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Experimental determination of stability constants of aqueous complexes

Lars-Olof Öhman

Department of Inorganic Chemistry, Umeå University, Umeå, S-901 87, Sweden

Abstract

Based on the use of thermodynamic data, chemical modelling offers a unique technique to predict and understand the chemistry of metal ions in aquatic systems. This paper discusses the necessary precautions that must be taken to evaluate these thermodynamic data as correctly as possible. The presentation addresses the methodology to be employed in equilibrium studies, emphasizing the need for a continuum between accurate solution preparation, via high quality measurements, to an unbiassed evaluation of the data. The process of extracting a speciation model (i.e., stoichiometric compositions and corresponding equilibrium constants) from potentiometric data is described in some detail. Examples from the authors work with aluminium (III) and silicon (IV) chemistry, conducted at 25° C, are used to illustrate some important aspects. The paper finally advocates the use of graphical representations to visualize the importance of different appearing complexes. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The aquatic behaviour of most metal ions can be affected by a variety of competing reactions, such as hydrolysis, complexation, precipitation/dissolution, oxidation/reduction, and sorption/desorption at the surfaces of particles. Since these reactions change the speciation of metal ions, they control to a large extent both their toxicity and mobility in a natural system. Speciation is therefore of central importance when studying metal ion behaviour in natural aquatic environments, in which these reactions can all occur simultaneously, but to highly different extents under different conditions.

The problem of quantifying metal speciation can in principal be approached by means of two different techniques: direct experimental measurements or computerized chemical modelling. The first technique, which involves the application of physicochemical separation procedures, is generally purely operational, sensitive to re-equilibrations during measurement and lacks predictive capability.

The second approach assumes an equilibrium state and uses a set of thermodynamic data, together with input concentrations (free or total) of reacting components, to compute the equilibrium concentrations (or activities) of the various species. The most appealing features of this technique are that (i) only a few input parameters are needed and (ii) effects of a change in input conditions can be foreseen. The technique, however, relies heavily on the assumption of equilibrium and on the validity and completeness

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of the thermodynamic database, i.e., on the equilibrium model and/or the equilibrium constants. The validity of the results obtained from these calculations, are therefore, directly correlated to the quality of the underlying thermodynamic database.

This article focuses on how to determine these thermodynamic data as accurately as possible. The actual experimental data discussed are predominantly ion-selective electrode data, and therefore, restricted to low temperature systems, but the mathematical procedures to extract an accurate equilibrium model can easily be adapted to other types of measurements also.

2. Mathematical formalism

Written in a general way, the appearance of soluble complexes in a metal ion–ligand equilibrium system can be described by the reaction:

$$p\mathrm{H}^+ + q\mathrm{Me}^{z+} + r\mathrm{H}_n\mathrm{L} \rightleftarrows \mathrm{H}_p\mathrm{Me}_q(\mathrm{H}_n\mathrm{L})_r^{p+qz} \qquad (1)$$

which obey the law of mass action:

$$\beta_{p,q,r} = \frac{\left\{\mathrm{H}_p\mathrm{Me}_q(\mathrm{H}_n\mathrm{L})_r^{p+qz}\right\}}{\{\mathrm{H}^+\}^p\{\mathrm{Me}^{z+}\}^q\{\mathrm{H}_n\mathrm{L}\}^r}$$

$$= \frac{\gamma_{\mathrm{H}_p\mathrm{Me}_q(\mathrm{H}_n\mathrm{L})_r}}{\gamma^p_{\mathrm{H}^+}\cdot\gamma^q_{\mathrm{Me}^{z+}}\cdot\gamma^r_{\mathrm{H}_n\mathrm{L}}}$$

$$\times \frac{\left[\mathrm{H}_p\mathrm{Me}_q(\mathrm{H}_n\mathrm{L})_r^{p+qz}\right]}{[\mathrm{H}^+]^P[\mathrm{Me}^{z+}]^q[\mathrm{H}_nL]^r} \qquad (2)$$

and in which $\{X\}$ is the activity of 'X', γ_X is the activity coefficient for 'X' and $[X]$ is the concentration of 'X'.

This mathematical formalism of describing complex metal–(in)organic ions and molecules in terms of a minimum number of reacting components may, at first sight, seem artificial but it greatly facilitates data analysis and computer modelling. If we consider a specific system, e.g., the system H^+–Al^{3+}-methylmalonic acid (ethane-1,1-dicarboxylic acid, $\mathrm{H}_2\mathrm{L}$), it was shown (Marklund and Öhman, 1990) that three dominant species characterized the system; AlL^+, AlL_2^- and AlL_3^{3-}. With the choice of H^+, Al^{3+} and $\mathrm{H}_2\mathrm{L}$ as reacting components, the formation of these species should be written:

$$\mathrm{Al}^{3+} + \mathrm{H}_2\mathrm{L} \rightleftarrows \mathrm{AlL}^+ + 2\mathrm{H}^+ \qquad (3a)$$

$$\mathrm{Al}^{3+} + 2\mathrm{H}_2\mathrm{L} \rightleftarrows \mathrm{AlL}_2^- + 4\mathrm{H}^+ \qquad (3b)$$

$$\mathrm{Al}^{3+} + 3\mathrm{H}_2\mathrm{L} \rightleftarrows \mathrm{AlL}_3^{3-} + 6\mathrm{H}^+ \qquad (3c)$$

