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OUTER-SPHERE INTERACTION IN AQUEOUS SOLUTIONS OF COMPLEX COMPOUNDS

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1. INTRODUCTION

The majority of chemical processes in nature and technology take place in aqueous solutions. These processes are closely linked with complex formation.

Ions in water are present as simple aquo-ions or mixed complexes: hydroxoaquo-, oxoaquo-, halogenoaquo-, and similar compounds. Complex formation in solutions involves the replacement of ligands in the inner sphere of the so called "free" central ion. This replacement may take place with or without change in the geometric configuration of the inner sphere[1,2].

Complex compounds in solution are defined as any associated species whose components are joined by a direct bond[3], whose energy of formation is greater than, or at least only slightly less than, the kinetic energy of the solvent molecules[4]. Associated species in which there is no direct bond between the ions are called outer-sphere complexes or associated species of the ion-pair type[5].

The results of many studies[3] show that complex formation in solutions is not restricted to the Werner[6] coordination sphere. Complex ions which according to Werner's theory are coordinatively saturated may still combine with ions with opposite sign[3] and polar molecules[7].

In a number of complexes the stability of the inner-sphere bonds is comparable to and even slightly less than the stability of the outer-sphere bonds[3,8,9]. This situation is often encountered in complex formation in concentrated ($> 1\ N$) aqueous solutions of inert salts, but is sometimes also found in dilute aqueous solutions of complex compounds[10,11].

Data have been published on outer-sphere interaction in aqueous solutions of complex compounds in the presence and absence of inert salts, but there are no reviews or monographs on this subject. Moreover, technologists and many research workers, following Bjerrum[12], consider that the influence of outer-sphere ions on complex formation in aqueous solutions is non-existent or negligibly small relative to the effect of inner-sphere interaction, although there are not always sufficient grounds for this.

The present paper is an attempt to examine critically published data on outer-sphere interaction in aqueous solutions of complex compounds. The problem of standardising conditions for the study of outer-sphere association is discussed, a procedure for calculating outer-sphere association constants for labile[13] and relatively unstable ionic

complexes is described, it is shown that outer-sphere association obeys the law of mass action, and the chief methods for studying outer-sphere interaction are described. In addition, a number of new regular features of outer-sphere association are formulated, the stabilities of outer-sphere and inner-sphere bonds in various complexes are compared, the possibility of predicting outer-sphere association constants in certain systems which have not been studied is demonstrated, and complex formation with allowance for associative interaction of the ions with the salt medium is discussed.

2. STANDARDISATION OF CONDITIONS FOR STUDYING OUTER-SPHERE ASSOCIATION IN AQUEOUS SOLUTIONS OF COMPLEX COMPOUNDS

Outer-sphere association in aqueous solutions of complex compounds is studied under the same standard conditions as the inner-sphere interaction[14,15]. The chief standard state for the study of complex formation in solutions is a hypothetical molal solution exhibiting the properties of an infinitely dilute solution[16]. In addition, in the past twenty years the state of solutions with high and constant ionic strength has been taken as standard state[15-18].

The low stability of outer-sphere complexes makes it impossible to obtain accurate values for their thermodynamic functions relating to an infinitely dilute solution, due to the difficulty of graphical or analytical extrapolation of the low values of the thermodynamic functions from real concentrated solutions to solutions with zero ionic strength[14].

Vasil'ev's work[19,20] improved the procedure for extrapolating the stability constants of ionic complexes to zero ionic strength. Vasil'ev replaced the two [adjustable ? (Ed. of Translation)] constants in the Debye–Hückel equation[21] by a single constant (the ion parameter a) and assumed that this constant has the value 4.9 Å in all systems. This assumption is hardly justified for all types of outer-sphere complexes, for which the ion parameter a may vary over a wider range than for ionic complexes.

