineral acid is suitably done from a concentrated high purity acid. To standardise the solution, titration against dried (80 °C) tris(hydroxymethyl)aminomethane (TRISMA base) is recommended. Commercial pellets of NaOH or KOH are inevitably contaminated with carbonate ions on their surfaces. The pre-preparation of a saturated NaOH solution ("oljelut", 50% NaOH and 50% H_2O) utilises the limited solubility product of Na_2CO_3 and makes it possible to reach a carbonate-"free" NaOH via filtration. The KOH is most suitably freed from carbonate via extensive washing in several portions of boiled, carbon dioxide free, distilled water. To standardise the hydroxide solution, titration against standardised mineral acid is recommended. The use of commercial NaOH or KOH ampoules cannot be recommended owing to the obvious risk of CO_2 contamination during storage.

The aluminium source can consist either of a salt with the desired anion or of a high purity metal foil which is dissolved in the desired strong mineral acid. The important point is, in both cases, that to avoid aging effects from aluminium hydrolysis and/or aluminium hydroxide precipitation, the solution must also be prepared to contain at least about 10^{-2} mol l^{-1} mineral acid. To standardise this solution with regard to its Al content, indirect titration with EDTA–$Pb(NO_3)_2$ and xylenol orange as indicator is recommended. The excess of mineral acid can be standardised through the use of potentiometric titration with strong base, but a prerequisite to avoid errors from transitory aluminium hydroxide precipitation is that the base additions are gentle, that the equilibration times between base additions are long and that the equivalent point is evaluated through the use of the Gran extrapolation method [14]. For this reason it is also recommended to standardise the anion content of the solution and to check this value against the value of $[H^+]+3[Al^{3+}]$.

The ligand generally consists of a weak acid and, depending on availability, purity, crystallinity, water solubility and so on, the acid or the corresponding base can be chosen. The standardisation of this solution is preferably combined with the determination of acidity constant(s) of the ligand. This means that the acidity constant(s) and the ligand concentration are simultaneously optimised on a series of potentiometric titration data and implies that the concentration determination is based on proton balance data. It is therefore vital that the resulting residuals from this optimisation are carefully checked in order to detect the presence of possible foreign protolytes ("dirt acids").

As will be discussed in the next section, an unbiased equilibrium analysis of a ternary system also necessitates an experimental area in which the activity coefficients of participating ions and molecules can be regarded constant. This is practically accomplished through the constant ionic medium approach [15], in which a high concentration (more than 10 times the equivalent concentration of the investigated compounds [16]) of an "inert" supporting electrolyte is added to all solutions under investigation. This high concentration implies that even relatively minor impurities in the electrolyte salt itself can cause substantial disturbances to the system under investigation. The purification and standardisation of this electrolyte with regard to its content of metal ions and protolytes are therefore of vital importance.

Once standardised, these few solutions can be used to generate solutions of any desired composition by volumetric mixing. To avoid transitory precipitates during this preparation, the order of mixing can sometimes be crucial. An analytically important aspect of the preparation is the use of volumes large enough so that the volume uncertainties do not add significantly to the uncertainties of the analytes.

3. Experimental constraints

The complete characterisation of an equilibrium system comprises (i) a determination of stoichiometry of species appearing in significant amounts and (ii) a determination of stability for species which appear as a function of (a) ionic strength, (b) temperature, and (c) pressure. A fundamental requirement for an equilibrium characterisation is thus to be able to define the actual species forming. As most methods for the study of equilibrium speciation are based on indirect macroscopic measurements, the process of equilibrium analysis must always be performed simultaneously with the equilibrium stability determination.

Written in a general way, the appearance of soluble complexes in an Al^{3+}–weak acid system can be described by the reaction

$$pH^{+} + qAl^{3+} + rH_nL \rightleftharpoons H_pAl_q(H_nL)_r^{p+3q} \tag{1}$$

and by

$$\beta_{p,q,r} = \frac{\{H_pAl_q(H_nL)_r^{p+3q}\}}{\{H^{+}\}^{p}\{Al^{3+}\}^{q}\{H_nL\}^{r}} = \frac{\gamma_{H_pAl_q(H_nL)_r}}{\gamma_{H^+}^{p}\gamma_{Al^{3+}}^{q}\gamma_{H_nL}^{r}} \frac{[H_pAl_q(H_nL)_r^{p+3q}]}{[H^{+}]^{p}[Al^{3+}]^{q}[H_nL]^{r}} \tag{2}$$

where {X} is the activity of X, γ_X is the activity coefficient for X and [X] is the concentration of X. The task is thus to evaluate significant (p, q, r) triplets and corresponding $\beta_{p,q,r}$ values from experimental data.

To be successful and scientifically convincing in such an analysis, a number of prerequisites must be fulfilled. First and perhaps obvious, the experimental data on which the analysis is based must be true equilibrium data. A necessary demand is thus that reversibility of the system has been certified (by measurements in formation as well as decomposition directions). Secondly, the subsystems underlying the system under investigation must be either well characterised (e.g. the acid–base properties of the ligand) through separate experiments or negligible (e.g. the metal ion hydrolysis) through the selection of suitable experimental conditions. Thirdly, as the equilibrium model is often based on indirect measurements, it must be evaluated from concentration ranges as broad as possible with regard to total metal ion and ligand concentrations, metal ion to ligand ratio and pH. Finally, it must be satisfactorily shown that the model presented really gives a good description of experimental data and that this model has been evaluated in an unbiased manner, i.e. that no other model gives a better fit to experimental data. If the equilibrium model is to be used for a specific purpose, e.g. modelling of biofluids or natural waters, it is, of course, also of vital importance that the model really could be expected to be valid under such conditions, i.e. at low ligand concentrations and near-neutral pH values.

An obvious complication in an equilibrium analysis of data collected in solutions of low ionic strength is the non-ideal behaviour of the dissolved species, i.e. the concentration-dependent activity coefficient values. Under these experimental conditions, the measured effects will be a simultaneous effect of γ values, β values and (p, q, r) triplets. Such data are therefore practically impossible to use for an independent evaluation of appearing stoichiometries. This problem can be circumvented by using the constant ionic medium method. In an early contribution from the Sille'n school [15] it was shown that, if a high and constant salt medium was added to the system under investigation, the activity coefficients of participating ions and molecules became practically constant. This was later shown to hold as long as the equivalent concentrations of the investigated compounds do not exceed about 10% of the salt medium concentration [16]. Depending then on whether mainly anionic or cationic complexes can be assumed to form in the system, the total cation or anion concentration of the medium can be chosen as being held constant, for example X mol Na(Cl) l^{-1} or Y mol (K)NO_3 l^{-1}. By using this approach, a concentration and ratio region is created in which the activity coefficients can be regarded as constant and, accordingly, in which the activities of participating species can be replaced by their concentrations. An experimental area is thus created where an unbiased search for the composition of resulting species can be performed. The obvious drawback with the approach is that the resulting equilibrium constants are only valid in the specific ionic medium chosen and that an electrolyte theory must be applied to obtain standard state thermodynamic data.