Since the protons in these reactions are situated on the right hand side of the equilibrium arrow, it is implied that protons should be subtracted when the complexes are formed and this corresponds to negative proton numbers in their (p,q,r)-notations, i.e., their stoichiometries become $(-2,1,1)$, $(-4,1,2)$ and $(-6,1,3)$, respectively. If, as an equally valid alternative, the reacting components had been chosen as H^+, Al^{3+} and L^{2-}, it is easily realized that no proton turnover is involved and that the (p,q,r)-notations would have become (0,1,1), (0,1,2) and (0,1,3), respectively. Since the numerical value of an equilibrium constant is intimately coupled to how the equilibrium reaction is written, it is always crucially important not to confuse the choice of reacting components and the values for the equilibrium constants.

The characterization of a particular three-component system, at a given temperature and pressure, can be described as comprising of three tasks:

(a) a determination of the stoichiometries, i.e., (p,q,r)-combinations, for the species that form in significant amounts

(b) a determination of the corresponding stabilities, i.e., $\beta_{p,q,r}$-values, characterizing the formation of these species and

(c) a determination of the non-ideal behaviour of the dissolved species, i.e., the concentration-dependent activity coefficient values.

Since most methods for studying equilibrium speciation are based on indirect macroscopic measurements, responding to a combined effect of these factors, the three tasks must furthermore be simultaneously solved. In practice, this is almost impossible because of the large number of variables that need to be determined simultaneously. However, by adopting the so-called constant ionic medium method (Biedermann and Sille'n, 1952), activity coefficient values can all be kept effectively constant. According to this method, a high excess of a low-valent electrolyte salt is added to the investigated solution, for instance NaCl, NaClO_4 or KNO_3, in addition to the substances of interest. These monovalent ions, which are chosen to be as 'inert' as possible, then dominate the ionic strength of the solution and set the activity coefficients for all ions and molecules forming in the system under investigation to be constant. In practice, this has been shown to hold as long as the equivalent concentrations of the investigated compounds do not exceed about 10% of the salt medium concentration (Biedermann, 1975). This corresponds to an upper limit of an experimental 'window', in which the activity coefficients can be incorporated into the β-values, and in which chemical concentrations can be used instead of activities. Within this window, the aim is now to vary the concentrations of the three reacting components within as wide ranges as possible, to create as favourable conditions as possible for the formation of all presumptive complexes.

This is best achieved by using five stock solutions, all containing the chosen ionic medium. Two of these solutions, the metal ion solution and the ligand solution, are obvious. The third and the fourth solutions contain a strong acid and a strong base, respectively, and are used to vary the total proton concentration. The fifth solution, finally, contain a pure ionic medium and is used to accomplish different degrees of dilution. After careful checks for concentration and absence of foreign impurities such as metal ions and protolytes, these solutions can be volumetrically used to generate a solution of any composition in the system. To avoid transitory precipitates during this preparation, the order of mixing can sometimes be crucial. An analytically important aspect of the preparation is also to use volumes large enough, so that the volume uncertainties do not add significantly to the uncertainties of the analytes.

Since the validity of the equilibrium model evaluated from these data strongly increases with the area experimentally covered, the aim should be to spread out these compositions as much as possible. For a given number of compositions, it is always a better choice to have them widely distributed in experimental 'space' than to have them as repeated checks for reproducibility or with small gradual steps in, for instance, total proton concentration. Furthermore, if the equilibrium model is to be used for a specific purpose, e.g., at near-neutral pH, it is vital that the experimental data covers that area.

3. Equilibrium measurements

A basic requirement for any analytical method used to determine the position in 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. This explains the predominant use of ion-selective electrodes for these measurements at lower temperatures and the most common ion to analyze for is the proton, by means of glass electrode or hydrogen gas electrode measurements. Metal-ion selective electrodes or metal-amalgam electrodes can also be used for certain metal ions, but these electrodes are seldom as precise or convenient as the hydrogen ion electrode. In the use of these electrodes, it is of critical importance that the electrode reading yields an accurate measurement of the corresponding free ion concentration. To achieve this, a number of requirements with regard to the measuring cell arrangement, the temperature control of the experiment and the calibration routine of the electrode must be fulfilled. This is discussed in detail by Öhman and Sjöberg (1996).

A great advantage with the use of ion-selective electrode measurements is that series of data can be easily collected through a titration procedure. From an initial analytical composition, stepwise changes with a burette are made with intervening electrode recordings. The time elapsed between these changes must be certained to be sufficient for equilibrium to be attained. A good method to check for this prerequisite, is to make repeated high-resolution electrode readings at predetermined time intervals, since this will make sluggish attainments of equilibrium clearly visible. Extended equilibration periods are frequently needed when polynuclear complexes are being formed, when the coordination number of the metal ion changes, when precipitates are being formed and when surface complexation phenomena are being studied.

