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The formation of weak complexes by metal ions in aqueous solutions

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ABSTRACT. The modern approaches to the determination of the composition and the stepwise stability constants of weak metal complexes (K_n = 0.1–5.0) with ionic and molecular ligands in aqueous solutions are discussed. The difficulties in the unambiguous separation of the effects of the medium from those of the short-range specific interaction, described by equilibrium constants, and the consequent unreliability of the lower values of the formation constants, even when the latter are selected on the basis of a critical assessment, are examined. It is recommended that the linear relations between the algebraic sums of the logarithms of the activity coefficients of the components of the equilibria investigated and the ligand concentrations, the standard isotherms, or the measurement of the properties of all the components of the complex formation equilibria be employed for the separation of the long-range and weak short-range interactions.

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I. Introduction

The majority of processes in nature, analytical chemistry, and chemical engineering take place in aqueous solutions. Many characteristic features of such processes are determined by weak ion–ion and ion–molecule interactions leading to the formation of relatively unstable complexes. These complexes are formed and decompose via rapid reactions so that many of their properties are determined by thermodynamic functions. The most important thermodynamic parameters of the complexes in solutions are the equilibrium constants of their formation processes.

The determination of the composition and stability constants of complexes in solutions is one of the problems in physicochemical analysis[1] and constitutes the basis of the chemical theory of solutions,[2] which relates the properties of the solution to its composition. In this theory, the solution is regarded as a system where there are equilibria, obeying the Law of Mass Action, between the initial components and the products of their chemical interaction. However, when weak complexes are formed in aqueous solutions, the effect of the specific interaction is difficult to separate from the influence of the aqueous salt medium whose composition varies.

The thermodynamic functions for the formation reactions of a large number of weak complexes have been compiled in modern handbooks.[3–6] Metal cations M^{z+} with z = 1–4 usually play the role of coordination centres in the compounds considered, while polar molecules A or anions A^{z-} with z = 1–3 serve as the ligands. Analysis of data in handbooks[6] and in original studies (quoted below) shows that the current information about the thermodynamics of weak complex formation and even about the composition of weak complexes in aqueous solutions is extremely contradictory. Even many of the critically selected[5] values of the stepwise stability constants of weak complexes, for example $TlNH_3^+$, are doubtful. This is considered in Section IV of the present review.

During the last 20 years, there has been a renewed growth of interest in the thermodynamics of weak complex formation by metals. Numerous studies of outersphere association,[7–11] detailed investigation of non-aqueous solutions,[12,13] and the development of the theory of homogeneous catalysis[9] played a major role in this connection. The improvement of the level of studies on weak complex formation has been promoted by the application of microwave spectroscopy and computer techniques[14,15] and also by the use of the method involving the measurement of the activities of individual ions.[16]

Numerous new investigations[17–26] have been carried out to revise the information on the thermodynamics of repeatedly investigated complexes with low stabilities. Bjerrum discussed[27,28] the limits of the possibilities for the estimation of low stability constants of associated species in aqueous solutions. A controversy has recently arisen[26,29,30] concerning the reliability and accuracy of the determination of the stepwise formation constants of the weak complexes $CuCl_n^{2-n}$ with n = 1–4. Studies have been published[31–40] in which it is recommended that the compositions of weak associated species be determined taking into account the non-ideality of aqueous solutions with high constant ionic strengths (0.5–4.0). A new standard state has been proposed[41–43] (isopiestic solutions) for the investigation of weak complex formation. The possibilities for the quantitative investigation of weak metal ammines have been expanded.[25,44–47] A similar approach has been extended[48–50] to other ion–molecule complexes with low stabilities. Numerous free energies of transfer of ions from water to non-aqueous and mixed solvents have been surveyed and analysed.[51–53] The practical role of the thermodynamic functions of individual ions has been demonstrated.[54–56]

The most common one-centre complex formation reactions of metal (M) ions with ligands (A) in aqueous solutions are represented by the following reaction equations at the present level of development of chemistry:

$$M(H_2O)_{N,\,solv} + nA_{solv} \rightleftarrows MA_n(H_2O)_{N-nd,\,solv} + ndH_2O_{solv}, \quad (1)$$

where N is the limiting coordination number according to Werner's theory and d is the number of water molecules displaced by one

ligand A from the hydration shell of the central cation M. The ionic charges in Eqn. (1) and whenever possible in the text below are omitted to simplify formulation. The subscripts *solv* in the reactants involved in equilibrium (1) show that the latter interact in a definite sequence with all the remaining components of the solution and in the first place with solvent (water) molecules and with the ions of the supporting electrolyte and the excess ligands. However, these interactions are not included in Eqn. (1) in order to simplify the treatment of the properties of the system. They are frequently referred to as non-specific and are assigned to the effect of the medium or to changes in the activity coefficients.[57]

The constants β_n^0 of type (1) equilibria are expressed by the following relation for any standard state (designated by the superscript 0):

$$\beta_n^0 = \frac{[MA_n(H_2O)_{N-nd}][H_2O]^{nd}}{[M(H_2O)_N][A]^n} \cdot \frac{y_{MA_n(H_2O)_{N-nd}} y_{H_2O}^{nd}}{y_{M(H_2O)_N} y_A^n} = \beta_n \left(\prod_i y_i^{\nu_i}\right)_n, \quad (2)$$

where the square brackets and y_i denote the equilibrium concentrations and the activity coefficients of reactants i, β_n is the product of the concentrations or equilibrium function (but is not a constant! [1]), and ν_i are stoichiometric coefficients. The values of β_n in type (2) equations remain constant only when the concepts of the reactants and the effect of the medium, included in the symbol *solv* or in the values of y_i, are assumed to be fixed. The quantities β_n^0 are standardised in terms of temperature, pressure, and the medium selected as the standard with $I = 0$, I = const., etc. (I = ionic strength).

Whatever the standard state chosen for the study of weak complexes in aqueous solutions, the constancy of the activity coefficients in Eqn. (2) cannot be maintained. Their variation must be taken into account in the determination of n and β_n^0 for type (1) equilibria from "property–composition" diagrams because β_n and $\left(\prod_i y_i^{\nu_i}\right)_n$ are frequently comparable when the stability of the associated species is low.

There is a limitation as regards energy[7] (p. 196) in the determination of the composition and formation constants of weak complexes in solutions using the thermodynamics of reversible processes. To a first approximation, the energy of the thermal motion of the solvent, i.e. water, molecules may be adopted as a measure of this limitation, because complex formation via reaction (1) is studied in an aqueous medium. The energy of the thermal motion of solvent molecules is minimal in the ideal gas model. Such energy is defined as $1.5RT$ and at 298 K it amounts to 3.7 kJ mol^{-1}. The energy of the thermal motion of water molecules in water is comparable to the strength of the hydrogen bond and is approximately equal to 20 kJ mol^{-1}. Assuming that the energies indicated (3.7 and 20 kJ mol^{-1}) are equal to the changes in the Gibbs free energy (ΔG_n°) (it is more correct to compare them with enthalpy changes) during the stepwise occurrence of reaction (1), we obtained from the relation

$$\Delta G_n^0 = -RT \ln {}^{y}K_n^0 \quad (3)$$

where ${}^{y}K_n^0$ are unitary stepwise constants of equilibrium (1), the values of $\lg {}^{y}K_n^0$ at T = 298 K, which lie in the range 0.7–3.5 if d in Eqn. (2) is unity and $[H_2O]$ = 55.5 M. Hence it follows that cratic stepwise stability constants, varying approximately from 0.1 to 50, correspond to the energy level of the thermal motion of solvent molecules in the ideal gas model and of water molecules under the conditions indicated. The tabulated stepwise stability constants of weak complexes[3–6] lie within these limits. The stepwise stability constants below 0.1, which are frequently quoted in handbooks,[3–6] cannot be regarded as an adequate demonstration of the formation of complexes, which has been emphasised by Krestov[58] and other investigators. Spectral additional justification of the occurrence of specific interactions is needed in systems with $K_n \leqslant 0.1$. In the absence of such justification, there is apparently no point in separating the measured effects from the changes in the activity coefficients.

The introduction of the concept of the formation constant of a complex always presupposes the presence in the solution of the initial reactants and of the molecules of the complex located at some statistical mean distance from one another. This situation is possible when there are delta-type relations between the potential energies of the associated species and the distance between M and A in reaction (1) and the separate existence of the reactants in the associated and dissociated states is likely only when the probability of the intermediate variants is zero. However, over a wide range of concentrations of electrolytes, such a situation does not arise—for example, when the ions have the electronic structure of noble gases. For systems of this kind, one should not determine the low formation cosntants of the complexes because such constants have no definite physical significance according to Kessler [see, for example, Valyashko and Kravchuk[59] (p. 7)].

This review was written with the aim of a critical consideration of the modern approaches to the determination of the composition and stability constants of weak metal complexes with ionic and molecular ligands in aqueous solutions, the analysis of a series of reliable data on the thermodynamics of weak complex formation reactions, and also the formulation of certain recommendations for new research into weak interactions in aqueous solutions.

II. Standardisation of conditions in the study of weak complex formation in aqueous solutions

The relation between the chemical potential of the component (μ_i) and its overall (c_i) and equilibrium ($\{[i]\}$) concentrations in a real solution at a constant temperature and pressure can be expressed by the equations

$$\mu_i = \mu_i^0 + RT \ln c_i y_i^* = \mu_i^0 + RT \ln [i]\, y_i, \quad (4)$$

$$\mu_i = \mu_i^0 + RT\left(\ln c_i + \sum_x b_{i,x}^* c_i^x\right) = \mu_i^0 + RT\left(\ln [i] + \sum_x b_{i,x} [i]^x\right) \quad (5)$$

where μ_i^0 are the standard chemical potentials, while $b_{i,x}^*$ or $b_{i,x}$ are virial coefficients whose values are independent of c_i or $[i]$. The differences between y_i^* and y_i and also between $b_{i,x}^*$ and $b_{i,x}$ consist in the fact that the coefficients marked with an asterisk represent the deviations in the behaviour of the reactants containing component i from ideality, while the coefficients without an asterisk in the superscript position express the analogous properties of only the conventionally free species i_{solv} constituting the system (1). If there is no chemical interaction, for example, no reaction (1), in the system considered, then $c_i = [i]$, $y_i^* = y_i$, and $b_{i,x}^* = b_{i,x}$. In any arbitrarily selected standard state for component i, we have $c_i = [i] = 1$ and $y_i^* = y_i = 1$, although it is frequently assumed that $y_i^* = y_i \to 1$ when $c_i \to 0$.