In the search for a thermodynamic model, it is highly recommended that the data are divided in subareas where (a) acid–base properties of the ligand, (b) binary metal ion–ligand complexes, and (c) ternary complexes can be successively evaluated. In the search of existing ternary complexes, access to a suitable least-squares computer program is a necessity (see Ref. [17] for references to suitable programs). By using such a program, the significance of evaluated equilibrium constants and the goodness of fit to experimental data is also readily obtained. With regard to the reliability of the evaluated thermodynamic model, it can be generally stated that it strongly increases with the width of the experimental region used for the evaluation. For this reason, the experimental data ranges should always be as broad as possible. It is always better to have a given number of data widely distributed in the experimental "space" than to have them as repeated checks for reproducibility or with small gradual steps in for instance pH.

The upper concentration limit in this "space" is regularly set by the maximum replacement of 10% of the ionic medium or, in other cases, by the solubility of the ligand. The lower limit is set by the loss of analytical precision either in solution preparation or in measurement. The upper limit with regard to the Al:ligand ratio is highly dependent on the complexation qualities of the ligand under study but is, in principle, set by the onset of slow hydrolytic reactions (hydrolysis and/or precipitation) of uncomplexed Al^{3+}. The lower limit is also highly system dependent and can be set either by the lower concentration limit for Al^{3+} as discussed above or by the dominance of pure binary proton–ligand effects in the measurable quantity.

4. Experimental methods of measurement

A basic requirement for any analytical method used to characterise a dynamic equilibrium system is that the measured quantity constitutes a well-defined sub-amount of the whole and that the measurement can be performed with a negligible disturbance of the equilibrium state. These measurements can be aimed at quantifying one or several of the free proton concentration, the free metal ion concentration, the free ligand concentration or, in cases when solid phases are formed, the total aqueous concentration of protons, metal ions and/or ligands. With spectroscopic methods, the measurements can also aim at determining the absolute concentration of one or several of the soluble complexes forming in the system. Among these different choices, the quantification of the free proton concentration by means of potentiometric measurements with the hydrogen or glass electrode is by far the most commonly employed technique. The major reasons for this popularity are the wide range of concentrations that can be studied (about 10–12 orders of magnitude) and the relative ease with which the measurement can be performed

Because of the very negative reduction potential of Al(III), and the absence of electrons with energy transfers in the UV–visible range, many of the experimental methods normally employed for metal ion measurement, such as polarography, ion-selective electrode measurements and light spectrophotometry, are not applicable to the Al^{3+} ion. These methods can of course still be usable, but then as a result of suitable qualities of the specific ligand under study. According to our experience, the only spectroscopic method possible to use for the quantitative aluminium characterisation in a dynamic equilibrium system is the ^{27}Al nuclear magnetic resonance (NMR) technique.

In systems involving the formation or dissolution of solid phases, extended equilibration times (days to months) are generally needed and, for this reason, such systems are regularly studied through the use of batch suspensions. The equilibrated suspension can then be exposed to a solvent extraction step, for analysis of the total aqueous metal ion concentration, or to a physical phase separation step. After phase separation, the total concentrations remaining in the aqueous phase can be determined using a number of analytical methods. Correspondingly, the solid phase should be characterised both crystallographically (powder diffraction) and for size (BET-area or PCS-analysis) to detect possible particle size effects on the recorded solubility. The physical separation of the solid phase can be performed through centrifugation or filtration, but both methods are susceptible to errors from ultrasmall particles that can pass the separation step. At low aqueous concentrations, the filtration method might also introduce errors due to filter adsorption. Other often overlooked problems in systems involving solid phases are the occurrence of metastable surface phases and the adsorption of metal ions and/or ligands onto the surface of the solid, processes which are highly pH dependent. It can therefore be concluded that both the collection and the interpretation of such data are associated with severe difficulties.

Another type of experimental method is those aiming at measuring gross physical properties, such as conductivity or calorimetry. The use of conductivity as a measuring probe is, however, prohibited by the use of the constant ionic medium method, since the major contribution to solution conductivity is given by the ionic medium itself. Calorimetry, on the contrary, can suitably be used to determine the enthalpies (i.e. ΔH values) for the complexes which appear. According to our experience, these experimental data are not decisive enough to allow for an unbiased equilibrium analysis, i.e. for a simultaneous optimisation of (p, q, r) triplets, $\beta_{p,q,r}$ values and $\Delta H_{p,q,r}$ values. Therefore, a prerequisite for such a determination is that the speciation model, i.e. (p, q, r) triplets and $\beta_{p,q,r}$ values, has already been established by means of other measurements, most commonly those of potentiometric $[H^+]$ determination and quantitative ^{27}Al NMR determination.

4.1. Potentiometric titrations

As already mentioned, the potentiometric determination of free proton concentration by means of hydrogen or glass electrode measurements is by far the most commonly used technique for the characterisation of aqueous aluminium complexation systems. This is a technique which, combined with an automated titration and data collection system, makes it possible to collect a large amount of high precision data within a reasonable short time period. Critically important in this work is to minimise errors in the $[H^+]$ determination, and this puts constraints on the temperature control and on the measuring cell arrangement as well as on the electrode calibration procedure.

Since equilibrium constants in general are temperature dependent, a variation in temperature during measurement would naturally have a deleterious effect on the quality of recorded data. Of much higher significance, however, is the fact that the measuring electrode itself is highly temperature sensitive, both with respect to its absolute potential E_0 and with respect to its response to changes ("slope") in $[H^+]$. The sum of these effects is usually of the order of 1 mV $°C^{-1}$ [18] and it is therefore vital that the experiments are performed with a temperature control of at least ± 0.05 °C. To achieve this, and to avoid unstable readings due to fluctuating electrical field gradients, the use of an oil-thermostatted set-up and an immersion type of vessel is recommended. Commercial double-walled vessels used together with circulating thermostatted water are much more sensitive to temperature variations and reading instability and cannot be recommended.

The measuring cell arrangement can be divided into three key parts; the measuring electrode, the reference electrode and the liquid junction between the measuring compartment and the reference compartment. The primary standard for the H^+-measuring electrode is the hydrogen electrode [19] but the development of reliable, fast response, easy-to-handle glass electrodes has today drastically reduced their use. It should, however, always be borne in mind that the glass electrode is a secondary standard with a limited applicability and that, therefore, their response should be examined frequently. The best way to do this is to perform a potentiometric titration in which the responses of one or several glass electrodes are matched against the response of the hydrogen electrode. By preparing an acidic solution containing equimolar concentrations of several buffers, as a suggestion phosphoric acid, acetic acid and boric acid, and titrating with strong base, quite a broad $-\log[H^+]$ range can be covered. From this titration deviations from theoretical slope and highest correctly measured $-\log[H^+]$ for each glass electrode can be readily identified. In the every day use, it is highly recommended always to use two glass electrodes simultaneously and to monitor the difference between their responses. This usage will immediately reveal the onset of "misbehaviour" in one of the electrodes.