The most convenient standard state for the study of outer-sphere association in labile and relatively unstable (first stability constant less than 100) ionic complexes is that of solutions with high and constant ionic strength[15] maintained with inert salts. The use of lithium perchlorate as an inert salt is recommended[3], since the ClO_4^- anion and Li^+ cation form the least stable associated species with the majority of singly-, doubly-, and triply-charged ionic complexes[22]. Ions with a lower tendency to undergo association than for example the ClO_4^- anion are known[23] but they are unfortunately unstable in aqueous solutions.

The Li^+ cation cannot be used as an inert ion in systems with anionic complexes whose charge exceeds three. On association, highly-charged ionic complexes break down the hydration sheath of the Li^+ cation and form more stable associated species with this cation than with the cations of the other alkali metals. Large cations of the type NR_4^+, where R = CH_3, C_2H_5, etc.[24,25], are inert with respect to highly-charged anionic complexes. The majority of salts with NR_4^+ cations are sparingly soluble in water, so that the outer-sphere association of highly-charged ionic complexes is usually studied[22] in dilute solutions with variable or constant ionic strengths and the thermodynamic functions are calculated for solutions with zero ionic strength. The hypothetical molal solution exhibiting the properties of an infinitely dilute solution can be used as a standard state for the study of the outer-sphere association of highly-charged ionic complexes, since the latter form extremely stable outer-sphere complexes.

If lithium perchlorate is used as an inert salt to establish the ionic strength, outer-sphere association is studied[3] in solutions with ionic strengths equal to three or four, since the low stability of the outer-sphere complexes necessitates high concentrations of outer-sphere ions for their formation, and in solutions with low ionic strengths this leads to a change in the activity coefficients of the reacting components. Studies in lithium perchlorate solutions with concentrations greater than 4 M are impossible, since the solubility of lithium perchlorate in water at 20° is 4.2 M.

The replacement of water by aqueous solutions of inert salts does not alter the significance of the laws of thermodynamics[18], so that solutions with high and constant ionic strengths and the hypothetical molal solution exhibiting the properties of an infinitely dilute solution can equally justifiably be regarded as standard states. Change from one standard state to the other changes the conditions under which the activity coefficients are equated to unity. Change in the conditions changes the composition of the associated species which include both "free" ions and ionic complexes[17].

In dilute aqueous solutions the concentration of free ions M (here and subsequently the charges of most ions are omitted for simplicity) is understood to be the concentration the species $\sum_{n=0}^{n=N} M(H_2O)_n$, where N is the maximum number of water molecules joined to M. X-Ray study of aqueous solutions[26], study of exchange with water containing the isotope ^{18}O,[27] magnetic and spectroscopic data[28], and their interpretation[29] from the viewpoint of ligand field theory show that in dilute aqueous solutions of most completely dissociated salts, N is the maximum coordination number of Werner's theory.

In concentrated solutions of inert salts, for example in lithium perchlorate solutions, the concentration of free M ions is understood to be the total concentration of associated species:

$$\sum_{x=0}^{x=X}\sum_{y=0}^{y=Y}\sum_{z=0}^{z=Z} M(H_2O)_x(ClO_4)_yLi_z, \qquad (1)$$

and the concentration of ionic complexes ML_n, where L is the ligand, is understood to be the concentration of the species

$$\sum_{n=0}^{n=N}\sum_{x=0}^{x=X}\sum_{y=0}^{y=Y}\sum_{z=0}^{z=Z} ML_n(H_2O)_x(ClO_4)_yLi_x \qquad (2)$$

where n lies in the range $1-N$. There is at present no information on the values of X, Y, and Z in species of types (1) and (2).

Outer-sphere associated species made up of ionic complexes of low stability have been studied chiefly in 3 M and 4 M $Li(ClO_4, L)$ and (Li, B)L solutions[3,8,9,30-46], where B represents the outer-sphere ions. The concentration of ligand in $Li(ClO_4, L)$ solutions was varied in a number of systems in the range 0–3 M and 0–4 M.