Logarithmic concentration functions enter into Eqns. (4) and (5); for this reason, real solutions with $c_i \to 0$ cannot be chosen as the standard state because $\mu_i \to -\infty$ when $c_i \to 0$. The hypothetical 1.0 M or 1.0 m (M and m represent the molarity and molality respectively) solutions, having the properties of infinitely dilute solutions, usually serve as the standard state for the determination of thermodynamic functions for the complex formation reactions. The choice of water, an aqueous salt solution at a constant of ionic strength or at a constant molarity, and also of any mixed solvent as the solvent for the system alters only the point from which the excess thermodynamic functions are reckoned or the factors designated by the subscript *solv* in Eqn. (1). A necessary requirement which must be met by the standard state is the constancy of these factors, i.e. the constancy of the concept of "*solv*" and of the quantity y_i. It must be emphasised that water is a fully legitimate reactant involved in equilibrium (1) and its concentration, which varies markedly in the study of weak complexes can be usefully expressed on the same concentration scale as that employed for the other reactants (in the study of complexes in solution, the molarity scale is usually employed) and not the mole fraction scale normally used. When the latter is used, it is incorrect to calculate ΔG_n° by Eqn. (3).[60]

It follows from Eqns. (4) and (5) that the relation between these two ways of taking into account the non-ideality of the behaviour of reactant i is defined by the relations

$$\ln y_i^* = \sum_x b_{i,x}^* c_i^x, \tag{6}$$

$$\ln y_i = \sum_x b_{i,x} [\mathrm{i}]^x, \tag{7}$$

the first of which refers to a system with complex formation, whose parameters are included in the quantity $\ln y_i^*$ or in $\sum_x b_{i,x}^* c_i^*$.

Measurable amounts of weak complexes are formed only at high concentrations ($>0.1-0.5$ M) of M and A or of one of these substances. The majority of studies on weak interactions have been carried out hitherto[3-6] at microconcentrations of M (at $c_M \leqslant 1 \times 10^{-2}$ M) and with wide variation of c_A. Complex formation was usually studied in aqueous solutions with variable (from 1×10^{-2} to 15 M) or constant (0.5, 1.0, 3.0, 4.0, and 6.0) ionic strength maintained by inert electrolytes. Sodium perchlorate and ammonium nitrate were usually employed as the latter.

The wide variations of the concentration c_A or c_M, required to investigate weak complexes whatever the choice of the standard state, alter the factors designated by the subscript *solv* in type (1) equilibria or contributing to the activity coefficients in Eqn. (2). Such changes must be taken into account in calculations of n and β_n^0.

After taking logarithms in Eqn. (2), we obtain

$$\lg \beta_n{}^0 = \lg \beta_n + \lg y_{\mathrm{MA}_n} + nd \lg y_{\mathrm{H_2O}} - \lg y_{\mathrm{M}} - n \lg y_{\mathrm{A}} =$$

$$= \lg \beta_n + \Delta (\nu_i \lg y_i)_n, \tag{8}$$

where the symbol Δ denotes the algebraic sum. Substitution of the general Eqn. (7) in Eqn. (8) affords

$$\lg \beta_n{}^0 = \lg \beta_n + \Delta \left(2.303 \nu_i \sum_x b_{i,x} [\mathrm{i}]^x\right)_n . \tag{9}$$

Application of Eqn. (9) to semi-ideal solutions,[61-63] i.e. the restriction of the sum in Eqn. (7) to the quantities $b_{i,1}$, leads to the equation

$$\lg \beta_n{}^0 = \lg \beta_n + \Delta (2.303 \nu_i b_{i,1})_n [\mathrm{i}]. \tag{10}$$

If the composition of the test solution changes only as regards the ligand A concentration, then Eqn. (10) simplifies and assumes the following form:

$$\lg \beta_n{}^0 = \lg \beta_n + \lambda_n [\mathrm{A}], \tag{11}$$

where λ_n is the algebraic sum of $b_{i,1}$ with allowance for the stoichiometric coefficients ν_i.

Potentiometric study of the equilibrium

$$\mathrm{Ac}^-_{solv} + \mathrm{H_2O}_{solv} \rightleftarrows \mathrm{HAc}_{solv} + \mathrm{OH}^-_{solv}, \tag{12}$$

where HAc is acetic acid, in 3.0 M aqueous Na(Cl→Ac) solutions with chromatographic determination of the activity coefficients of acetic acid molecules made it possible to estimate[32] the contributions of the non-ideality of the behaviour of all the reactants as the salt composition of the medium is varied. It is seen from the data in Table 1 that the replacement of chloride ions by acetate ions increases to the maximum extent (compared with other reactants) the activity coefficients of hydroxide ions, but there is at the same time an appreciable increase in the activity coefficients of acetate ions and a significant fall of y_{HAc}. On the other hand, the algebraic sum of the logarithms of the activity coefficients of the reactants ($\Delta \lg y_i$) involved in equilibrium (12), i.e.

$$\Delta \lg y_i = \lg y_{\mathrm{OH^-}} + \lg y_{\mathrm{HAc}} - \lg y_{\mathrm{Ac^-}} \tag{13}$$

varies appreciably less than the activity coefficients of any individual reactant. The ratio $\Delta \lg y_i / c_{\mathrm{Ac^-}}$ then remains almost constant and amounts to 0.07 ± 0.01 at all the concentrations of chloride and acetate ions.

Table 1. The logarithms of the activity coefficients of the reactants involved in equilibrium (12) in 3.0 M Na(Cl→Ac) solutions at 298 K.

$c_{\mathrm{Ac^-}}$, M	$\lg y_{\mathrm{OH^-}}$	$\lg y_{\mathrm{Ac^-}}$	$-\lg y_{\mathrm{HAc}}$	$-\lg y_i$ from Eqn. (13)	$-\lambda_i = \Delta \lg y_i / c_{\mathrm{Ac^-}}$
0.5	0.07	0.04	0.07	0.04	0.08
1.0	0.14	0.08	0.13	0.07	0.07
2.0	0.30	0.20	0.24	0.14	0.07
3.0	0.45	0.30	0.33	0.18	0.06

Calculations have shown[31] that β_1, approximately equal to unity, changes by almost 100% if λ_1 in Eqn. (11) amounts to only ~0.2, as happens in many mixtures of uni-univalent electrolytes with I = const. Hence it is clear that, in the study of weak acido-complexes in aqueous solutions with I = const., it is essential to determine both β_n and λ_n in Eqn. (11).

The study of the behaviour of non-electrolytes in aqueous solutions of the majority of inorganic salts with variable and constant ionic strengths has recently[61] led to the equation

$$\lg y_i = \sum_j b_{i,j}^* c_j, \tag{14}$$

where the Sechenov's constants $b_{i,j}^*$ depend only on the nature of the non-electrolyte i and the ions j. Eqn. (14) is valid for all systems without strong interactions between the molecule i and the ions j.

The activity coefficients of the ion i are expressed by the following equation over a wide range of ionic strengths:

$$\lg y_i = -Az_i^2\sqrt{I}/(1 + B\mathring{a}\sqrt{I}) + b_i^*I, \quad (15)$$

where A and B are the Debye–Hückel constants calculated theoretically, $\mathring{a}$ is the conventional ionic radius, and b_i^* is the second virial coefficient. The first term on the right-hand side of Eqn. (15) is constant at I = const. if it is assumed that $\mathring{a}$ is invariant. By analogy with Eqn.(14), it is suggested that one assumes[33] that the activity coefficients of the ions and ionic strengths, which are constant in magnitude but variable as regards composition, are described by the equation

$$\lg y_i = F_i(I) + \sum_j b_{i,j}^* c_j, \quad (16)$$

in which F_i(I) are characteristic constant functions of the ion i independent of the nature of the ion j.

The applicability of Eqn. (16) to mixtures of uni-univalent electrolytes with a constant molarity or molality has been repeatedly confirmed.[18,19,31] Eqn. (16) is frequently valid for mixtures of uni-bivalent and bi-univalent electrolytes of the type of sodium sulphate or barium chloride for constant overall molar concentrations[33] but not constant ionic strengths I.

Throughout many years, the model of semi-ideal solutions was used successfully[23,64] in the study of copper(II), cobalt(II), and iron(III) chloride complexes as well as other weak associated acido-species formed by reaction with the cations M in 3–12 M solutions of hydrochloric acid and lithium, magnesium and calcium chlorides as well as similar solutions[26] with variable ionic strengths. The corrections for the variation of the activity coefficients in such solutions were introduced in terms of averaged system parameters (y_{av}) expressed by the relation

$$\lg y_{av} = a + bc_{Cl^-}, \quad (17)$$

where a and b are constants for a specific salt medium with a variable ionic strength. The similarity of the methods used to take into account the non-ideality of the solutions with constant ionic strengths I = 0.5–6.0 and for variable ionic strengths $I \geqslant 3$ is clearly seen from the comparison of Eqns. (16) and (17).

The need to take into account the changes in the activity coefficients of the Cd^{2+} ions in 3.0 N aqueous solutions of sodium sulphate and perchlorate arose already in the old investigations of cadmium sulphate complexes.[65] It was established that the measured activities of sulphate ions can be accounted for by the hypothesis of the formation of only the $CdSO_4$ complexes with a stability constant of 7 ± 2, while the activities of the cadmium cations in the same solutions are reproduced by the hypothesis that the complexes $Cd(SO_4)_n^{2-n}$ [sic] are formed with ν_n = 8 ± 1, 10, and 110 for n = 1, 2, and 3 respectively.

McKay[66] cast doubt on the low thermodynamic functions for complexes standardised using solutions with high and constant ionic strengths immediately after the publication of the first edition of the Handbook of Stability Constants.[3] Pitzer and Brewer[67] pointed out as early as 1961 that there is no point in using solutions with high and constant values of I for the study of weak acido-complexes, since the Harned coefficients for I = const. = 0.1–3.0 are approximately constant.