Since the potential of single electrodes cannot be measured directly, the potential difference, or e.m.f., between the glass electrode and a reference electrode is always determined. Next to the hydrogen electrode, the silver–silver chloride (Ag/AgCl) electrode is probably the most reproducible and certainly the most reliable and convenient electrode. It can easily be prepared [20], has short response times and gives constant potentials within ±0.1 mV. This electrode is therefore the obvious choice for use as reference electrode. There are in principle two different ways in which this electrode and the glass electrode can be interconnected to form a galvanic cell: (i) a chemical cell without liquid junction, in which both electrodes are immersed in the same solution, and (ii) a cell with a liquid junction, in which the two electrodes are in contact with two different solutions but connected through a salt bridge. Since an obvious prerequisite for obtaining a stable and constant potential from the Ag/AgCl electrode is that the surrounding solution contain a stable and constant concentration of Cl^- (or Ag^+), the second alternative is by far the most commonly used. At the liquid junction then, in which two solutions of different composition join, diffusion of ions will occur and, as a consequence, a liquid junction potential E_j is formed. The e.m.f. of this cell can thus be written:

$$E = E_+ - E_- + E_j \tag{3}$$

where E_j is the potential caused by the diffusion of ions across the liquid junction. It is therefore vital that this liquid junction is constructed in such a way that predictable and reproducible potentials are obtained. We have found that the half-cell of the so-called "Wilhelm" type [21] (Fig. 1) is more or less ideal in this respect. The junction potential of this cell has been found to be in fair agreement with the values predicted by the simple Henderson equation [22] and accurate expressions for its ionic medium dependence, with respect to H^+ and OH^- ions, have been experimentally determined [15,23]. The complete cell arrangement can therefore be written:

$$- \text{ Ag/AgCl} \mid I \text{ mol NaCl l}^{-1} \mid \; \mid \begin{array}{c}\text{equilibrium}\\ \text{solution}\end{array} \mid \text{glass electrode } +$$

where I denotes the concentration of the background medium.

The e.m.f. of this cell (expressed in millivolts) can, at 25 °C and with the application

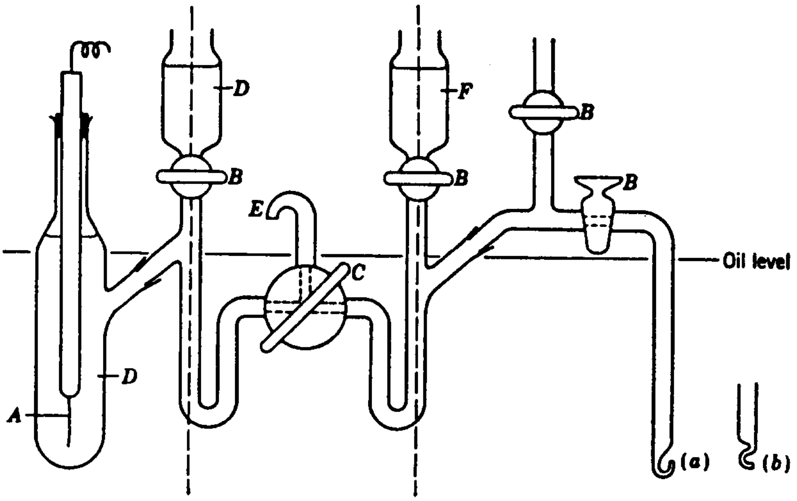

Fig. 1. “Wilhelm”-type reference half-cell with liquid junction (the parts outside the broken lines may conveniently be bent perpendicular to the plane of the paper): A, Ag/AgCl electrode; B, two-way stopcocks; C, three-way stopcock; D and F, 1 mol NaCl l^{-1} (these solutions may be of different compositions with D containing a well-defined Ag^+ or Cl^- concentration and F the chosen ionic medium); E, to waste; (a) J-shaped liquid junction; (b) S-shaped liquid junction. Reproduced by permission of McGraw-Hill Publishing Co.

of the constant ionic medium approach, be written as

$$E = E_0 + 59.157 \log [\mathrm{H}^+] + E_\mathrm{j} \tag{4}$$

The expression for the liquid junction potential E_j is [23]

$$E_\mathrm{j}\,(\mathrm{mV}) = -49.7I^{-1}[\mathrm{H}^+] + 21.4I^{-1}K_\mathrm{w}[\mathrm{H}^+]^{-1} \tag{5}$$

where $\log K_\mathrm{w} = -14.013 + 1.022I^{1/2}/(1 + I^{1/2}) - 0.22I$, and K_w is the ionic product of water.

In comparison with the commercial “combination” glass electrode cell, this cell has two important advantages, both connected to the construction of the liquid junction. In the combination electrode, this junction consists of a semipermeable diaphragm which is continuously supported with fresh solution from the reference electrode compartment. This implies that a concentrated salt solution (most commonly 3 mol KCl l^{-1} or saturated KCl) is continuously added to the equilibrium solution, thereby altering both its volume and its salt content. It also implies that much of the diffusion gradients is moved from inside a thin stable capillary (cf. Fig. 1) out to the equilibrium solution itself. The result of this is that resulting liquid junction potential will be sensitive to external factors such as turbulence and stirring rate and therefore is neither predictable nor reproducible.

Good e.m.f. data are also dependent on good electrode calibration procedures. The application of the constant ionic medium approach implies, as indicated above, that a concentration scale with respect to H^+ (and other species) is used. Therefore, the calibration is regularly conducted through a series of e.m.f. measurements in solutions of known H^+ concentration. Since an internal calibration routine definitely is more reliable than an external routine (i.e. with separate calibration solutions), the recommended titration procedure is started with pure strong acid in the vessel. To this solution, then, 5–10 successive additions of strong base with intervening e.m.f. readings are made, until the solution is nearly neutralised. Since $[H^+]$ can be stoichiometrically calculated for each of these points, 5–10 calibration points are thus created and the apparatus constant E_0, cf. Eq. (4) above, can be evaluated as the mean of these measurements. After that, the desired volumes of ligand and/or Al^{3+} solution are added to the vessel, and the titration is continued. This procedure can be regarded as a general calibration routine but, depending on the actual system under study, it can sometimes be simplified. Thus, if the ligand exhibits negligible acid–base properties for $-\log[H^+] \leqslant 3$–3.5, it can suitably be present during the calibration. If, in addition, also the aluminium ion complexation is negligible below this point, the calibration is best performed in the presence of both metal ion and ligand.

At this point it should also be noted that, as an alternative to titrating with strong base, coulometry offers a very precise method to change the composition of the solution gradually. In this case, a second Wilhelm bridge equipped with an Ag foil is connected to the titration vessel and a Pt net is immersed into the solution. When an electrical current is passed through this cell (in the correct direction), protons will be reduced to hydrogen gas at the platinum cathode, while silver will be oxidised to silver ions and precipitate as silver chloride at the anode. Since the amount of reduced protons is equal to the amount of electrons passed through the cell and, since this amount can be calculated from the Faraday law, i.e.

$$n_{e^-} = It/(96\,485 \text{ A s mol}^{-1}) \tag{6}$$

this implies that highly controlled changes in H^+ content can be effected through accurate measures of electrical current and time. At our department, we have achieved this by connecting a high precision constant-current unit with an electronic timer. This equipment has been of great value to us, especially at low concentration titrations, since it also allows very small "additions" to be made with high accuracy. It should, however, be noted that a prerequisite for its use is that the ligand under study must not be reducible. Therefore, as a point of security, we always initiate the study of a new ligand with parallel strong base and coulometric titrations to certify that identical results are obtained.