In addition, other experimental techniques are sometimes available. For example, if the metal ion or the ligand is coloured, and the colour changes (in intensity and/or frequency) upon complexation, spectrophotometry can be used. If the metal ion is diamagnetic, or if the ligand contains a suitable nucleus, nuclear magnetic resonance (NMR) is an attractive method. This latter method, which ideally gives one separated signal for each unique chemical surrounding, can provide information not only on the free metal ion or ligand concentration, but also on the number of species and their respective concentrations for a given analytical composition. Furthermore, since the positions of these signals are susceptible to protonation/deprotonation reactions, they can also be used to gain information on acid/base reactions at the ligand and at the complexes. Unfortunately, the precision of NMR-data is only in the range of ±5–10% and, to the authors experience, they are often too unprecise to allow for an independent data analysis. However, when combined with the high-resolution proton measurements described above, they permit analysis of very complicated equilibrium systems with confidence (e.g., Pettersson et al., 1986; Öhman, 1989; Selling et al., 1994).

4. Evaluation of the equilibrium model

As the equilibrium analysis is initiated, a set of reacting components defining the equilibria of the system must be chosen. This choice of components then also defines a zero level, from which the analytical total concentrations are calculated. Thus, in the analysis of a proton-metal ion-weak acid ligand system, which is a three-component system, two of the components should be the proton and the metal ion while the third component should be chosen as one of the protonation degrees of the weak acid, cf. the discussion in Section 2.

The corresponding equilibria can then be represented by three general reactions:

$$p\mathrm{H}^+ + q\mathrm{Me}^{z+} + r\mathrm{H}_n\mathrm{L} \rightleftarrows \mathrm{H}_p\mathrm{Me}_q(\mathrm{H}_n\mathrm{L})_r^{p+qz};\ \beta_{p,q,r} \tag{4a}$$

$$p\mathrm{H}^+ + q\mathrm{Me}^{z+} \rightleftarrows \mathrm{H}_p\mathrm{Me}_q^{p+qz};\ \beta_{p,q,0} \tag{4b}$$

$$p\mathrm{H}^+ + r\mathrm{H}_n\mathrm{L} \rightleftarrows \mathrm{H}_p(\mathrm{H}_n\mathrm{L})_r^{p};\ \beta_{p,0,r} \tag{4c}$$

where reaction (4a) represents the formation of three-component complexes, while (4b) and (4c) represent two underlying two-component systems, i.e., the metal ion hydrolysis and the acid/base reactions of the ligand, respectively.

The zero level with respect to total proton concentration, as defined from this choice of reacting components, becomes neutral water, uncomplexed metal ions and the chosen protonation degree of the weak acid. Since hydroxide ions can be neutralized to water with an equivalent amount of strong acid, they appear with a negative sign in the total concentration equation:

$$\begin{aligned}[\mathrm{H}]_{\mathrm{tot}} = [\mathrm{H}^+] - [\mathrm{OH}^-] &+ \Sigma p\left[\mathrm{H}_p\mathrm{Me}_q^{p+qz}\right] \\ &+ \Sigma p\left[\mathrm{H}_p(\mathrm{H}_n\mathrm{L})_r^{p}\right] \\ &+ \Sigma p\left[\mathrm{H}_p\mathrm{Me}_q(\mathrm{H}_n\mathrm{L})_r^{p+qz}\right]\end{aligned} \tag{5a}$$

$$\begin{aligned}[\mathrm{Me}]_{\mathrm{tot}} = [\mathrm{Me}^{z+}] &+ \Sigma q\left[\mathrm{H}_p\mathrm{Me}_q^{p+qz}\right] \\ &+ \Sigma q\left[\mathrm{H}_p\mathrm{Me}_q(\mathrm{H}_n\mathrm{L})_r^{p+qz}\right]\end{aligned} \tag{5b}$$

$$\begin{aligned}[\mathrm{H}_n L]_{\mathrm{tot}} = [\mathrm{H}_n\mathrm{L}] &+ \Sigma r\left[\mathrm{H}_p(\mathrm{H}_n\mathrm{L})_r^{p}\right] \\ &+ \Sigma r\left[\mathrm{H}_p\mathrm{Me}_q(\mathrm{H}_n\mathrm{L})_r^{p+qz}\right]\end{aligned} \tag{5c}$$

In these equations, the total concentrations $[\mathrm{H}]_{\mathrm{tot}}$, $[\mathrm{Me}]_{\mathrm{tot}}$ and $[\mathrm{H}_n\mathrm{L}]_{\mathrm{tot}}$ are known in each data point from solution preparation and the right-hand side expressions constitute the conditions for conservation of mass. All terms on the right-hand side of these equations can be expressed in terms of β-values and free concentrations of H^+, Me^{z+} and $\mathrm{H}_n\mathrm{L}$, cf. Eq. (2). Therefore, by measuring, for instance, $[\mathrm{H}^+]$ or $[\mathrm{Me}^{z+}]$ in each of these data points, the resulting equation system can be used to determine β-values.