Kul'ba and Mironov[68] noted in 1963 that the values of n and β_n for the weak acido-complexes TlA_n^{1-n} with $n > 1$, where A^- = Cl^-, Br^-, I^- or SCN^- are conventional thermodynamic parameters which include both the short-range specific interaction of Tl^+ with A^- and the changes in the activity coefficients of ions reacting in 3.0 or 4.0 M aqueous solutions of Na(ClO_4→A). It has been shown[31] that the changes in the composition of the majority of uni-univalent electrolyte solutions with I = const. make it possible to determine the stepwise stability constants of acido-complexes of ~10 with an error not less than 10% without taking into account the variability of the activity coefficients, the error increasing with decrease in K_n.

Eqn. (11) was first used for a detailed study of weak multistep acido-complex formation by Vierling,[34,69] who investigated lead(II) chloride and bromide complexes in 4.0 M aqueous Na(ClO_4→A) solutions, where A^- = Cl^- or Br^-, with complete replacement of perchlorate ions by halide ions. Potentiometric, solubility, and spectrophotometric methods were used as the basis for these investigations. Unfortunately, the relevant communications do not give a mathematical analysis of the reliability of the simultaneous calculation of β_n^0 and λ_n on the basis of Eqn. (11). The necessity to analyse the different hypotheses concerning the formation of weak acido-complexes in connection with the determination of β_n and λ_n in aqueous solutions with high ionic strengths was first confirmed by Belevantsev et al.[40] This conclusion was reached from the applicability to solutions with constant molarities and molalities of the Harned rule with a single virial coefficient α' in the general equation

$$\lg y_{\pm}^{(I+II)} = \lg y_{\pm}^{(I)} - \alpha' c_{II} - \alpha'' c_{II}^2 \quad (18)$$

where $y_{\pm}^{I+II)}$ and $y_{\pm}^{(I)}$ are the mean ionic activity coefficients in mixtures of electrolytes (I) and (II) with I = const. and in the pure electrolyte (I) with the same ionic strength, c_{II} is the concentration of electrolyte (II) in the mixture, and α' and α'' are Harned coefficients, usually with $\alpha' \gg \alpha''$. However, the limited applicability of the Harned rule is generally known.[70,71] At the same time, Eqn. (11) is valid for many aqueous salt systems. This contradiction can be accounted for by the fact that λ_n is the algebraic sum of the Harned coefficients. The high values of the latter, as well as the terms quadratic in c_{II}, cancel out in this sum judging from the data in Table 1. It is important that Eqn. (11) is frequently applicable to solutions with variable ionic strength as a result of the applicability of the Storonkin–Lagunov rule[72] to these systems. It has been noted[40] that the values of λ_n in Eqn. (11) as well as those of $\lg y_{\pm}$ can be divided into components corresponding to individual ions. At the same time, accurate calculations of the λ_n from the mean ionic activity coefficients are by no means always possible, while the Harned coefficients for individual ions are extremely useful for the estimation of the effects of non-ideality.

The values of λ_1 for equations of type (11) have been determined[36,73] in the study of solutions with microconcentrations of outer-sphere tris(phenanthroline)iron(II) monoperchlorate complexes, keeping the ionic strength I, the normality N, and the molarity M constant using mixtures of two salts and also at a constant activity of water a_{H_2O}. It was found (Table 2) that the replacement of the constant parameters in the sequence I, N, $M \simeq a_{H_2O}$ reduces significantly the value of λ_1, i.e. diminishes the effect of non-ideality. The changes in I or N in the range 0.25–0.75 have little influence on λ_1, but none of the methods of standardising the conditions in the study of weak perchlorate complexes indicated ensures the constancy of the activity coefficients. The replacements Na(F→Cl), Na(F→Ac), and (Na_2→Li_2)SO_4, i.e. of one singly-charged ion by another singly-charged ion, had little influence on λ_1, while the replacement of fluoride or chloride ions by divalent sulphate ions did exert a significant influence.

It has been established[74–79] that the coefficients λ_1 are almost constant for the equilibria in the formation of microamounts of

$H^+ - A^{z-}$ associated species and certain metal acido-complexes in mixtures of $NaClO_4$ with NaCl, NaBr, NaI, $NaNO_3$, and $LiClO_4$ at constant ionic strengths I = 0.5, 1.0, 2.0, 3.0, 4.0, and even 6.0 (Table 3). The constancy of λ_1 is maintained also for 3.0 M Na(Cl→Ac) solutions[32] in which 0.1–3.0 M acetate ions (Ac^-) are protonated, i.e. the process takes place under the conditions of an ionic automedium (Table 1).

Table 2. The coefficient λ_1 (accuracy to within ±20%) in Eqn. (11) [36,39,73] for tris(phenanthroline)iron(II) monoperchlorate complexes.

Supporting salt	λ_1 at				
	I=0.25	I=0.75	N=0.25	M=0.25	a_{H_2O}=0.99
Na(F→0.5SO_4)	3.9	2.7 *	2.6	1.5	1.8
Na(Cl→0.5SO_4)	3.6	–	2.7	1.5	1.6
Na(F→Cl)	–	0.1	–	–	–
Na(F→CH_3COO)	–	0.9	–	–	–
(Na_2→Li_2)SO_4	–	0.35	–	–	–

*At N = 0.75.

Table 3. The values of λ_n in Eqn. (11) for I = const. and T = 298 K.[78,79]

Reaction	I	Salt in the medium	$\lambda_n \pm \sigma$
$H^+ + Ac^- \rightarrow HAc$	1.0	Na(ClO_4→Cl)	0.081±0.005
	2.0	Na(ClO_4→Cl)	0.082±0.002
	4.0	Na(ClO_4→Cl)	0.069±0.004
	1.0	Na(ClO_4→Br)	0.027±0.007
	3.0	Na(ClO_4→Br)	0.036±0.005
	1.0	Na(ClO_4→I)	−0.022±0.009
	3.0	Na(ClO_4→I)	−0.021±0.003
	6.0	Na(ClO_4→I)	−0.015±0.03
	1.0	Na(ClO_4→NO_3)	0.072±0.007
	3.0	Na(ClO_4→NO_3)	0.087±0.004
	3.0	(Na→Li)ClO_4	0.068±0.003
$H^+ + HCOO^- \rightarrow HCOOH$	3.0	Na(ClO_4→Cl)	0.070±0.003
	3.0	Na(ClO_4→Br)	0.023±0.003
	3.0	Na(ClO_4→NO_3)	0.076±0.003
$H^+ + Cit^{3-} \rightleftarrows HCit^{2-}$ *	2.0	Na(ClO_4→NO_3)	0.073±0.03
$H^+ + Cit^{3-} \rightleftarrows HCit^{2-}$	3.0	Na(ClO_4→NO_3)	0.06±0.01
$2H^+ + HCit^{2-} \rightleftarrows H_3Cit$	3.0	Na(ClO_4→NO_3)	0.10±0.01
$H^+ + OH^- \rightleftarrows H_2O$	2.0	Na(ClO_4→NO_3)	0.075±0.005
$H^+ + C_2O_4^{2-} \rightleftarrows HC_2O_4^-$	3.0	Na(ClO_4→Cl)	0.075±0.003
$2H^+ + C_2O_4^{2-} \rightleftarrows H_2C_2O_4$	3.0	Na(Cl_4→Cl)	0.14±0.02
$H^+ + NH_3 \rightleftarrows NH_4^+$	0.5	Na(ClO_4→NO_3)	0.016
	1.0	Na(ClO_4→NO_3)	−0.013
	2.0	Na(ClO_4→NO_3)	0.017

*Cit^{3-} = citrate ion.

In order to reduce the activity coefficients λ_1 in Eqn. (11), recommendations have been formulated[80] concerning the rational selection of electrolytes for the study of weak acido-complexes. According to these recommendations, the difference between the logarithms of the mean ionic activity coefficients ($\Delta \lg y_\pm$) and the activities of water (or osmotic coefficients) in solutions of an inert electrolyte BX and the ligand-supplying salt BA should be minimal. Analysis of the parameters

$$\Delta \lg y_\pm = (\lg y_{\pm BX} - \lg y_{\pm BA})\, m^{-1}, \quad (19)$$

$$\Delta\varphi = (\varphi_{BX} - \varphi_{BA})\, m^{-1}, \quad (20)$$

where m is the molality and φ are osmotic coefficients, showed[63,70,71] that, for $\Delta \lg y_\pm$ and $\Delta\varphi$ tending to zero, the microcomponents of the type (1) equilibria in BX + BA mixtures induce a minimal change in the activity coefficients. For example, such changes have been observed for acetic acid (Table 3) and also for thallium(I) [24] and lead(II) [81] chloride complexes in isopiestic $NaClO_4$ + NaCl solutions which are nearly isomolar.

Krigintsev[82] and Ryazanov suggested[41–43] isopiestic solutions of mixtures of BX with BA as a new standard state. It is recommended that, when the latter is used, the entire experimental effect be included in the thermodynamic functions for equilibrium (1). On this assumption, no account is taken of the differences between the following parameters:

$$\Delta \lg y_\pm = (\lg y_{\pm MX_z} - \lg_{\pm BX})\, m^{-1}, \quad (21)$$

$$\Delta \lg y_\pm'' = (\lg y_{\pm MX_z} - \lg y_{\pm BA})\, m^{-1}\ . \quad (22)$$

The main feature is that one neglects the difference between the degrees of associaiton of ions in mixtures of the BX and BA salts, which makes an appreciable contribution even to the properties of 1.0 M Na(Cl→F) solutions[83] owing to the different strengths of the $Na^+(H_2O)_xCl^-$ and $Na^+(H_2O)_xF^-$ ion pairs.

A novel, purely chemical approach to complex non-ideal solutions put forward by Poppi[84,85] is noteworthy. It is based on allowance for the formation of solvates and transformation distributions. The non-ideality of such solutions is taken into account in terms of the hypothesis of an ideal solution of a continuous set of solvates. However, this procedure for taking into account non-ideality has not so far undergone the necessary tests on a sufficient number of specific examples. This also applies to a promising unified concept within the framework of which reduced ionic activity coefficients are used as characteristics of the non-ideality of the solutions.[86]

In many systems, the quantities λ_n in Eqn. (11) remain virtually constant when constant ionic strengths are varied in the range 0.5–4.0 (Table 3). The constancy of λ_n has been frequently demonstrated in relation to the behaviour of weak acids in mixtures of two electrolytes. The values of λ_n for the stepwise protonation of anions, i.e.

$$nH^+ + A^{z-} \rightleftarrows H_nA^{n-z} \quad (23)$$

were determined for systems with z = −1, −2, and −3. On the basis of the constancy of λ_n at constant ionic strengths I in the range 0.5–4.0, a method was developed for the separation of the medium effect from the effect of weak complex formation.