4.2. *Quantitative ^{27}Al nuclear magnetic resonance measurements*

From the strict aspect of NMR receptivity, the ^{27}Al nucleus belongs to one of the ten most sensitive nuclei of the periodic table. This implies that, under favourable conditions, good signal:noise ratios can be obtained also from highly dilute (below 0.0001 mol l^{-1}) solutions [24]. Also, since ^{27}Al is a quadrupolar nucleus ($I = 5/2$; $Q = 0.149 \times 10^{-28}$ m^2), the relaxation times are generally short and this implies that high pulse repetition rates can be used without losing quantitative information from appearing resonances.

In fact, the major experimental shortcoming of ^{27}Al NMR is due to the appearance of complexes with extremely short relaxation times. These short relaxation times (i.e. efficient relaxation mechanisms) are connected to asymmetries (electrical field gradients) in the species causing the signal and are manifested as a signal broadening. Therefore, the reported linewidths of different aluminium(III) resonances range from a few hertz for highly symmetric octahedral or tetrahedral complexes up to linewidths so high that they easily pass the limit of detection [25]. An implicit problem with these wide and/or undetected signals is that the integrated area of detected signals does not correspond to the total Al(III) concentration in the sample. This is an obvious fact for undetected signals while, for broad but detected signals, it results from a partial relaxation during the dwell time between excitation pulse and data acquisition. Other, more operational, problems when dealing with NMR spectra containing overlapping broad and narrow resonances are to suppress the occurrence of baseline roll and to identify correctly the baseline position, tasks which are by no means trivial.

Because of these difficulties, one should always relate the ^{27}Al spectrum of an unknown sample to that of an external standard of known concentration and containing all Al in a single species with a narrow resonance line. By comparing the integrated area from this signal with the sum of the integrated area from the sample, conclusions with regard to "missing Al" can be drawn.

Furthermore, the absolute concentration of each resolved resonance can be evaluated. Also here overlapping resonances pose a difficult problem which, to some extent, can be solved using spectral deconvolution techniques. However, one resonance that is always discernible is the signal from free Al^{3+} and it can therefore be stated that ^{27}Al NMR, even in the worst case, always functions as an unique "ion-selective electrode" for Al^{3+} [26,27].

The best choice for the external standard is probably an acidic solution of aluminium perchlorate (e.g. 0.1 mol $Al(ClO_4)_3$ l^{-1} in 0.1 mol $HClO_4$ l^{-1}) (linewidth, 2 Hz for $Al(H_2O)_6^{3+}$) which might then also serve as chemical shift standard. Another standard in use is an alkaline aluminate solution but for this standard the resonance is broader (linewidth, 10 Hz for $Al(OH)_4^-$); its excess of alkali slowly dissolves Si from glass with the risk of aluminosilicate complex formation and the standard must be protected from contamination of atmospheric CO_2 to avoid $Al(OH)_3(s)$ precipitation.

There are in principle two ways in which the external standard can be applied. Either the time domain of the free induction decay (FID) is employed by calibrating the area of the reference FID for a given number of transients and spectral width (i.e. running the spectrometer in the absolute intensity mode) or the frequency domain is employed by arranging the standard in a capillary in the centre of the sample tube. The relative ratio between the two compartments can, in this second case, be determined by measuring the $Al^{3+}:Al(OH)_4^-$ integral ratio when the compartments are filled with the two standards described above and contain equal Al(III) concentrations.

It should also be pointed out, as an operational warning, that many of the modern NMR spectrometers have probes manufactured from an aluminium-containing ceramic material and that these solid state Al(III) ions give rise to a broad downfield resonance. Therefore, when working with samples containing broad signals, this resonance must be subtracted by running a blank sample or erroneous conclusions will be drawn.

5. Mathematical treatment of data

As the equilibrium analysis is initiated, a set of components defining the equilibria of the system has to be chosen. From these components a zero level is assigned above which the concentration conditions are given.

Since the Al(III) ion is a "hard" acid, it is most strongly bound to ligands with "hard" donor groups. Organic ligands which have been found to be very effective in binding Al(III) in aqueous solutions quite often contain basic alkoxide or phenoxide donor groups coordinating in a chelating mode (often with one or several carboxylate groups as neighbouring binding sites). These groups typically exhibit (logarithmic) protonation constants around 14 (alkoxide) and 10 (phenoxide) which implies that accurate values of these protonation constants are difficult to obtain from potentiometric titration data. This in turn implies that the fully deprotonated form of the ligand should not be chosen as a component because these uncertainties will then be included in the overall stability constants. Instead a protonated form of the ligand should be used which implies that formation constants $^*\beta$ defining reactions with displacement of protons will be determined.

5.1. Mass balances

The equilibria in an aqueous Al(III) system characterised by the components H^+, Al^{3+} and a ligand H_nL can be described by three general reactions:

$$pH^+ + qAl^{3+} \rightleftharpoons H_pAl_q^{p+3q};\quad \beta_{p,q,0} \tag{7a}$$

$$pH^+ + rH_nL \rightleftharpoons H_p(H_nL)_r^p;\quad \beta_{p,0,r} \tag{7b}$$

$$pH^+ + qAl^{3+} + rH_nL \rightleftharpoons H_pAl_q(H_nL)_r^{p+3q};\quad \beta_{p,q,r} \tag{7c}$$

where reaction (7a) refers to the aluminium hydrolysis, reaction (7b) refers to the deprotonation of the ligand and reaction (7c) refers to the formation of three-component complexes. The law of mass action and the conditions for the concentrations applied to these reactions give the following equations, where h, b and c are the "free" concentrations of H^+, Al^{3+} and H_nL respectively:

$$H = h + \sum p\beta_{p,0,r}h^pc^r + \sum p\beta_{p,q,0}h^pb^q + \sum p\beta_{p,q,r}h^pb^qc^r - K_wh^{-1} \tag{8a}$$

$$B = b + \sum q\beta_{p,q,0}h^pb^q + \sum q\beta_{p,q,r}h^pb^qc^r \tag{8b}$$

$$C = c + \sum r\beta_{p,0,r}h^pc^r + \sum r\beta_{p,q,r}h^pb^qc^r \tag{8c}$$

In the potentiometric titration, the total concentrations H, B and C of protons, aluminium and ligand respectively are generally known from chemical analysis, while h is measured by using a cell as described above.

The computational problem now involves a determination of sets of unknown (p, q, r) triplets and the corresponding equilibrium constants $\beta_{p,q,r}$ that "best" fit the experimental data. The recommended procedure here is to assume that the two-component systems (7a) and (7b) are exactly known (either from one's own results or from the literature) and that all effects above this level are caused by the three-component complexes. However, it is also recommended that a sensitivity analysis is performed in which the proposed equilibrium model is being tested against expected error limits of the subsystems as well as uncertanties in h, H, B and C.

A great number of computer programs are now available that are able to handle computational problems as outlined above [17].