This computational problem involves a determination of sets of unknown (p,q,r) triplets and corresponding equilibrium constants $\beta_{p,q,r}$ that 'best' fit the experimental data. Before addressing this problem, however, it is good practice to analyze the two subsystems ((4b) and (4c)) separately, so that these can be treated as exactly known when effects from three-component complexation are analyzed.

Often of great benefit in the analysis of data is the use of two types of graphical diagrams, the Z-plot and the $\bar{n}$-plot. The function Z is defined as the average number of hydroxide ions reacted (or, of equal meaning, number of protons released) per total metal ion (Z_B) or total ligand (Z_C). The letters B and C are in this context used to represent $[\mathrm{Me}]_{\mathrm{tot}}$ and $[\mathrm{H}_n\mathrm{L}]_{\mathrm{tot}}$, respectively. These functions can, if the ionic product of water is known, be directly calculated from $[H]_{tot}$, $[Me]_{tot}$, $[H_nL]_{tot}$, $-\log[H^+]$ data with the expressions $Z_B = ([H^+] - [OH^-] - [H]_{tot})/[Me]_{tot}$ and $Z_C = ([H^+] - [OH^-] - [H]_{tot})/[H_nL]_{tot}$, respectively. If Z_C is plotted vs. $-\log[H^+]$ for a series of $H^+ - H_nL$ data, an 'ordinary' weak acid/base titration curve will occur with buffer minima at integer Z_C-values and maxima at half integer values. If metal ions are added to this weak acid solution at some Z_C-value, and these ions react with the ligand via proton displacement (e.g., $Me^{z+} + HL \rightleftarrows MeL^{z-1} + H^+$), the protons released will shift the Z_C curve towards a lower $-\log[H^+]$ value. These $Z_C(-\log[H^+])$ curves can accordingly be used to gain information about the $-\log[H^+]$ range, and the extent, of significant metal complexation.

Furthermore, since the maximum value of Z_C for H_nL is n, (i.e., the deprotonation can not proceed beyond L^{n-}), experimental areas in which metal hydroxo and/or mixed ligand/hydroxo species are formed, can be clearly identified from those Z_C-data exceeding this value. Fig. 1 represents experimental data in the H^+–Al^{3+}-oxalic acid (ethanedioic acid, H_2L) system (Sjöberg and Öhman, 1985) and illustrates all of the aforementioned characteristics of the $Z_C(-\log[H^+])$ curves. Thus, the titrations in absence of Al^{3+}, which are illustrated by filled symbols, show that the upper limiting value of 2, and corresponding to a dominance of the species L^{2-}, is approached at a $-\log[H^+]$ of ~ 5. The unfilled and half-filled symbols represent corresponding data in presence of various Al_{tot} concentrations and various Al_{tot}/H_2L_{tot} ratios. As seen, the displacement of these curves from those in absence of Al, increase with increasing Al_{tot} concentration and increasing Al_{tot}/H_2L_{tot} ratios and this indicates an increasing degree of complex formation. Finally, with regard to half-filled symbols, it can be seen that Z_C-values exceeding 2 are registered at $-\log[H^+]$ above approximately 4, and this is a direct evidence that hydroxide ions are involved in complexation in this range. Fig. 2 represents data in a restricted part of the H^+–$Si(OH)_4$-tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one,HL) system (Sjöberg et al., 1985) and shows that, in this particular data range, all curves are coinciding independent of $(Si(OH)_4)_{tot}$ concentration. From this information, it can be concluded that no complexation with proton displacement is occurring in that part of the data space.

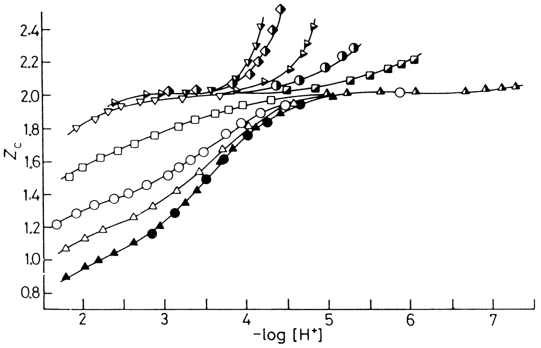

Fig. 1. Part of the experimental data in the H^+–Al^{3+}-oxalic acid system (Sjöberg and Öhman, 1985) plotted as $Z_C(-\log[H^+])$ curves. Different symbols denotes different $[Al]_{tot}$, $[H_2Ox]_{tot}$ combinations expressed in $mmol/dm^3$: (●) 0, 1; (▲) 0, 16; (△) 1, 16; (○) 2, 16; (□) 2, 8; (▽) 2, 4; (triangle half-filled up) 3, 24; (◪) 10, 25; (◑) 10, 20; (diamond half-filled) 10, 10; (triangle half-filled down) 10, 5; and (triangle half-filled right) 1, 1. The full curves were calculated using the proposed equilibrium model by means of the computer program SOLGASWATER (Eriksson, 1979). Reproduced by permission of The Royal Society of Chemistry, UK.