It is important to stress that the coefficients λ_n are constants even in those systems where the values of $\lg y_i$ in Eqn. (8) depend significantly on the constant ionic forces in mixtures of two electrolytes. The abolition of the differences between the values of $\lg y_i$ as a result of the cancellation of the third virial coefficients in equations of type (5) explains this finding. According to data in handbooks,[87] the quantities $b_{i,1}$ are almost constant for 0.1–0.6 m aqueous Na(ClO_4→A) solutions with A^- = Cl^-, Br^-, or I^-, but

decrease appreciably with increase in the molality of mixtures of $Li(ClO_4 \rightarrow A)$ and $K(F \rightarrow A)$. Mixtures of MSO_4 (M = Zn, Cu) with sodium, potassium, magnesium, and bismuth(II) sulphates as well as sulphuric acid can be divided into three groups as regards the nature of the dependences of $\Delta \lg y_{\pm}$ on I:[88] for the first group, the dependence has a maximum, for the second it has a minimum, and for the third the values of $\Delta \lg y_{\pm}$ remain almost constant over the entire range of ionic strengths I.

Potentiometric determinations of the activity coefficients of microamounts of tris(ethylene diamine)cadmium(II) [89] from the e.m.f.'s of cells with transport in 1 M aqueous $Li(ClO_4 \rightarrow A)$ solutions showed that b_i [Eqn.(16)] varies with increase in I in the same way as $y_{\pm}$ for $LiClO_4$ + LiA mixtures.

The influence of the charge of the ion A^{z-} in equilibrium (23) on λ_n in Eqn.(11) is of interest. There exists the view that the relation[79,90]

$$\lambda_n \simeq n\lambda_1 \qquad (24)$$

is valid, as can be seen from the data for oxalic acid, or that $\lambda_1 \simeq \lambda_2 \simeq \lambda_3$, as can be seen from the values of λ_n for citric acid (Table 3). Preference is usually given to Eqn.(24), but, unfortunately, the experimental data concerning the influence of ionic charges in equilibrium (1) on the λ_n are not unambiguous[90] and have been obtained only in isolated studies. In a new investigation,[26] Bjerrum notes that the following relation is valid for weak acido-complexes in solutions with high variable ionic strengths:

$$(y_{M^{z+}}y_{A^-})/y_{MA^{z-}} \approx (y_{MA^{z-1}}y_{A^-})/y_{MA_2^{z-2}} \approx \ldots \approx y_{MA_n^{z-n}}y_A/y_{MA_{n-1}^{z-n+1}}.$$

Allowance for the non-ideality of solutions with the aid of Eqns.(4), (5), or (11) does not meet the entire set of Guggenheim's requirements[61] (p. 5) for semi-ideal mixtures. This set includes the requirement that the solutions, for example, of BX and BA, at constant temperatures and pressures be mixed without a heat or volume change. Comparison of the data in Tables 3 and 4 shows that the substitution $Na(ClO \rightarrow A)$ at constant values of I in the range 1.0 – 6.0 hardly affects the values of λ_1 in Eqn.(11) but does alter appreciably $\lambda_{1(H)}$ in the equation

$$\Delta H_1^{\circ} = \Delta H_1 + \lambda_{1(H)}c_{Ac^-} \qquad (25)$$

where ΔH_1 and ΔH_1° are the enthalpy changes standardised by I M $NaClO_4$ and $Na(ClO_4 \rightarrow A)$ solutions, while $\lambda_{1(H)}$ are coefficients taking into account the influence of the non-ideality of the behaviour of H^+ and Ac^- in $Na(ClO_4 \rightarrow Ac)$ solutions on the coefficient λ_1. It is important to note that the values of $\lambda_{1(H)}$ are much higher than those of λ_1 (see the data in Tables 3 and 4).

Analysis of the heats of protonation of NH_3 and OH^- shows[91] that $\lambda_{1(H)}$ for ammonia is appreciably lower than for the OH^- ion, while the influence of the ionic strength I on these coefficients $\lambda_{1(H)}$ is consistent with the equation of Pitzer's theory (with the exclusion of concentrated nitrate solutions).

The absence of an appreciable influence of constant ionic strength on λ_1 at I = 0.5–6.0 (Table 3) led to the conclusion[40,79] that it is desirable to investigate weak acido-complexes at high ionic strengths of solutions with the replacement of a small proportion (< 10–20%) of the inert anions by the ligand ions. This conclusion is valid because the ions of any inert salts are little inferior to reactants forming weak complexes as regards their capacity for complex formation. In the light of the Storonkin–Lagunov rule[72] and Bjerrum's studies,[18,29,64] solutions with a variable ionic strength are more suitable as the standard state for the study of weak acido-complexes in aqueous solutions than a medium with a constant ionic strength. A correction for the non-ideality of the behaviour of the reactants involved in the type (1) equilibrium on formation of weak acido-complexes can be introduced, to a first approximation, on the basis of Eqn.(11) even at $I \neq$ const.

Table 4. The value of ΔH_1^0 for the reaction $H^+ + Ac^- \rightleftharpoons HAc$ and $\lambda_1(\Delta H)$ for I M aqueous solutions of NaA and $Na(ClO_4 \rightarrow A)$ at 298 K.[78]

I	A	ΔH_1^0, kJ mol^{-1}	$-\lambda_1(\Delta H)$
1.0	Cl^-	0.83	0.16±0.02
3.0	Cl^-	3.34	0.42±0.04
1.0	Br^-	0.72	0.07±0.03
3.0	Br^-	3.20	0.35±0.02
1.0	I^-	0.69	0.04±0.03
3.0	I^-	2.83	0.26±0.02
6.0	I^-	5.17	0.52±0.05
1.0	ClO_4^-	0.65	0
3.0	ClO_4^-	2.05	0

III. Classification of experimental methods

Various classifications of experimental methods for the study of complex formation in solution have been proposed in the literature,[3,92–94] but they do not take into account the specific features of the weak interaction in terms of type (1) reaction equations. The latter include four types of substances: (1) a simple or complex coordination centre M; (2) a ligand A; (3) the complex MA_n or the complexes $\sum_n MA_n$ formed; (4) the solvent H_2O. Measurement of the equilibrium concentrations [M], [A], [MA_n] or $\sum_n [MA_n]$, and [H_2O], i.e. of any of the reactants, and also of the functions $F\{[M]\}, F\{[A]\}, F\{[MA_n]\}$ or $F(\sum_n [MA_n])$, and $F\{[H_2O]\}$ sets limits, in our view, to the first group of methods for the study of weak complex formation in aqueous solutions. The second group comprises methods in which measurements are made of the acitivities (designated by braces) of the reactants or the functions of their activities, i.e. $F(\{M\})$, $F(\{A\})$, $F(\{MA_n\})$ or $F(\sum_n \{MA_n\})$, , and $F(\{H_2O\})$. This is the group of methods involving the measurement of activity.

The approaches to the mathematical analysis of experimental data for weak complex formation, for example, the determination of n and β_n^0, change on passing from concentration methods to activity measurement methods. The separation of experimental methods into the group of concentration methods and the group of activity measurement methods is associated with the need to take into

account the changes in the activity coefficients of the reactants in Eqn. (2) for any choice of standard state.

In a number of studies[7,37,95–98] on weak acido-complexes, fundamentally different information has been obtained about the values of n and β_n^0 for type (1) equilibria, which can be explained by failure to take into account the specific features of the experimental methods, noted above, in the mathematical treatment of the results. The differences are observed most often[95–98] when data obtained by the $F(\{M\})$ methods, for example the potentiometric method using an electrode reversible with respect to M, are compared with data obtained by the $F(\{A\})$ or $F\{[A]\}$ methods, for example the potentiometric method using an electrode reversible with respect to A or the method involving the measurement of solubility. The contribution of the disregarded changes in the activity coefficients of the ions M in the $F(\{M\})$ methods has frequently led to higher values of n and β_n^0 for halide, thiocyanate, and sulphate complexes than those obtained by treating the data in terms of the $F(\{A\})$ methods. A similar difference has been observed in the analysis of the results obtained by the $F\{[M]\}$ and $F(\{M\})$ methods or the $F\left(\sum_n [MA_n]\right)$ and $F(\{M\})$ methods.[7,97] The conventional parameters of the complex formation equilibria, involving both chemical interaction and the effect of the medium, have been determined in numerous investigations,[7] although their conventional nature has been rarely mentioned. The differences between the values of n and β_n^0 considered usually disappeared in the mathematical analysis of the experimental data using Eqns. (11) or (17). However, additional parameters then appeared in the form of the quantities λ_n or "b", whose values depended on the type of experimental method.[96]

An unusual case of the scatter of the values of n and β_n^0 for weak complexes has been observed[99–101] when the extraction method was used. The replacement of one extractant by another frequently alters the thermodynamic parameters of the equilibria investigated in the aqueous phase. For example, the extraction of traces of tris(phenanthroline)ruthenium(II) perchlorate from 0.75 M aqueous solutions of sodium sulphate with chloroform or acetophenone led[101] to significantly different values of the logarithms of the stepwise formation constants of the outer-sphere complexes $[RuPhen_3](ClO_4)_n^{3-n}$ (Phen = phenanthroline) for $n = 1$ and 2; these values proved to be 2.38 and 1.73 or 5.43 and 2.49 for extraction with chloroform and acetophenone respectively. Such differences are caused by the change in the standard conditions on replacement of the type of extractant. Aqueous solutions saturated by the extracting solvent constitute the standard state when extraction methods are used to investigate complex formation in aqueous solutions.

In an attempt to obtain more objective information about weak complexes in aqueous solutions, investigators have sometimes used[81] in Eqn. (2) the concentrations of some of the reactants involved in equilibrium (1) and the activities of others. Such calculations yielded estimated thermodynamic parameters of the type (1) equilibrium, the extent to which they are conventional being difficult to estimate.

For the experimental study of weak complex formation by concentration methods, it is useful to employ in the mathematical treatment of the experimental data the activity coefficients of one or several (but not all) components of the equilibria. In particular, one should avoid using the mean ionic activity coefficients in the study of weak stepwise complex formation, although some investigators[102] do not agree with this claim. From our point of view, their information about the stability constants of weak complexes can be regarded as merely qualitative but not quantitative.