5.2. *Formation curves*

It is sensible to process any exploratory set of measurements by some graphical methods in order to obtain a general view of the behaviour of the system. We can detect the presence of polynuclear or ternary complexes in this way and we can learn much about mononuclear systems from the shape of the formation curves.

Plots of formation curves are also useful for revealing errors. Random "bad" points can be discarded and plateaux at non-integral values of the formation curve indicate systematic errors which should be sought out and eliminated.

$Z(-\log[H^+])$ *curves*

In order to visualise the experimental data, $Z(-\log[H^+])$ curves can easily be calculated. Z is defined as the average number of H^+ bound per B (Z_B) or C (Z_C) and is given by the expression (cf. Eqs. (8))

$$Z_C = (H - h + K_w h^{-1})/C \tag{9}$$

A comparison between such Z_C curves in the absence and presence of Al(III) clearly reveals in what pH range and to what extent complexation with aluminium is significant. Furthermore, the formation of mixed hydroxo Al species also becomes obvious from many of these graphs. Good examples here are Al systems with the monocarboxylic acids [28,29], phthalic acid [30] and oxalic acid [31] (Fig. 2), all systems in which a deprotonation beyond the L^{n-} state can be observed.

$\bar{n}(\log[L])$ *curves*

To find out to what extent series of AlL_n complexes are formed, the calculation of $\bar{n}(\log[L])$ curves has been found to be most useful. This plot is often referred to as the 'Bjerrum plot" [32]. From experimental H, B, C, h data and known protonation constants of the ligand as well as K_w of water, $\bar{n}(\log[L])$ data can be calculated by using the expression

$$\bar{n} = [C - (H - h + K_w h^{-1})/Z_C]/B \tag{10}$$

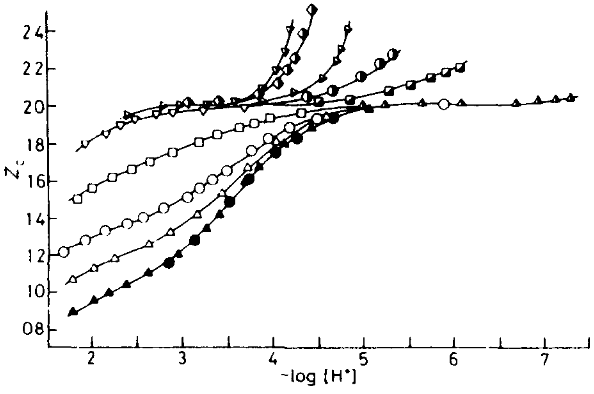

Fig. 2. Part of the experimental data in the H^+–Al^{3+}–oxalic acid (H_2L) [31] system plotted as $Z_C(-\log [H^+])$ curves. Z_C is defined as the average number of hydroxide ions bound per C.——, calculated from the set of proposed formation constants. Reproduced by permission of The Royal Society of Chemistry, UK.

(here, Z_C is defined as the average number of protons bound per C and H is calculated from the zero-level H_2O, Al^{3+}, L^{n-}).

Assuming now that only mononuclear binary (AlL_n) complexes are formed, it can be shown that these $\bar{n}(\log [L^+])$ plots will coincide independent of B and C. This will also be the case if homonuclear (Al_qL_n) species are formed, providing the 'free' Al^{3+} concentration is negligible. If binary or ternary hydroxo complexes are formed in significant amounts, deviations from the homonuclear curve will be observed (because the assumption above is no longer valid). This will also be the case if heteronuclear or protonated ($H_pAl_qL_r$) species are formed.

The formation of a series of prevailing mononuclear AlL_n complexes has been found in systems in which the ligand forms quite stable species with Al(III). Another prerequisite is that the ligand is present in excess to suppress the hydrolysis of aluminium and/or the formation of mixed hydroxo complexes. The weaker the complexes that the ligand forms, the higher the excess of ligand must be. This behaviour is evident from results obtained in several Al systems, e.g. with catechol [33], oxalic acid [31], methylmalonic acid [34] (Fig. 3), maltol and kojic acid [35] and several pyridones [36].

5.3. *Evaluation of the equilibrium model*

On the basis of the information obtained from the different types of formation curves, a strategy for the equilibrium analysis can be outlined.

From experimental $Z_C(-\log [H^+])$ data, protonation constants of the ligand can be evaluated (from data with $B = 0 \text{ mol } l^{-1}$). Furthermore, a determination of C as well as possible protolytic impurities of the ligand solutions can be characterised.

If coinciding $\bar{n}(\log [L])$ curves are obtained, the corresponding data set can be

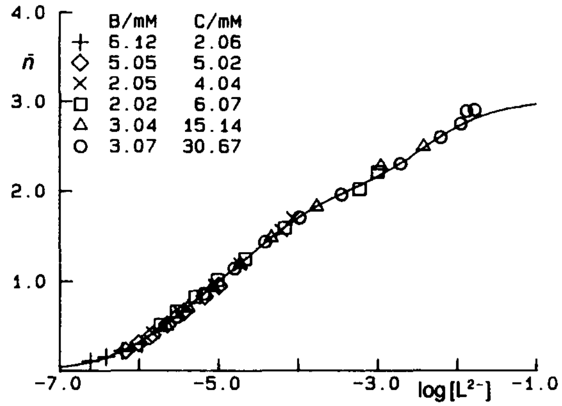

Fig. 3. Experimental data and calculated $\bar{n}(\log [L^{2-}])$ curve illustrating AlL_n ($n = 1, 2, 3$) formation with methylmalonic acid [34]. Reproduced by permission of Acta Chemica Scandinavica.

used to calculate composition and stability of complexes belonging to the series AlL_n (alternatively Al_qL_r).

The third step in the equilibrium analysis implies an interpretation of deviations from the "mononuclear curve" which are observed. Usually these deviations are found at low *C*:*B* ratios indicating the formation of mononuclear and/or polynuclear mixed hydroxo species (Fig. 4). The search for a model explaining these data can be performed by means of a procedure called *p*, *q*, *r* analysis. In this procedure it is assumed that, within a certain part of the data space, only one new complex $H_pAl_qL_r$ is formed and different combinations of *p*, *q*, *r* integers are systematically tested (involving a refinement of the corresponding formation constant $\beta_{p,q,r}$). That combi-

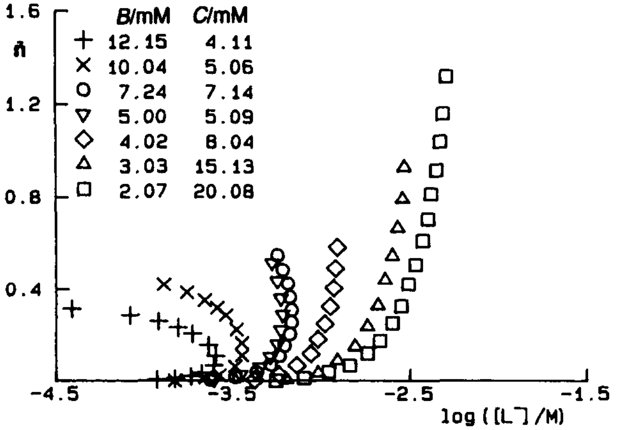

Fig. 4. Experimental data from the propionic acid [28] system plotted as $\bar{n}(\log [L^-])$ curves. An example of a system where no coinciding curves were obtained. Reproduced by permission of Acta Chemica Scandinavica.

nation giving the lowest error squares sum

$$U = \sum (H_{\text{calc}} - H_{\text{exp}})^2 \quad \text{or} \quad U = \sum (Z_{calc} - Z_{\text{exp}})^2$$

is considered to be the "best". This p, q, r combination may then be the true stoichiometry of the missing species, but it may also represent the best possible average composition of two or several coexisting complexes. It is therefore essential to examine carefully the resulting $\Delta H(-\log[\text{H}^+], B, C, C/B)$ residuals $\Delta H = H_{\text{calc}} - H_{\text{exp}}$ to see whether these are within experimental uncertanties or whether systematic deviations between experimental data and the equilibrium model still remain.