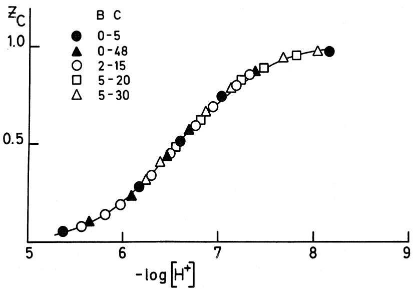

Fig. 2. Part of the experimental data in the H^+–$Si(OH)_4$-tropolone system (Sjöberg et al., 1985). *B* and *C* denote the total silicic acid and tropolone concentrations, expressed in $mmol/dm^3$, respectively. Reproduced by permission of Elsevier Science Publishing.

The function n̄ is defined as the average number of ligands, as L^{n-}, bound per total metal ion. The value of n̄ can be calculated from experimental $[H]_{tot}$, $[Me]_{tot}$, $[H_nL]_{tot}$, $-\log[H^+]$ data, cf. Rossotti (1969), if the acid/base constants of the ligand and the ionic product of water are known. These values plotted against $\log[L^{n-}]$ result in a graph regularly referred to as a 'Bjerrum plot' after the Danish solution chemist Jannik Bjerrum (1941).

It can be mathematically shown that if the system of interest is characterized by a series of MeL–MeL$_x$ complexes only, these $\bar{n}$-curves will all coincide, independent of $[Me]_{tot}$, $[H_nL]_{tot}$ and $[Me]_{tot}/[H_nL]_{tot}$. If, on the other hand, more complicated compositions appear among the species formed, each combination in total concentrations will result in a unique $\bar{n}$-curve. The $\bar{n}$-plot can thus be used to gain insight into the complexity of a system studied and Figs. 3 and 4 illustrate two end members in this respect. Thus, in Fig. 3, which illustrates data in the system H^+–Al^{3+}-methylmalonic acid (ethane-1,1-dicarboxylic acid, H_2L) (Marklund and Öhman, 1990), all curves are seen to coincide independent of total concentrations and ratios. This is a direct graphical evidence that complexation in this system is characterized by the formation of simple AlL_n^{3-2n} species. Furthermore, from the information that $\bar{n}$ has an upper limiting value of 3, it can be concluded that the last complex in the series is AlL_3^{3-}. In contrast, the $\bar{n}$-curves shown in Fig. 4, which were obtained in the system H^+–Al^{3+}-propionic acid (ethanemonocarboxylic acid, HL) (Marklund et al., 1989), are all unique and this graphically proves that simple AlL_n^{3-n} complexes are of minor or negligible importance in the system.

In many systems, both binary and true three-component complexes can form in different parts of the experimental data range. The $\bar{n}$-plot can, under such circumstances, provide the means to determine compositional regions in which ‘simple’ and ‘complicated’ complexes dominate, respectively. To interpret the ‘complicated’ equilibrium data ranges, the use of a non-linear least-squares computer program is highly recommendable. These programs, many of which are reviewed by Hartley et al. (1980), generally allow for the optimization of one or several equilibrium constants to reach the ‘best possible’ fit between data and model. The type of experimental data fitted to can often be selected, and common choices are Z_C, $[H]_{tot}$ or $-\log[H^+]$.

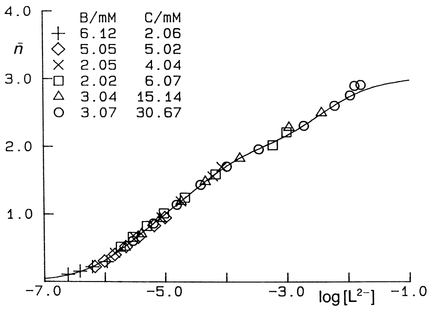

Fig. 3. Experimental data and calculated $\bar{n}(\log[L^{2-}])$ curve illustrating AlL_n^{3-2n} ($n=1$, 2, 3) formation in the H^+–Al^{3+}-methylmalonic acid system (Marklund and Öhman, 1990). *B* and *C* denote the total aluminum and methylmalonic acid concentrations, expressed in mmol/dm^3, respectively. Reproduced by permission of Acta Chemica Scandinavica.

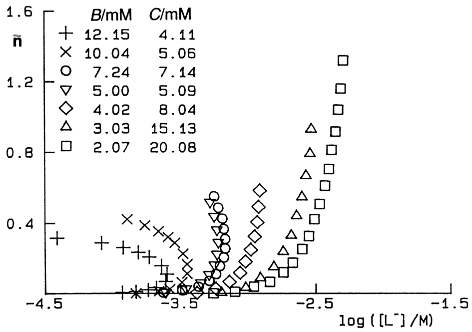

Fig. 4. Experimental data from the H^+–Al^{3+}-propionic acid system (Marklund et al. (1989) plotted as curves $\bar{n}(\log[L^-])$. *B* and *C* denote the total concentrations of aluminum and propionic acid, respectively. Reproduced by permission of Acta Chemica Scandinavica.