The application of experimental activity methods is complicated by the need to carry out all the calculations in terms of activities or to obtain additional information about the activity coefficients of the reactants whose activities have been measured experimentally. The determination of reliable values of n and β_n^0 for weak complexes by the activity methods involves direct or indirect determination of the activity coefficients of both molecules and individual ions.[25]

The $F\left(\sum_n [MA_n]\right)$, methods, in which measurements are made for example, of the optical densities of solutions, chemical shifts, heats of reaction, etc., are sometimes (especially for $n = N = 1$) most useful for the experimental study of weak complex formation. However, these methods, which yield the dependence of the given parameter $\bar{P}$ on c_A, entail the necessity to solve equations of the type

$$\bar{P} = \sum_{n=0}^{N} (P_n [MA_n])/c_M, \qquad (26)$$

where P_n are the molar coefficients of the parameter $\bar{P}$ of the complexes MA_n. The solution of type (26) equations for weak complexes is associated with the need to find simultaneously n, β_n^0, and λ_n, as well as P_n and $\lambda_{n(P)}$, where the coefficients $\lambda_{n(P)}$ reflect the influence of the medium on the values of P_n. Judging from data (Table 4) for the influence of the medium on the enthalpy of protonation of acetate ions, the values of $\lambda_{1(\Delta H)}$ in this system are several times higher than the values of λ_1. Hitherto, in studies on weak complexes by the $F\left(\sum_n [MA_n]\right)$ methods, the influence of the medium on $\lambda_{n(P)}$ was usually disregarded. Such neglect of the values of $\lambda_{n(P)}$ has frequently led to significant differences between the constants for the protonation of strong acid anions in aqueous solutions[103] (p. 40) in calculations based on values of $\bar{P}$ obtained by different methods. The simultaneous determination of n, β_n^0, P_n, λ_n, and $\lambda_{n(P)}$ from a single smooth curve relating P to [A] for $n > 1$ has not been carried out and, judging from the first attempts,[90] is scarcely possible. The use of the $F\left(\sum_n [MA_n]\right)$ methods for the study of type (1) equilibria can be specially recommended in combination with the measurements of λ_n, P_n, and $\lambda_{n(P)}$ independent of the parameter $\bar{P}$. Such experimental methods must be sought. Electrodes reversible with respect to weak complexes MA_n may be useful, in addition to different types of molecular, microwave, and ultrasonic spectroscopy, but in such experiments it is essential to take into account the influence of the medium on the standard potentials.

IV. Complexes with molecular ligands

Ammonia is a classical ligand of the molecular type. The study of the formation of metal ammines in aqueous solutions by Bjerrum[104] determined the development of a large series of modern aspects of the chemistry of complex formation in condensed phases. However, in Bjerrum's studies the majority of problems concerning the formation of weak ammines in solutions were not solved. Until recent years, the very marked dependence of the formation constant of the complex $MgNH_3^{2+}$ on the type of magnesium salt[104] (p. 154) from the solubility of which in aqueous ammonia solutions the constant had been calculated was not understood. The solubilities at

291 K of magnesium naphthalene-β-sulphonate, cinnamate, and oxalate, led to $\lg\beta_1$ = 0.02, −0.13, and −0.66 respectively for the $MgNH_3^{2+}$ ion.

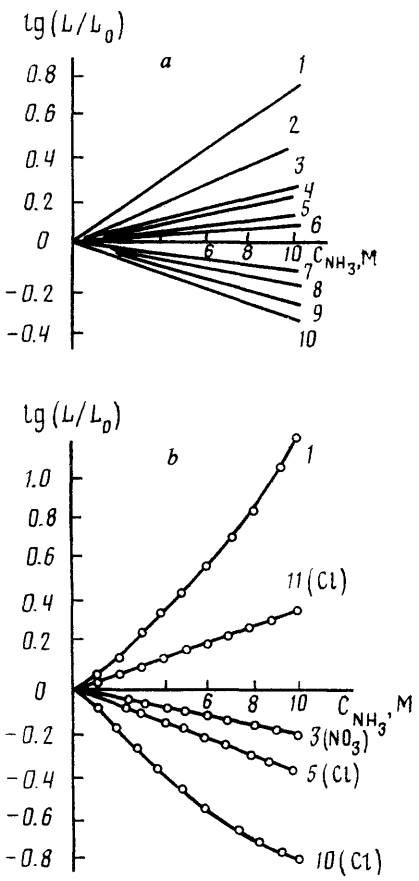


Figure 1. Dependences of the logarithms ($\lg L/L_0$) of the relative solubilities of thallium(I) salts (*a*) and hexamminecobalt(III) salts (*b*) on the ammonia concentration in 1.0 M aqueous solutions of ammonium perchlorate (nitrate (NO_3) or chloride (Cl)] at 298 K (L_0 represents the solubilities of the salts at c_{NH_3} = 0): *1*, perchlorates; *2*, iodides; *3*, nitrates; *4*, bromides; *5*, chlorides; *6*, bromates; *7*, carbonates; *8*, sulphates; *9*, oxalates; *10*, iodates; *11*, hexacyanoferrates.[25]

The decrease in the stability constant of the complex $TlNH_3^+$ with increase in ammonia concentration in aqueous solutions could not be explained[104] (p. 183). The value of this constant was unjustifiably included also among critically selected constants.[5] The marked increase in the solubility of $[Co(NH_3)_6](ClO_4)_3$ with increase in ammonia concentration in solution[105] in practical applications in the hydrometallurgy of non-ferrous metals[106,107] and the marked decrease in the solubility of $[Co(NH_3)_6]_2(SO_4)_3$ with increasing concentration of ammonia in water remain unexplained.

Systematic studies have been recently carried out[25,44–47,108–110] on the formation of weak ammines in relation to ammonia solutions of thallium(I) lithium, sodium, magnesium, calcium, strontium, barium, hexammine- and tris(ethylenediamine)cobalt(III), and a number of other simple and complex cations, which do not hydrolyse appreciably at pH < 11, in aqueous solutions with c_{NH_3} = 0−10 M. The principle standard state in the majority of these investigations consisted of 1.0 M solutions of ammonium perchlorate, nitrate, or chloride at 298 K. A number of experiments have also been carried out in 0.25, 0.50, 2.0, and 4.0 M solutions of ammonium salts at 293, 298, 303, and 308 K. A distinctive feature of the series of studies considered was the simultaneous measurement of the equilibrium concentrations or activities of the central cations, ammonia, the complexes, and water, i.e. the properties of all the reactants involved in type (1) equilibria. Electrodes reversible with respect to M and NH_3, measurements of the solubility of sparingly soluble salts, extraction, electronic spectroscopy, and NMR were used.

It is clear from the data in Fig. 1 and similar relations that the solubility of sparingly soluble salts in aqueous ammonia solutions at I = const. cannot be used to determine n and β_n^0 for type (1) reactions without taking into account the influence of the anion of the dissolved salt, although the anions considered are not appreciably associated with the cations M^{z+}.[3–6] Experiments designed to measure the vapour pressure of ammonia over aqueous salt solutions showed[44] that the potassium cation and the ClO_4^- anion do not influence appreciably the activity of ammonia in its aqueous salt solutions. Taking into account the fact that the potassium cation does not form ammines in aqueous solutions[3–5] while the solubility of $KClO_4$ in 1 M NH_4ClO_4 solutions with c_{NH_3} = 0−10 M is constant (0.040 M at 298 K),[47] a new extrathermodynamic assumption was introduced on the basis of the above postulate:

$$y_{K^+} = y_{ClO_4^-} = 1, \qquad (27)$$

where y_{K^+} and $y_{ClO_4^-}$ are the activity coefficients of the ions K^+ and ClO_4^- in aqueous ammonia solutions at 298 K. Assumption (27) served as the basis of a quantitative characterisation of the stepwise formation of weak ammines of a number of metals in aqueous solutions at c_{NH_3} = 0.1−10 M and also of the calculation of the activity coefficients of individual ions in aqueous-salt ammonia solutions. The calculation showed that the logarithms of these coefficients (Table 5) are positive for anions but negative for the majority of cations, including NH_4^+. Under these conditions, hydroxopentamminecobalt(III) has a zero value of the logarithm of the activity coefficient in 0.1−10 M ammonia solutions, i.e. ammonia is not appreciably bound by the cation, while the $Coen_2CO_3^+$ cation (en = ethylenediamine) actually salts out ammonia, like the anions.

A nearly zero value of the activity coefficient of the iodide ion combined with the similarity of the behaviour in aqueous ammonia solutions of potassium and caesium cations suggest that the extrathermodynamic assumption (27) is in many respects identical with the usual assumption[111,112] that the activity coefficients of the I^- and Cs^+ ions are equal. However, for the study of weak metal ammines in aqueous solutions, assumption (27) is better justified and more convenient[25,44] than the caesium iodide ionic scale.

On the basis of assumption (27), the composition and formation constants of thallium(I) ammines have been calculated[25] from the solubilities L of the salt $TlClO_4$ (Fig. 1) adjusted to a constant ionic strength of 1.0 based on the sum of the salts NH_4ClO_4 and $TlClO_4$.

The calculations were performed by the method of least squares on the basis of the equation

$$(L/L_0 - 1)\{H_2O\}\{NH_3\}^{-1} = K_1^0 + K_1^0 \cdot K_2^0\{NH_3\}\{H_2O\}^{-1}, \quad (28)$$

where L_0 and L are the solubilities of $TlClO_4$ in 1.0 M (NH_4 + Tl)ClO_4 solutions in the absence or presence of ammonia. The activities of water and ammonia (on the molarity) scale, required for the solution of Eqn. (28), were expressed in terms of the molarity scale.

Table 5. The logarithms of the activity coefficients of individual ions in 1.0 M aqueous ammonia solutions of NH_4A at c_{NH_3} = 10 M and 298 K.[25,44]

Ions	lg y	A^- in NH_4A	Ions	lg y	A^- in NH_4A
Tl^+	−0.95	ClO_4^-	NO_3^-	0.45	NO_3^-
$Co(NH_3)_6^{3+}$	−1.24	ClO_4^-	Cl^-	0.67	ClO_4^-
$Co(NH_3)_6^{3+}$	−0.94 *	ClO_4^-	Br^-	0.53	ClO_4^-
$Co(NH_3)_6^{3+}$	−1.23 **	ClO_4^-	I^-	0	ClO_4^-
$Co(NH_3)_5OH^{2+}$	0	ClO_4^-	IO_3^-	1.50	ClO_4^-
$Coen_2CO_3^+$	0.24	ClO_4^-	SO_4^{2-}	2.4	ClO_4^-
NH_4^+	−0.56	ClO_4^-	$Fe(CN)_6^{3-}$	0.51	NO_3^-

*At I = 0.50.
**At 309 K.