Instructive examples are found in several Al(III)–monocarboxylic acid systems [28,29], where one single complex, i.e. $\text{Al}_2(\text{OH})_2\text{L}^{3+}$, was found to dominate all experimental data (Figs. 5 and 6).

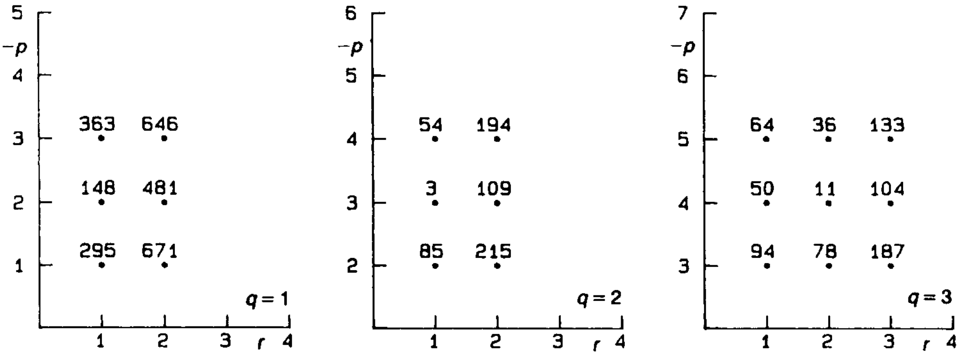

Fig. 5. Results of a p, q, r analysis using data from the H^+–Al^{3+}–propionic acid system [28]. The figures give error squares sums assuming one ternary complex. Reproduced by permission of Acta Chemica Scandinavica.

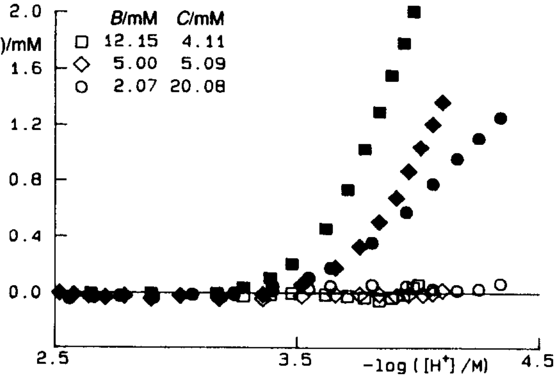

Fig. 6. Residual plot from the propionic acid system [28] showing the fit to experimental data with (open symbols) and without (filled symbols) the $-3, 2, 1$ ($\text{Al}_2(\text{OH}_2)\text{L}^{3+}$) species added to the speciation scheme. Reproduced by permission of Acta Chemica Scandinavica.

Sometimes, especially if the data space is too limited, two or more *p*, *q*, *r* combinations can be found to give an equally good fit to data. In the citrate system [37], the *p*, *q*, *r* analysis performed using a data set with $C/B \geqslant 2$, clearly indicated that a dominating species with an r/q quotient equal to 1 was formed. It was, however, impossible to judge whether the species formed was tri- or tetranuclear. As a consequence, complementary data were collected at $C/B=1$. On the basis of these new data, it was then possible to rule out the tetranuclear complex.

Often the additional complex cannot fully explain experimental data and systematic residuals $H_{\mathrm{calc}}-H_{\mathrm{exp}}$ (or $Z_{\mathrm{calc}}-Z_{\mathrm{exp}}$) still remain. The strategy for how to proceed in such a situation is not fully straightforward. A systematic testing of two or more *p*, *q*, *r* triplets implies a vast number of combinations if an unbiased search is aimed at.

Alternatively, the data set can be divided into smaller subsets defined by C/B ratios (or specified $-\log[\mathrm{H}^+]$ intervals) followed by new *p*, *q*, *r* analyses. In this way one complex at a time can be added to the speciation scheme as given by the different subsets. Finally, a covariation of all stability constants using the complete data set is necessary to verify a good fit within the whole data space.

As the formation of polynuclear mixed hydroxo complexes seem to be more of a rule than an exception in the presence of Al(III), the data evaluation becomes complicated. Quite often several models turn out to give comparable fits. The option of using some modelling program, e.g. SOLGASWATER [38], to find the "concentration window" in the data space, where the differences in calculated titration curves for the different models are greatest, is highly recommended. By performing additional measurements within this concentration window new possibilities to distinguish between different possible models are opened. An illustrative example is found in alkaline Al(III)–citrate solutions, as studied by Öhman [39] (Fig. 7).

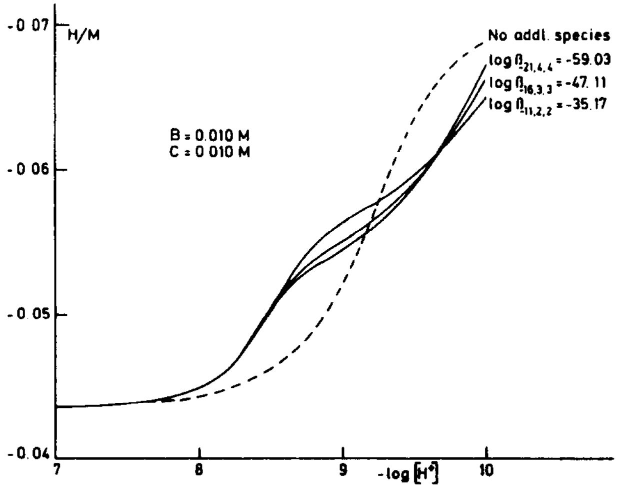

Fig. 7. Theoretical *H* vs. $-\log[\mathrm{H}^+]$ curves, with different polynuclear Al–citrate species assumed to be present [39]. Reproduced by permission of American Chemical Society.

A program such as SOLGASWATER should also be used to calculate theoretical $Z(-\log [\mathrm{L}])$ and $\bar{n}(\log [\mathrm{H}^+])$ curves to give a visual presentation of the model fit to experimental data. Such a program can also be used to give a qualitative and quantitative presentation of the speciation in the form of distribution diagrams or predominance area diagrams.

This program has also been used to calculate solubility products of different solid phases formed. In the oxalate [40] and phthalate [30] systems precipitation boundaries were characterised from pH and tyndallometric data. With tropolone [41], the solubility product of a highly insoluble $\mathrm{AlL_3}$ phase was determined. In all these systems manual least-squares calculations were performed in which the error squares sum

$$U = \sum (\mathrm{pH_{calc}} - \mathrm{pH_{exp}})^2$$

was minimised by systematically varying the solubility product according to a "pit mapping" procedure, described by Dyrssen et al. [42].