For each data point, the program compares the experimental value with its calculated counterpart and computes an error squares sum over all data, a *U*-value according to $U=\Sigma(X_{calc}-X_{exp})^2$. The equilibrium constant is then varied and the value resulting in the lowest possible *U*-value is identified. This numerical value then becomes the optimized value of β.

This ‘lowest possible’ value of *U* is of course also dependent on the (p,q,r)-stoichiometry assumed for the species in question, and the technique we have developed in Umeå to search for the best stoichiometry possible, has been named ‘(p,q,r)-analysis’.

The basic initial assumption made in this search, is that one single species is formed in the data range considered. All relevant integer (p,q,r)-combinations are then tested, one at the time, and in each case the corresponding ‘lowest possible’ *U*-value is recorded. Finally, these *U*-values are plotted in (p,q,r)-space and the combination resulting in the globally lowest value is identified.

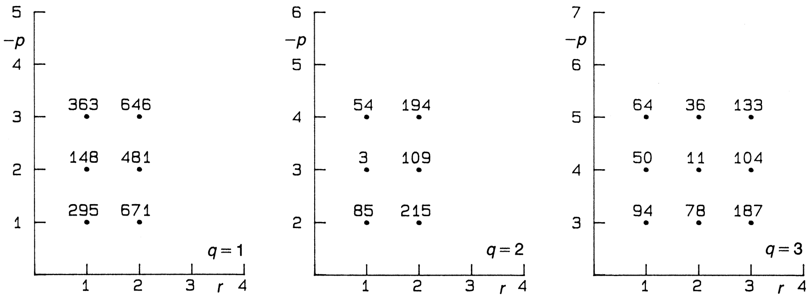

Fig. 5. Results of a (p,q,r)-analysis of data in the H^+–Al^{3+}-propionic acid system (Marklund et al., 1989). The figures give error squares sums assuming the formation of one ternary complex. Reproduced by permission of Acta Chemica Scandinavica.

The result of such an (p,q,r)-analysis, for the previously illustrated H^+–Al^{3+}-propionic acid system (Marklund et al., 1989), is shown in Fig. 5. As already indicated by the $\bar{n}$-plot, this unbiassed search shows that the tentative formation of binary AlL^{2+} and AlL_2^+ complexes, i.e., $(p,q,r)=(-1,1,1)$ and $(-2,1,2)$ respectively, both results in high error squares sums. Instead, the best fit to data is obtained by the stoichiometry $(-3,2,1)$ and, since propionic acid has only one dissociable proton, this implies that the two other protons released must originate from dissociated water molecules. We can therefore write the corresponding equilibrium reaction as: $2Al^{3+} + HL + 2H_2O \rightleftarrows Al_2(OH)_2L^{3+} + 3H^+$, i.e., the formation of a dinuclear mixed-hydroxo complex is being indicated. At this point, it might be noted that the same specific stoichiometry has been shown to give the best fit also in several other Al-monocarboxylic acid systems (Öhman, 1991). This complex might now be the sole species forming in the system, but it might also represent only the best possible average of two or several co-existing complexes. To judge between these two alternatives, a detailed inspection of the deviations remaining between data and model, cf. Fig. 6, is highly informative. Thus, if the first alternative is true, and the stoichiometry identified truly represents a sole dominant complex, these deviations should all rest within the experimental uncertainties, as depicted by the open symbols in Fig. 6. If, on the other hand, this stoichiometry only represents an average value, these deviations will show upon a systematic behaviour, at least in some parts of the experimental 'space'.

If this second alternative is the case, the equilibrium analysis may proceed along two alternative routes. One route implies that combinations of two or more complexes, with an average composition at or close to the one identified, are simultaneously fitted to the data. This route thus implies that a vast number of combinations must be tested, if an unbiassed search is aimed for.

The second alternative is to divide data into smaller sub-sets, with respect to for instance $-\log[H^+]$ interval or $[Me]_{tot}/[H_nL]_{tot}$ ratio interval, and that the (p,q,r)-analysis is restarted from the sub-set at one end of the data space. In this way, one complex at the time might be added to the speciation scheme as the analysis proceeds from one sub-set to another. At the end of this procedure, i.e., when the last sub-set has been analyzed, it is also of vital importance to co-optimize the equilibrium constants for all identified complexes on the full data set. This

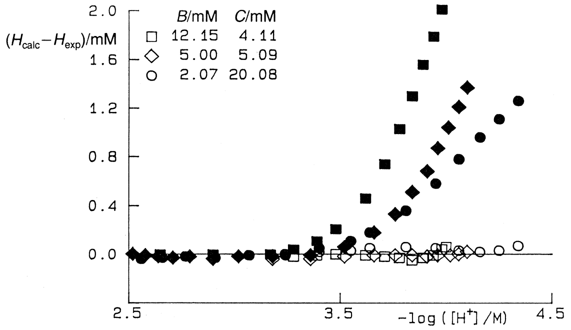

Fig. 6. Deviation plot from the H^+–Al^{3+}-propionic acid system (Marklund et al., 1989) showing the fit to experimental data without (filled symbols) and with (open symbols) the 'best' fitting species $(-3,2,1)$ $(Al_2(OH)_2L^{3+})$, c.f. Fig. 5, included in the speciation scheme. The letter H is used to represent $[H]_{tot}$ on the ordinate while B and C represent $[Al]_{tot}$ and $[HL]_{tot}$, respectively. Reproduced by permission of Acta Chemica Scandinavica.