The potentiometric measurements of the activities of thallium(I) ions with the aid of the Tl(Hg) electrode in aqueous ammonia solutions led to values of K_n^0 for the thallium(I) ammines which agreed with those found for the solubility of $TlClO_4$ only after correcting the measured e.m.f.'s of the cells with transport for the liquid-junction potentials arising at the interfaces between the solutions: 1 M NH_4ClO_4|1M NH_4ClO_4 + x M NH_3. These potentials, determined with the aid of iodide and perchlorate membrane electrodes, were 3.0 mV for 1.0 M ammonia.

The Bjerrum formation functions $\bar{n}'$ of thallium(I) ammines were calculated by means of the following equation from the experimental values of $\{NH_3\}$ and y_{NH_3} in the studies under consideration:

$$\bar{n}' = (c_{NH_3} - \{NH_3\}/y_{NH_3})/c_{Tl^+}, \quad (29)$$

which led to negative values of $\bar{n}'$ for c_{NH_3} = 0.1−10 M. Additional measurements of $\{NH_3\}$ and y_{NH_3} were performed for aqueous ammonia solutions of the potassium salts KX. The corrections Δn were applied to $\bar{n}'$ on the basis of the above data in accordance with the equation

$$\Delta\bar{n} = (c_{NH_3} - \{NH_3\}/y_{NH_3})/c_{KX}. \quad (30)$$

The Bjerrum functions $\bar{n}$, from which the compositions and formation constants of the complexes $Tl(NH_3)_n^+$ were calculated, had been determined from the relation

$$\bar{n} = \bar{n}' - \Delta\bar{n}\ . \quad (31)$$

The values of $\Delta\bar{n}$ from Eqn. (30) were more negative than the values of $\bar{n}'$ found from Eqn. (29). Hence the values of $\bar{n}$ based on Eqn. (31) were positive and the least squares solution of the equation

$$\sum_n (\bar{n} - n)\{NH_3\}^n\{H_2O\}^{-n}\beta_n^0 = 0 \quad (32)$$

led to formation constants agreeing (Table 6) with the above parameters obtained with the aid of the $F(\{Tl^+\})$, $F([Tl^+])$, $F(\{NH_3\})$, and $F\left(\sum_n [Tl(NH_3)_n^+]\right)$ methods. ^{205}Tl NMR was employed as the last method. The constants K_n were calculated from the chemical shifts of the ^{205}Tl signal taking into account the influence of ammonia on σ_2' in accordance with the equation

$$\sigma_0 = \sigma_0' + \alpha_0 c_{NH_3} \quad (33)$$

where σ_0' and σ_0 are the chemical shifts in aqueous solutions without ammonia and at an ammonia concentration c_{NH_3}, while α_0 are coefficients taking into account the influence of ammonia on the chemical shift of ^{205}Tl present as the aquo-complex.

Table 6. Data on the compositions and stepwise stability constants of the complexes $Tl(NH_3)_n^+$ in 1.0 M NH_4ClO_4 solutions at 298 K.[25,44]

lg $K_n \pm 3\sigma$		Experimental method	Type of method according to classification in Section III
n=1	n=2		
0.85±0.10	0.4±0.1	Solubility	$F([Tl^+])$
−0.89	−1.4	Ditto	Ditto with allowance for $[H_2O]$ on the mole fraction scale
1.2±0.3	0.3±0.1	Potentiometry with ammonia electrodes*	$F(\{NH_3\})$
1.2±0.3	0.3±0.1	Extraction of ammonia into chloroform*	$F(\{NH_3\})$
0.60±0.01	–	Potentiometry with a Tl(Hg) electrode	$F(\{Tl^+\})$
1.04±0.09	0.3±0.1	Ditto with a correction for the liquid junction potential	Ditto
−0.70±0.09	−1.3±0.1	Ditto	Ditto with allowance for $[H_2O]$ on the mole fraction scale
0.98±0.08	0.3±0.1	^{205}Tl NMR	$F([MA_n])$
0.4±0.2	–	Electronic spectra**	$F([MA_n])$

*$I \simeq$ 1.2 M NH_4ClO_4 + $TlClO_4$.
**At $c_{NH_3} \leqslant$ 5.0 M.

The low accuracy of the measurement of small changes in the optical density ($\Delta\overline{D}$) of Tl^+ solutions due to added ammonia precluded the determination of K_n for $Tl(NH_3)_n^+$ from electronic spectra in agreement with data produced by other methods (Table 6). This finding has already been explained.[113] The contribution of the formation of $Tl(NH_3)_2^+$ to $\Delta\overline{D}$ led to a low value of K_1 calculated from $\Delta\overline{D} = F(\{NH_3\})$.

The study of the influence of the ionic strength I of the solutions on the formation constant of the complex $TlNH_3^+$ afforded[44] the equation

$$\lg K_1^0 = \lg K_1 - 0.065I, \quad (34)$$

where K_1^0 is the constant at 298 K and $I \to 0$.

Tests of the possibility of determining the composition and stability of weak inner-sphere ammines of thallium(I) and a number of other metals with the aid of a wide range of experimental methods have made it possible to apply a similar approach to the study of the outer-sphere interaction of ammonia with coordinatively saturated inert cobalt(III) complexes. The calculations showed (Table 7) that hexammine- and tris(ethylenediamine)cobalt(III) combined with up to four ammonia molecules in the outer sphere in aqueous solutions. The binding strength of each succeeding molecule compared with the previous one diminishes in conformity with the statistical effects $S_{n,n+1}$ [104] for the limiting coordination number $N = 4$.

Table 7. The logarithms of the stepwise stability constants of the outer-sphere ammonia complexes of cobalt(III) in aqueous solutions at I = const. and 298 K and the statistical and average general effects.[25,44]

n	$\lg K_n^0 \pm 3\sigma$		$n, n+1$	$T_{n,n+1}$	$S_{n,n+1}$	
	$[Co(NH_3)_6](NH_3)_n^{3+}$	$[Coen_3](NH_3)_n^{3+}$			$N=4$	$N=8$
1	0.95±0.09 *	1.46±0.09 **	–	–	–	–
1	0.84±0.10 ***	0.85±0.07 ***	–	–	–	–
2	0.53±0.08	1.00±0.08	1.2	0.41	0.43	0.36
3	0.28±0.12	0.64±0.07	2.3	0.35	0.35	0.34
4	–	0.20±0.06	3.4	0.44	0.43	0.21

*The values of $\lg K_n^0$ were obtained from the solubility of hexamminecobalt(III) perchlorate in 1.0 M ammonium perchlorate solutions.

**The values of $\lg K_n^0$ were obtained from the averaged data for the extraction of ammonia into chloroform and potentiometric data obtained using an ammonia electrode at $I \simeq 2$.

***From electronic spectra t $I = 1$.

The low solubility (3×10^{-4} M at 298 K) of hexamminecobalt(III) perchlorate in 1.0 M NH_4ClO_4 solutions made it possible to investigate the outer-sphere ammonia derivatives of this complex only by the $F(\{M\})$, $F\{[M]\}$, and $F\{[MA]\}$ methods. The high solubility of tris(ethylenediamine)cobalt(III) perchlorate made it possible to investigate its ammonia derivatives in terms of the activity of ammonia, i.e. by the $F(\{A\})$ method, at $I \simeq 2$. In the study of hexamminecobalt(III) derivatives, it was observed[25,44] that the influence of ionic strength in the range 0.1–1.0 is represented by the relation

$$\lg K_1^0 = \lg K_1 + 0.54I. \quad (35)$$

Extrapolation in terms of Eqn. (35) to $I = 2$ yielded $\lg K_1 = 1.49$. Within the limits of error, this value agrees with that (Table 7) found for the outersphere complex $[Coen_3](NH_3)^{3+}$. This finding suggests that the $Coen_3^{3+}$ and $Co(NH_3)_6^{3+}$ ions have approximately the same ability to combine with ammonia in aqueous solutions.

The formation constants of the outer-sphere ammonia derivatives of hexamminecobalt(III) and the ionic activity coefficients in aqueous ammonia solutions (Table 7) provide a quantitative idea[106] about the increase in the solubility of $[Co(NH_3)_6](ClO_4)_3$ and the decrease in the solubility of $[Co(NH_3)_6]_2(SO_4)_3$ [107] in aqueous solutions with increase in the concentration of ammonia.

The method for the study of ammonia derivatives of metals considered above was extended to weak methylamine, pyridine, ethylenediamine and other relatively unstable complexes of cations with molecules in aqueous solutions.[25,44,48–50]

V. Acido-complexes

Careful studies of the stepwise formation reactions of weak acido-complexes of metals in aqueous solutions by different methods indicate the impossibility of obtaining a single set of stepwise stability constants with the representation of the experimental data obtained by different experimental methods. This situation has been demonstrated recently in relation to zinc chloride complexes.[114] It is entirely reasonable because the values of K_n^0 for these complexes leads to values of $\Delta_r G_n^0$ comparable to $1.5RT$, while reliable unambiguous isolation of the small contribution of the specific interaction of Zn^{2+} with Cl^- against the background of inevitable significant changes in the ionic acitivity coefficients is virtually impossible. However, only allowance for the changes in the activity coefficients in 3.0 M aqueous $(Na \to H)ClO_4$ solutions with the aid of an equation of type (11) led to the possibility of describing the complex form of the solubility curve for molybdenum(VI) oxide.[32] Other conceivable ways of explaining this curve with a complex shape did not lead to its quantitative representation in terms of the constants of the Law of Mass Action.

Data obtained solely by thermodynamic methods for the investigation of weak stepwise formation of acido-complexes without extrathermodynamic assumptions usually do not permit an unambiguous differentiation between the changes in the activity coefficients and the formation of the complex MA_{n+1} after the real formation of the associated species MA_n. Under favourable conditions, such differentiation can be achieved[31] on the basis of spectroscopic measurements at several wavelengths but that too is not unambiguous because no account is taken of the influence of the composition of the ionic medium on the molar extinction coefficients of the reactants.