5.4. *Combined potentiometric and ^{27}Al nuclear magnetic resonance data*

Although the potentiometric titration method is one of the most powerful techniques available to study complicated equilibria, it is an indirect method and it seems advisable that some complementary method should be used whenever possible. NMR measurements have found many applications in this respect. By interpreting spectra in a quantitative way, the concentrations of different species can be directly obtained. In several complicated vanadium [43] as well as phosphorus [44] systems, combined potentiometric and NMR data were found necessary to enable an interpretation of the speciation schemes. Also, in several Al(III) systems quantitative ^{27}Al NMR data have been of great value. The possibility of measuring the concentration of "free" $\mathrm{Al^{3+}}$ has been utilised in several systems. For example, the stability constants of $\mathrm{AlHL^{2+}}$ and $\mathrm{AlL^{+}}$ in the oxalate system [31] could not be obtained with any accuracy from potentiometric pH data as these species are formed in too acidic solutions. However, on the basis of combined pH and quantitative ^{27}Al NMR data, good estimates of these constants were obtained. In a similar way, an unambiguous solution with regard to speciation and equilibria in the $\mathrm{Al^{3+}}$–$\mathrm{MoO_4^{2-}}$ system [45] (Fig. 8) has been presented. Validation of proposed models using the NMR technique has been successful in other Al(III) systems, i.e. with monocarboxylic acids [28,29] ascorbic acid [26] and lactic acid [46].

5.5. *Al(III) complexation to hydrous particle surfaces*

Over the last 15–20 years, the application of solution coordination chemistry concepts to describe the interaction of metal ions and inorganic–organic ligands at the particle–solution interface has been very successful. It is well known that functional groups such as —OH and —COOH on particle surfaces represent complex-forming donor groups which may coordinate metal ions or metal complexes from

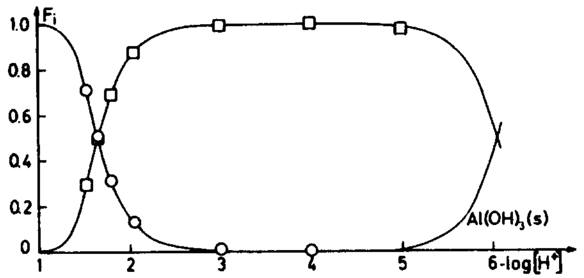

Fig. 8. Fraction of Al(III) in Al^{3+} (○) and $Al(OH)_6Mo_6O_{18}^{3-}$ (□) as a function of $-\log[H^+]$ at $B = 0.01$ mol l^{-1} and $C = 0.06$ mol l^{-1}. ——, proposed equilibrium model. Reproduced by permission of American Chemical Society.

the bulk solution. These donor groups may also be replaced by other coordinating ligands. Several types of surface species may be formed in this manner, e.g. binary and ternary metal ion complexes as well as ligands coordinated to the surface in bridging and chelating modes.

Collection and interpretation of experimental data from these heterogeneous systems follow very much the guidelines outlined above. A more detailed description of how to apply the potentiometric technique to study complexation reactions at the particle–solution interface is found in Ref. [47].

At present, very few studies have been published where Al(III) complexation to hydrous particle surfaces has been interpreted in terms of surface complexation models. Complexation at the surface of goethite (α-FeO(OH)) has been studied by Lövgren et al. [48]. The results reveal upon an adsorption edge around $-\log[H^+] = 4$ (Fig. 9). Furthermore, the formation of the surface species $\equiv FeOAl(OH)^+$ and $\equiv FeOAl(OH)_2$ were established. Recently, similar surface speciation models with montmorillonite and silica have been presented [49].

The sorption of Al(III) onto goethite in the presence of phthalic acid has also

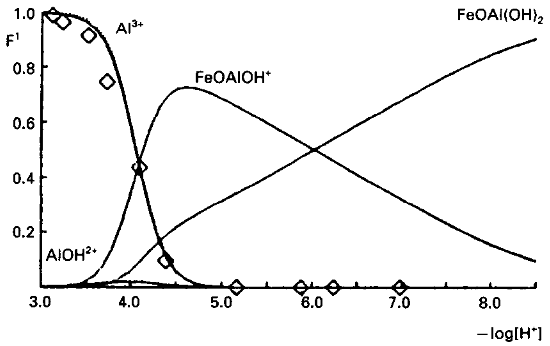

Fig. 9. Distribution diagram showing calculated distribution of aqueous and surface Al complexation. ◇, total concentration of Al(III) in solution as determined colorimetrically. Reproduced by permission of Elsevier Science Ltd.

been studied [50]. Here the equilibrium analysis showed formation of two surface species with $\equiv$FeOAlL and $\equiv$FeOAl(OH)L$^-$ stoichiometries. Thus, as in homogeneous solutions, Al^{3+} ions also tend to form mixed hydroxo species at particle surfaces.

6. The effects of ionic medium

A prerequisite for accurate speciation models, based on chemical equilibria, is access to reliable thermodynamic data. At present stability constants are frequently determined using the constant ionic medium method. A high electrolyte concentration is used to be able to keep variations of the activity coefficients at a minimum. Especially in systems where polynuclear complexes are formed and where the charge of the species are high, precise thermodynamic data can only be obtained provided an inert electrolyte of fairly high concentration (0.1 M and above) is used. Several good examples are found in aqueous Al(III) systems, e.g. the hydrolytic species $Al_3(OH)_4^{5+}$ and $Al_{13}O_4(OH)_{24}^{7+}$. The following questions now arise. How are stability constants obtained in media of constant and high ionic strength to be extrapolated to low ionic strength (e.g. $I = 0$)? How are stability constants obtained in a variety of ionic media of different ionic strengths to be correlated? Methods for estimating activity coefficients are of two basic types: those for low ionic strength solutions (0.1 M and below) and those for higher ionic strength solutions.

In the first category the Debye–Hückel assumption, stating that the deviations from ideal behaviour in dilute solutions are primarily caused by long-range electrostatic interactions, is frequently applied. Several methods based on the Debye–Hückel assumption are in use: extended Debye–Hückel, Guntelberg and Davies. Descriptions of these are found in many textbooks, e.g. Ref. [51], and are not outlined here.

The methods most frequently used for estimation of activity coefficients in concentrated electrolyte solutions with short range interactions are the ion association and specific ion interaction models.

The specific interaction theory (SIT) was introduced in 1922 by Brønsted [52] and later developed by Scatchard [53] and Guggenheim [54]. According to the SIT the activity coefficient γ_j of an ion of charge z_j in a solution of ionic strength I may be expressed by the equation

$$\log \gamma_j = -z_j^2 D + \sum_k \varepsilon(j, k, I) m_k \tag{11}$$

where

$$D = \frac{0.51 I^{1/2}}{1 + 1.5 I^{1/2}} \tag{12}$$

represents the Debye–Hückel term, and the summation extends over all the ions k present in the solution at the molarity m_k. The ε terms, the so-called interaction coefficients, are set to zero if the ions j and k are of the same charge sign. By using Eq. (11) one can make good estimates of ionic activity coefficients in electrolyte solutions as concentrated as 3–4 molal, provided that the interaction coefficients are known. Interaction coefficients involving simple ions can usually be determined from tabulated data of mean activity coefficients of electrolytes or from the corresponding osmotic coefficients. Interaction coefficients for complexes must be determined experimentally or estimated from the size and charge of the ion.