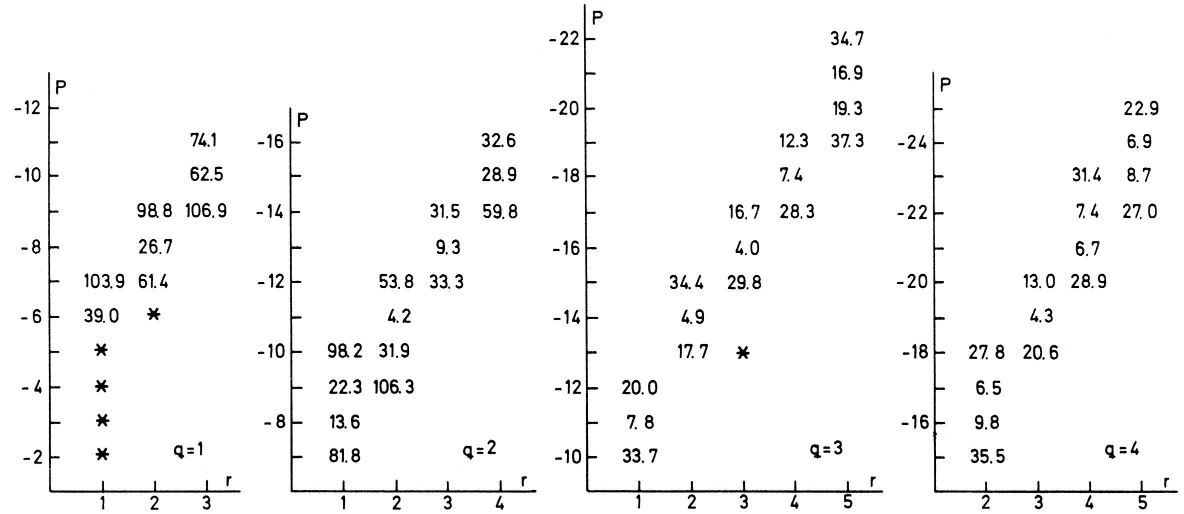

Fig. 7. Results of a (p,q,r)-analysis of data in a restricted part of the H^+–Al^{3+}-citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid, H_3L) system (Öhman, 1988). The figures give error squares sums assuming the formation of one additional complex and positions marked by stars are compositions already included in the model. Reproduced by permission of American Chemical Society.

will then make it possible to certify that all the identified complexes are significant and that no artefacts have been introduced via the mathematical procedure. From the output of this calculation, it will also be possible to check that this final model results in low remaining deviations over the entire data space.

A problem which sometimes occurs, especially if a restricted data range is treated, is that two or more (p,q,r) combinations result in comparably low U-values. This is illustrated in Fig. 7, showing the results of a (p,q,r)-search in alkaline Al^{3+}-citrate solutions (Öhman, 1988). In such situations, the access to a computerized simulation program, e.g., SOLGASWATER (Eriksson, 1979), is highly valuable. By means of such a program, it is possible to generate theoretical titration curves assuming each of these tentative species to form, one at the time. The result of such a simulation is illustrated in Fig. 8 and, as expected, the 'best' alternative stoichiometries, cf. Fig. 7, also result in closely resembling titration curves. There are, however, certain regions in which the different alternatives predict a difference in behaviour and, from the calculations, it is possible to judge where these are at the greatest. Accordingly, by performing additional measurements under those conditions, in the specific example at a $-\log[H^+]$ of around 9, new possibilities are opened to distinguish between the alternative models.

To validate the proposed speciation model, and to gain a graphical credibility for it, such a simulation

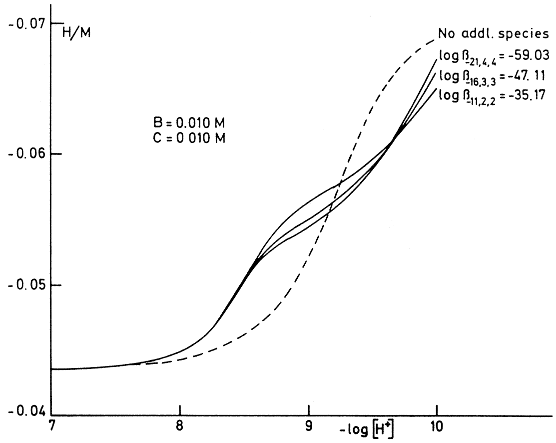

Fig. 8. Theoretical titration curves, as $[H]_{tot}$ (denoted H) vs. $-\log[H^+]$, in the H^+–Al^{3+}-citric acid system (Öhman, 1988) assuming the formation of different alternative polynuclear Al–citrate complexes with stoichiometries and equilibrium constants as labeled in the figure. The curves were constructed by means of the simulation program SOLGASWATER (Eriksson, 1979) at $[Al]_{tot} = [H_3L]_{tot} = 10\ mmol/dm^3$. Reproduced by permission of American Chemical Society.