Many weak inner-sphere and outer-sphere acido-complexes have been investigated[3–6] by the potentiometric method with the aid of electrodes reversible with respect to the proton or the central ion of the complex using cells with transport. In studies of this type, corrections were frequently introduced for the liquid junction potentials.[115] The correct application of such corrections led to the experimental determination of the activities or equilibrium concentrations of individual ions, M. The liquid junction potentials have been usually assumed to be proportional to the ligand concentrations and the proportionality coefficients b_A have been determined from experimental data. Such calculations have been carried out, for example, in the study of weak hydroxo-complexes of calcium, strontium, and barium in 3 M $Na(ClO_4 \to OH)$ solutions[116]

and of lead(II) and cadmium acetate and benzoate complexes in 1.0 M (Na, H)(ClO_4→A) solutions, where A represents acetate or benzoate ions,[117] and in a number of other systems.[3-5] The changes in the e.m.f.'s of the cells investigated as a function of the ligand concentration were attributed in the above studies to the contributions by β_n^0 and b_A. The calculations showed (Table 8) that variation of the coefficients b_A alters appreciably the calculated values of β_n^0 and even the values of n. The scale of the influence of the liquid junction potentials increases sharply[118] with decrease in the association constants determined. When an unreliable correction is applied for the liquid junction potentials, the constants have the significance of only semiquantitative characteristics of weak complex formation equilibria,[117] although they represent satisfactorily [with the differences $\sigma(E) \leqslant 0.1$ mV] the experimental data. A combination of different values and different corrections for diffusion potentials does not influence appreciably $\sigma(E)$, which hinders the selection of reliable information about the systems investigated.

Table 8. The compositions and stability constants of $Pb(Ac)_n^{2-n}$ in 1.0 M aqueous $Na(ClO_4 \rightarrow Ac)$ solutions at $c_{Ac^-} \leqslant 0.2$ M.[117]

method used to take into account E_d^*, mV	$\beta_1^0 \cdot 10^{-2}$	$\beta_2^0 \cdot 10^{-3}$	$\beta_3^0 \cdot 10^{-3}$	$\sigma(E)$, mV
No allowance for E_d^*	0.95±0.04	1.37±0.06	–	0.36
2.6 [HAc] – 7.2 [Ac$^-$]	0.99±0.02	1.23±0.03	–	0.17
2.6 [HAc] – 7.2 [Ac$^-$]	1.03±0.02	1.06±0.05	1.1±0.3	0.10
1.4 [HAc] – 13.6 [Ac$^-$]	1.00±0.01	1.11±0.01	–	0.09
1.4 [HAc] – 13.5 [Ac$^-$]	1.02±0.01	1.05±0.04	0.38±0.02	0.08
(2) [HAc_2^-] + [H_2Ac_2]	1.01±0.01	1.28±0.02	–	0.10
(6) + [HAc_2^-]	0.996±0.01	1.27±0.01	–	0.08
5.4 [HAc] – 13.6 [Ac$^-$]	1.029±0.004	1.11±0.02	–	0.03

*E_d = diffusion potential.

Vierling[34,69] studied the equilibria

$$Pb^{2+} + nA^- \rightleftarrows PbA_n^{2-n} \qquad (36)$$

where A are chloride and bromide ions and $n_{max} \geqslant 4$ according to the e.m.f.'s of cells with transport [containing Pb(Hg) electrodes] on the basis of Eqn. (11) without corrections for liquid function potentials. In the calculations of n, β_n^0, and λ_n, use was made of up to a thousand experimental e.m.f.'s at different ligand concentrations. The system (36) was investigated in 4.0 M $Na(ClO_4 \rightarrow A)$ solutions at $c_{A^-} = 0-4.0$ M.

The traditional expression for the complex formation function Φ is

$$\Phi = c_{Pb^{2+}}/[Pb^{2+}] = 1 + \sum_{n=1}^{N} \beta_n [A]^n \qquad (37)$$

and includes β_n standardised by variable composition $Na(ClO_4 \rightarrow A)$ solutions. Vierling replaced it by the relation

$$\Phi = 1 + \sum_{n=1}^{N} \beta_n^0 [A]^n \exp(\lambda_n [A]), \qquad (38)$$

where β_n^0 were standardised with 4.0 M $NaClO_4$ solutions and the quantities β_n, β_n^0, and λ_n were linked by relations (11). The contributions of the diffusion potentials in such calculations enter into the quantities λ_n. The parameters of Eqns. (37) and (38) were calculated from the dependences of ΔE on [A] using at $T = 298$ K the equation $\Delta E = 59.2 \lg \Phi$, where ΔE is the experimental e.m.f. The method of least squares with the minimisation of $\delta(E)$ led Vierling[34] to the data compiled in Table 9. It was found that the employment of a gigantic set of accurate experimental data makes it possible to represent the latter (within the limits of the error of the determination of ΔE) both by Eqn. (37) and by Eqn. (38) with different variations of β_n and λ_n. However, the application of Eqn. (38) yielded a series of values of β_n^0 for all the values of n equal to 1, 2, ..., N, while the application of Eqn. (37) frequently led to zero values of β_n for certain values of n. The λ_n found had different signs and did not depend regularly on the values of n. Only when the potentiometric study of equilibrium (36) was supplemented by solubility and spectrophotometric data did Vierling arrive at the unambiguous, from his point of view, conclusion[34] that in 4.0 M $Na(ClO_4 \rightarrow A)$ solutions with [A] = 0–4.0 and at $T = 298$ K, all the complexes PbA_n^{2-n} with $N = 4$ for A = Cl^- and $N = 5$ for A = Br^- are formed in succession. However, the very high values $\lambda_n = 0.232$, 0.244, 0.151, 0.399, and 0.309 for $n = 1-5$ were obtained for $PbBr_n^{2-n}$ from the measurements of the solubility of lead(II) bromide, in contrast to the potentiometric data (Table 9).

Table 9. Data for the formation of the complexes $PbCl_n^{2-n}$ and $PbBr_n^{2-n}$ obtained with the aid of Hg(Pb) electrodes in 4.0 M $Na(ClO_4 \rightarrow Cl)$ and $Na(ClO_4 \rightarrow Br)$ solutions at 298 K.[34,39]

n	Version (1)*			Version (2)*		
	lg β_n without λ_n	lg β_n^0 with λ_n	λ_n	lg β_n without λ_n	lg β_n^0 with λ_n	λ_n
Chloride complexes						
1	1.14	1.277	0.002	1.31	1.294	−0.006
2	1.93	1.574	0.001	1.34	1.473	−0.003
3	1.97	2.285	−0.036	2.37	2.330	−0.038
4	1.84	1.433	0.096	**	1.134	0.038
5	–	–	–	1.20	0.959	0.021
$\sigma(E)$, mV	0.37	0.15	–	0.12	0.14	–
Bromide complexes						
1	1.56	1.431	−0.021	1.53	1.505	−0.019
2	**	2.000	−0.050	**	1.443	−0.002
3	3.01	2.885	−0.237	3.03	2.996	−0.096
4	**	2.987	0.159	2.36	2.692	0.054
5	2.94	–	–	2.69	2.653	0.064
6	–	–	–	2.01	–	–
$\sigma(E)$, mV	0.55	0.21	–	0.15	0.16	–

*Versions (1) and (2) differ by the maximum values of n.
**$\beta_n \leqslant 0$ were obtained.

The system of thiocyanate complexes $(Nibipy_3)(SCN)_n^{2-n}$, investigated on the basis of the solubility of tris(2,2'-bipyridyl)-nickel(II) in 4.0 K (F→SCN) solutions, was analysed[63] in terms of Eqns. (37) and (38) using 12, 40, and 86 experimental solubilities.

The picture observed for the complexes PbA_n^{2-n} (Table 9) was in many respects repeated (Table 10) for the tris(2,2'-bipyridyl)nickel(II) thiocyanate complexes but, in contrast to the $PbBr_n^{2-n}$, the values of λ_n found were comparatively low, amounting to 0.04 ± 0.01 for all the values of n. Calculations for this system showed that a small set of comparatively accurate (errors of about ±1%) data, usually provided by the solubility method, does not permit the determination of reliable values of stepwise stability constants equal to 1.0 and below for $n \geqslant 3$ in combination with λ_n. The errors in the determination of the values of K_n^0 in Table 10 for $n \geqslant 3$ are comparable to the constants themselves. The high correlation of the quantities n, β_n^0, and λ_n with one another in equations of type (38) hinders an unambiguous and reliable calculation of all these functions from smooth $\Phi\{[A]\}$ curves for $n \geqslant 3$. Detailed analysis of the methods for the calculation of all the parameters of Eqn. (38) in systems of relatively unstable complexes has been correctly referred to as estimation of these parameters.[35] A reliable determination of β_n^0 and λ_n is possible only for $n = 1$; when $n \geqslant 3$, it is difficult to hope (Table 8) for the selection of a single reliable series of values of β_n^0 and λ_n with low errors of the determination of these functions. The validity of this conclusion has been confirmed by careful investigation.[35] However, the use of the values of λ_n found in independent experiments or calculations can increase the accuracy of the determination of the stepwise stability constants of the complexes by Eqn. (38).

Table 10. Data for the formation of the outer-sphere complexes $[Nibipy_3](CNS)_n^{2-n}$ obtained by the solubility method in 4.0 M K(F→SCN) solutions at 298 K.[63]

n	$\lg \beta_n$		$\lg \beta_n^0$	$\lg K_n^0$	λ_n
	r*=12	r=40	r=86		
0	−9.13±0.03**	−9.061±0.026**	−9.02**	–	0.05
1	1.98±0.11	1.445±0.13	1.50	1.50	0.04
2	***	3.045±0.032	2.98	1.48	0.03
3	2.97±0.19	2.544±0.19	2.34	−0.64	0.04
4	***	***	2.18	−0.16	0.03
5	2.23±0.12	2.419±0.036	2.02	−0.16	0.04

*r is the number of experimental values of the solubility used in the calculations.