At present, only a few studies have been performed in which the medium dependence of Al complexation in aqueous solutions has been studied. This is somewhat surprising bearing in mind the great need for accurate thermodynamic data of relevance to natural water conditions ($I = 0.7$ M in sea-water; close to $I = 0$ M in fresh waters) as well as conditions of body fluids ($I = 0.17$ M). However, the hydrolysis of Al(III) has been studied in detail and some of the results reported will be commented.

Mononuclear hydrolytic species of Al(III)

Much of the confusion and conflicting evidence regarding the monomeric speciation of aluminium is a result of the sluggish formation and decomposition as well as the high stability of polynuclear complexes formed at low total Al concentrations. For instance, Furrer et al. [55] have shown that the Al_{13} polymer can form under conditions resembling those of soil waters. They also demonstrated that the solubility of aluminium(oxy)hydroxides such as gibbsite, boehmite and bayerite reveals solubility characteristics given by the mononuclear species $Al(OH)_n^{3-n}$, $n = 1$–4.

In a recent paper, Wesolowski and Palmer [56] presented a consistent model for the distribution of monomeric Al hydrolysis species and the solubility of gibbsite in 0–5 molal NaCl solutions in the 0–100 °C range. The data were modelled using the Pitzer ion interaction treatment [57] and the following pK[$Al(OH)_{n-1}^{4-n}$] values at infinite dilution (25 °C) were suggested: 4.94, 5.6, 6.7 and 5.6.

Polynuclear hydrolytic species of Al(III)

Hedlund [58] performed precise potentiometric studies of the medium dependence of the hydrolytic species $Al(OH)^{2+}$ and $Al_3(OH)_4^{5+}$ in Na(Cl) and Na(ClO_4) media of different ionic strength (0.1–3.0 mol l^{-1}). These measurements were performed in homogeneous Al solutions to allow the formation of polynuclear species to take place and were restricted to a pH range in which the formation of a precipitate could be neglected. By using the SIT approach stability constants valid at infinite dilution as well as interaction coefficients between the cationic species and Cl^- and ClO_4^- ions respectively were evaluated. In a similar way, the medium dependences for the ternary aluminium–hydroxo–carbonato species $Al_2(OH)_2CO_3^{2+}$ and $Al_3(OH)_3CO_3^{4+}$ were determined.

A comparison of the results obtained reveals that some regularities can be observed in the magnitude of the different ε_i values. Thus, by plotting the different ε_i values against the charge z_i of the different cationic complexes, approximately linear relationships were found. In Na(Cl) media $\varepsilon_i = 0.16z_i$ and in Na(ClO_4) media $\varepsilon_i = 0.33z_i$. This offers an opportunity to estimate interaction coefficients for cationic Al complexes for which direct experimental information is missing.

7. The effects of temperature

Changes in the temperature may have some significant influences on the equilibrium properties and cause spontaneous changes in aquatic systems. Aqueous equilibria may be shifted to the right or to the left by an increase in temperature. The direction and magnitude of the shift are given by the sign and magnitude of the heat of the reaction as a function of temperature. From the expression

$$\mathrm{d}\ln K/\mathrm{d}T = \Delta H_0/RT^2 \tag{13}$$

the approximate magnitude of change in $\log K$ per degree is 0.0029 ΔH at 0 °C, 0.0025 ΔH at 25 °C and 0.0021 ΔH at 50 °C.

The enthalpy changes accompanying complex formation can be obtained directly through calorimetric measurements, or indirectly from the temperature dependence of the stability constants via the van't Hoff equation (13).

The accuracy of ΔH values based on calorimetric measurements is generally higher than those based on the temperature dependence of $\log K$ values. However, many parameters influence the accuracy of calorimetric data, e.g. the enthalpy of dissociation of water, the dilution of heat etc. [59].

Application of the temperature dependence of $\log K$ generally requires the determination of very accurate stability constants over as wide range in temperature as possible. However, the wider the range employed, the greater the uncertainty in the calculated values, because of the temperature dependence of the enthalpy values. If the temperature dependence of the enthalpy values is neglected (i.e. $\Delta C_p = 0$), the stability constants for any temperature can be calculated by using the equation

$$\ln(K_2/K_1) = (\Delta H_0/R)(1/T_1 - 1/T_2) \tag{14}$$

Enthalpy and to some extent heat capacities have been reported for inorganic aluminium species with the ligands OH^-, F^- and SO_4^{2-}. These data are mainly derived from $\log K(T)$ data and have been critically evaluated by Nordstrom and May [60]. At present, data for organic aluminium species seem to be lacking.

8. Conclusions

This presentation has focused on some important details that have to be considered as an equilibrium analysis is undertaken by applying the potentiometric titration technique. As good experimental data often will outlive the researchers that produce them, great efforts should be made to collect data with as high quality as possible. This is often a time-consuming tough job but there are no short cuts in this respect.

We would like to stress the importance of the following points:

(i) The purity of reagents and solvents must be checked carefully. The concentration of possible "dirt acids" must be kept at a minimum and whenever necessary the solvent and reagents have to be purified.

(ii) The composition of the solutions with respect to the total metal and ligand concentrations should be varied within as wide ranges as possible.

(iii) Good e.m.f. data are dependent on good electrode calibration procedures.

The response of the electrode system has to be checked as described above and the reproducibility of liquid junction potentials has to be verified.

(iv) Reproducibility and reversibility criteria of the titrations have to be demonstrated. This is obvious to everyone but is frequently overlooked in practice.

(v) The search for the equilibrium model must be unambiguous. The search for the speciation scheme should be based on graphical and computerised methods.

(vi) The fit to experimental data should always be visualised as theoretical curves, e.g. $Z(-\log [H^+])$ or $\bar{n}(\log [L])$ plots.

(vii) As a service to the reader, speciation and equilibria should be visualised in the form of diagrams, e.g. distribution and/or predominance area diagrams.

(viii) Whenever possible the proposed equilibrium model should be validated by using some supplementary method.

Equilibrium studies of aqueous Al(III) systems are met with several difficulties. The Al^{3+} ion starts to hydrolyse in acidic ($pH \geqslant 3.5$) solutions, which complicates the calibration procedures. Furthermore, the sluggish formation of polynuclear species and different precipitation processes emphasise a careful and proper design of the experimental conditions. The interpretation of experimental data is not straightforward owing to the complexity of the speciation schemes frequently found. However, by sharing our experience and by following the guidelines listed above we hope that we have opened possibilities to tackle yet-unsolved complicated systems including the Al(III) ion.

Acknowledgement

The Swedish Natural Science Research Council is acknowledged for their financial support for the different Al(III) studies that have been undertaken at our department.

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