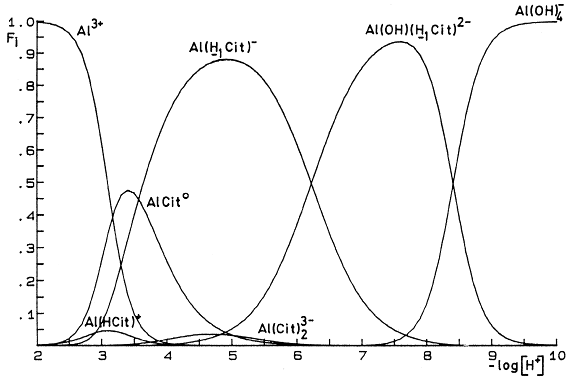

Fig. 9. Distribution diagram in the H^+–Al^{3+}-citric acid system constructed at conditions representative for blood plasma of man; $[Al]_{tot} = 0.001$ mmol/dm^3 and $[H_3L]_{tot} = 0.1$ mmol/dm^3. F_i is defined as the ratio between Al in a species and total Al concentration and the diagram was constructed by means of SOLGASWATER. Reproduced by permission of American Chemical Society.

program should also be used to generate theoretical $Z_C(-\log[H^+])$ and/or $\bar{n}(\log[L^{n-}])$ curves, i.e., curves generated from the final speciation model. By displaying these curves together with the experimental data, cf. Figs. 1–3, the conformity of the model to the data can be easily visualized.

Furthermore, the simulation program could also be used to construct several types of diagrams, such as distribution diagrams, solubility diagrams and predominance area diagrams. These graphical representations are exemplified for the H^+–Al^{3+}-citric acid system (Öhman, 1988) in Figs. 9–11, and allow the non-specialized reader to make judgements about the significance of the different proposed aqueous complexes.

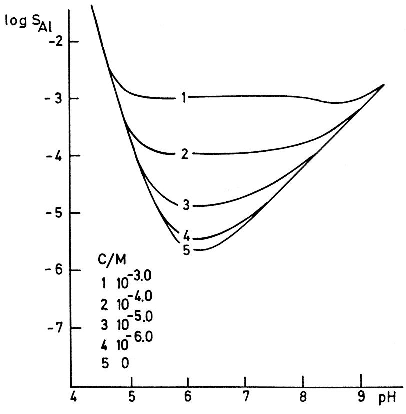

Fig. 10. Solubility diagram in the system H^+–Al^{3+}-citric acid. The diagram is constructed assuming the presence of a highly amorphous aluminum hydroxide phase and shows the logarithm of the total aqueous Al concentration as a function of $-\log[H^+]$ at different $[H_3L]_{tot}$, denoted *C*. Reproduced by permission of American Chemical Society.

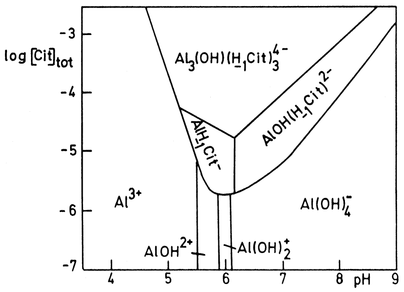

Fig. 11. Predominance area diagram in the system H^+–Al^{3+}-citric acid. The diagram shows predominating aqueous species in a suspension containing a highly amorphous aluminum hydroxide phase, as a function of $-\log[H^+]$ and $\log[H_3L]_{tot}$. The diagram illustrates the importance of hydrolysis products at low citrate concentrations, the formation of mononuclear Al–citrates at intermediate concentrations and the formation of polynuclear Al–citrates at high concentrations. This figure could be read in conjunction with Fig. 10 to elucidate the identity of the species predominantly responsible for the solubility enhancing effect of citrate under different conditions. Reproduced by permission of American Chemical Society.

5. Concluding remarks

This paper has reviewed the design and interpretation of experiments to characterize aqueous speciation. The presentation is by no means exhaustive; more comprehensive treatments dealing with aluminium(III) complexation and surface complexation, respectively, can be found in Öhman and Sjöberg (1996) and Sjöberg and Lövgren (1993). Since all succeeding steps of the equilibrium analysis are fully dependent on good experimental data, great efforts should be made to collect these with the highest quality possible and within the widest experimental ranges possible. In addition, reproducibility and reversibility criteria must be demonstrated and, whenever possible, complementary measuring methods should be applied. The process of collecting good equilibrium data is often time-consuming and tedious, but there are no short-cuts in this respect. The analysis of data should be performed in an un-biassed manner, in which graphical methods and computerized optimizations should both be utilized to reach the correct speciation scheme. The goal should always be to find a model with deviations from data that rest within the experimental uncertainties. Finally, since numerical values of equilibrium constants by nature are very abstract and also strongly depend on the choice of reacting components, the use of various forms of diagrams to illustrate the significance of different species under varying conditions, can be highly recommended.

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