**The logarithms of the solubility product of tris(2,2'-bipyridyl)-nickel(II) thiocyanate.

***$\beta_n \leqslant 0$.

The application of Eqn. (38) to a series of systems investigated previously demonstrated convincingly the conventional significance of many of the values of β_n for weak complexes with $n > 1$, which was noted in previous studies.[68] For example, the results of potentiometric measurements with the $Coen_3^{2+}$, $Coen_3^{3+}|Pt$ electrode in $NaClO_4 + Na_2SO_4$ solutions at constant ionic strengths, which were interpreted previously in terms of the hypothesis of the formation of a series of outer-sphere complexes $[Coen_3](SO_4)_n^{3-2n}$ (n = 1, 2, 3), were reproduced by means of the quantities β_1^0 and λ_1 with a high correlation coefficient (>0.995).[98] The validity of this treatment of potentiometric data has been confirmed by measurements of the activity of the sulphate ion and by thermochemical studies. A similar situation has been noted for other weak acido-complexes.[37,98,119]

The linear relation between $\lg\Phi$ and [A] in systems with formation of the acido-complexes MA_n in the absence of appreciable changes in the slopes of the above straight lines as a function of constant ionic strengths has been suggested[40,79] as proof of the absence of complex formation. This proof is based on the identification of the virial coefficients $b_{i,1}$ and $b_{i,1}^*$ in Eqn. (5) and on the claim that they are not influenced by the variation of constant ionic strengths in the range 0.5–4.0. Numerical data similar to those in Tables 3 and 11 were used by the authors[40,79] as a basis for such identification. In reality, for linear relations between $\lg\Phi_M$ and [A] or between $\lg y_M$ and [A], it is not permissible to differentiate on the basis of the data considered the effect of non-ideality and complex formation[31] without resorting to extrathermodynamic assumptions or additional experimental studies.

Table 11. The changes in the conventional diffusion potentials (E_d') and the contribution to the latter of the hydrogen ion activity coefficients (y_{H^+}) at 298 K.[115]

I	Composition of medium	$E_d'[H^+]$, mV mol litre^{-1}	$y_{H^+}[H^+]$, mV mol litre^{-1}
1.0	(Na → H)ClO_4	686	6
0.5	(Na → H)ClO_4	133	4
1.0	(Na → H)ClO_4	69	4
3.0	(Li → H)ClO_4	16	0.45
3.0	(Na → H)ClO_4	18	3
3.0	(K → H)Cl	10	4
1.0	(K → H)Cl	66	3
0.5	(K → H)Cl	123	5
0.5	Na(ClO_4 → OH)	615*	0.9*
3.0	Na(ClO_4 → OH)	8*	1.2*
0.5	Na(Cl → OH)	41*	0.2*

*Per 1.0 mol of OH^- litre^{-1}.

However, re-examination[120] of the Debye–Hückel theory taking into account the shielding of ions by water molecules leads to the possibility of partitioning the experimental values of the second virial coefficient. Such partitioning has already been achieved[121] in relation to a large set of experimental data for aqueous magnesium sulphate solutions with variable ionic strengths in the temperature range 273–423 K. The forces of attraction between the Mg^{2+} and SO_4^{2-} ions were expressed in terms of their association constants and only the effects of repulsive forces were included in the second virial coefficient. Unfortunately the subdivision was based on mean ionic activity coefficients which consist of unequal contributions by cations and anions, even in dilute solutions of ions with very similar electrostatic properties, for example, NH_4^+ and Cl^-.[15] Furthermore, it has been shown that $y_{M^{z+}}$ and y_{Cl^-} vary in fundamentally different ways with increase in the concentrations of aqueous solutions of

ammonium, nickel, and cadmium chlorides. This fact is associated with the increase in the stability of MCl_n^{2-n} in this series of M^{z+}. In view of the need for the summation of $\lg y_{M^{z+}}$ and $\lg y_{Cl^-}$ in order to find $\lg y_{\pm}$, it is difficult to find from the values of the latter the real values of n and β_n for weak acido-complexes. The linear relations between $\lg y_{\pm}$ and for example, concentrations in solutions of alkali metal or alkaline earth metal chlorides are replaced by non-linear relations for y_{H^+} and y_{Cl^-}. This usual phenomenon[54] indicates the desirability of determining n and β_n^0 for equilibrium (1) from the activities of individual ions, the specific features of the behaviour of which are obliterated in the mean ionic functions.

It is frequently forgotten[7,102] that the vast majority of modern data on equilibria of type (1) have been obtained from the activities of the cations and not from the mean ionic parameters. About 40% of the known values of β_n [3-6] have been calculated from the e.m.f.'s of cells with transport incorporating M^{z+}/M^0 indicator electrodes. The changes in the e.m.f.'s (ΔE, mV) of such cells after the introduction of ligands into the test solutions at 298 K are expressed by the equation

$$\Delta E = E_d + 59.2/z \lg C_u/\{M^{z+}\}, \quad (39)$$

where E_d is the liquid junction potential. The relative activities of the ions M^{z+} enter into Eqn. (39) within the quantity E_d.[54] These ionic activities are standardised by solutions in relation to which the values of ΔE have been measured.

The data in Table 11 show how the activity coefficients y_{H^+} vary in aqueous solutions at constant ionic strengths. These changes have been calculated from conventional diffusion potentials (E'_d), which are related to E_d in Eqn. (38) by the expression

$$E'_d = E_d + 59.2/z \lg y_{M_{z+}}.$$

Judging from Table 11, the variation of the constant ionic strengths from 0.5 to 3.0 does not affect appreciably the changes in y_{H^+} as well as the changes in λ_n (Table 3). The transition from 3.0 M (Na→H)ClO_4 solutions to 3.0 M (Li→H)ClO_4 solutions alters y_{H^+} by 4.5 $[H^+]$ mV mol litre^{-1}, i.e. $\lg y_{H^+}$ changes by 0.065, which agrees with λ_1 for the protonation of the acetate ion in 3.0 M (Na→Li)ClO_4. It has been recommended[115] that the numerical y_{H^+} data in Table 11 be used for the selection of ionic media, the variation of the composition of which causes minimal changes in the activity coefficients of the individual ions. The effect of these changes for y_{H^+} in (Li→H)ClO_4 media is much smaller than in (Na→H)ClO_4. The replacement of Cl^- or ClO_4^- by OH^- affects y_{H^+} less than the replacement of Na^+ by H^+, etc.

The need to use the ionic activities, and not mean ionic parameters, to characterise weak acdio-complex formation has been recently demonstrated by Yagodin, Solovkin, and co-workers.[122,123] Equations were proposed for the calculation of the activity coefficients of individual ions in media at constant ionic strengths and the errors in the extrapolation of β_n to I→0 on the basis of the Debye–Hückel theory were estimated. It must be emphasised that in systems with highly charged cations, for example Zr^{4+}, the detection of a whole series of weak complexes having the composition $Zr(NO_3)_n^{4-n}$ was a consequence only of the neglect of the changes in the ionic activity coefficients following the change in the composition of the salt medium.[123] It may be that the detection of stepwise acido-complex formation in M^{5+} solutions[124] is also associated with the contributions by the inconstancy of the activity coefficients like part of the experimentally determined effect described by the β_1 in similar systems.[125]

Bjerrum compared the available information about β_n and n for weak acido-complexes in 10 M H(ClO_4→Cl) and 1–10 M Cl^- solutions. The constancy of the activity coefficients of the Cl^- ions is taken into account with the aid of second virial coefficients. Spectrophotometric and extraction data, which make it possible to measure the MA_n concentrations, were used by Bjerrum in the study of weak acido-complexes,[18,20,26] but the influence of the salt media on the partition coefficients and the molar extinction coefficients of the complexes MA_n was not taken into account. Studies on weak acido-complexes based on the Bjerrum approach merit further expansion but it would be desirable to base future research on Eqn. (11) or on allowance for the second and third virial coefficients. The Storonkin–Lagunov rule[72] suggests that the applicability of Eqn. (11) extends over a wide range of variable concentrations (from 0.1–1 to 5 M) of the anions in aqueous solutions. The activity of water in the test solutions with $I \neq$ const. can be sometimes more usefully employed in equations of type (11) [126] rather than the concentrations of the ligand anions.

VI. Conclusion

The properties of aqueous solutions involving the formation of weak complexes of metal ions are characterised by formal activity coefficients (the conventional physical model) or the contribution due to the occurrence of complex formation reactions is isolated from the latter[121] (the conventional chemical model). The physical model alone frequently reproduces more accurately the properties of the solutions than does allowance for its chemical component, but one must remember that the initial model is based on several empirical parameters. The results obtained by thermodynamic methods do not provide procedures for the unambiguous separation of the experimental properties into the "physical" and "chemical" components when the stability of the complexes MA_n is low without resorting to extrathermodynamic assumptions. However, when account is taken of the two components of the second virial coefficient,[121] such separation is sometimes possible. The simplest assumption involves the attribution of the entire weak interaction in accordance with the type (1) equation to the physical model if the latter can be reproduced by the second virial coefficient alone.

However, on the basis of the determination of the activities of all the individual ions and molecules involved in the equilibria investigated and also with the aid of standard isotherms,[1] the second virial coefficient of the activity can be sub-divided into contributions due to the changes in the activity coefficients and the formation of complexes with a definite composition. A similar subdivision is possible when account is taken of the shielding of ions by water molecules[120] for complex formation in aqueous solution.

The attempts to isolate the contribution of chemical interactions on the basis of spectroscopic data are frequently unreliable because they are based on the assumption of the constancy of the spectroscopic molar parameters in solutions with very different compositions. A reliable separation of the effect of changes in these parameters from the effect of the formation of complexes is hardly possible, which has been demonstrated in the determination of the association constants of ions in aqueous solutions of strong acids.[103] Only the unitary stepwise association constants in excess of 1–5 can serve as reliable thermodynamic indicators of the formation of weak complexes subject to the condition that these constants have been determined from data obtained by a fundamentally different experimental method in accordance with the classification in

Section III of the present review. The information about the formation of weak complexes based on low values of K_n^0, presented in the new international handbooks as critically selective,[5] is frequently unreliable.

Naturally a property of systems with very weak complexes ($k_n < 0.1$) cannot be considered in isolation from the kinetics and mechanisms of the formation of the complexes[127,128] because the formation reactions of such complexes do not obey the principle of the minimisation energy and the Law of Mass Action is not applicable to them. The fluctuation theory, the thermodynamics of non-equilibrium systems, and molecular-kinetic models should be used more widely in the future for the study of systems of this kind, typical examples of which are aqueous solutions of alkali metal halides, nitrates, sulphates, and a number of other salts. The empirical and extrapolation methods for the determination of the stabilities of weak complexes in such systems[129] cannot be regarded as reliable. Furthermore very large errors in the determination of low formation constants are inevitable (for example, $\lg K_5$ for $AuCl_5^{2-}$ is -2.0 ± 1.0).[130]

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