The replacement of any quantity of perchlorate or other inert anions by ligand anions leads unavoidably to a change in the activity coefficients of the reactant and product ions

in solutions with high and constant ionic strength[47]. However, the activity coefficients of M, L, and ML_n are assumed[15,17,35,36,48] to be constant in 1–4 M $Li(ClO_4, L)$ and $Na(ClO_4, L)$ solutions for replacement of less than 10–15% of the perchlorate ions by singly-charged ligand anions, since the low accuracy of present experimental methods does not permit a change in activity coefficients to be observed under the above conditions. The replacement of more than 20% of the perchlorate anions by ligand anions produces a significant change in the activity coefficients of the reacting ions in the great majority of systems studied in 1–4 M $Li(ClO_4, L)$ and $Na(ClO_4, L)$ solutions, the logarithms of the activity coefficients being directly proportional to the logarithms of the ligand anion concentrations[3,49,50].

The extent of the change in the activity coefficients of M and L in solutions with high (greater than 0.1 M) and constant ionic strength is influenced markedly by the nature of the reacting ions[3,15,48]. The extent of this change is often determined[15,35,36,48] from the deviation from constant values shown by $a_{M^{j+}}[L^-]^j$ or $[M^{j+}]a_{L^-}$ (a is the activity†) for sparingly soluble salts containing M and L, in solutions saturated with such salts. These data indicate that increase in the charge of M or in the differences between the electrostatic characteristics of L and the inert anion leads to an increase in the deviations of the activity coefficients of M and L from constant values. For example, the complete replacement of perchlorate anions by chloride, bromide, thiocyanate, and iodide anions in 4 M $Na(ClO_4, L)$ solutions at 25° alters the value of $a_{Tl^+}[L^-]$, which changes in the same sense as the activity coefficients of M and L, by 36, 12, 9, and 3% respectively[48]. $a_{Tl^+}[L^-]$ changes to almost the same extent when ClO_4^- is replaced by L in 4 M $Li(ClO_4, L)$ solutions[3,15]. The values of $a_{Pb^{2+}}[L^-]^2$ in 3 M and 4 M $Li(ClO_4, L)$ and $Na(ClO_4, L)$ solutions change by 74% and 35% on complete replacement of perchlorate anions by chloride and bromide ions respectively[3,35].

The nature of the alkali and alkaline earth metal cations has little influence on the values of $a_{M^{j+}}[L^-]^j$ in 3 M and 4 M (Li, B)L solutions, where B represents alkali and alkaline earth metal cations[15,35,36]. It may be assumed[3] that the replacement of Li^+ cations by B cations alters the values of $[M^{j+}]a_{L^-}$, but there is no published information on these quantities.

One of the main disadvantages of both standard states (the hypothetical molal solution and solutions with high and constant ionic strength) used in the study of the stability of ionic and outer-sphere complexes is the change in the activity coefficients of the reacting ions with change in the salt composition of the medium being studied. In solutions with high and constant ionic strength the activity coefficients are more nearly constant than in solutions with varying ionic strengths. It is, however, easier at present to make allowance for the change in the activity coefficients in dilute ($< 0.2\ N$) solutions with varying ionic strength than in solutions with high and constant ionic strength. The values of the thermodynamic functions for relatively unstable associated species cannot be determined with high accuracy whatever method is used to allow for activity coefficients[3].

The advantages and disadvantages of the standard states for studying equilibria in aqueous solutions have been discussed many times[3,5,15,17,18]. The great majority of accurate studies of equilibria in solutions have been made in the past twenty years[22] by the constant ionic strength method[51] and the self-medium method[52]. Where possible, equilibria should be studied in solutions at several constant ionic strength values, after which various methods should be used to calculate the values of the thermodynamic functions for solutions with zero ionic strength. This applies equally to the thermodynamic functions of ionic[20] and outer-sphere complexes[20]. An unambiguous comparison of the thermodynamic functions of standardised solutions with the same high and constant ionic strength can be made only when the same inert salt is used.

† Calculated on the assumption that $a_{L^-} = [L^-]$ or $a_{M^{j+}} = [M^{j+}]$.

3. PROCEDURE FOR CALCULATING THE OUTER-SPHERE ASSOCIATION CONSTANTS FOR LABILE COMPLEXES

To determine the composition and calculate the outer-sphere association constants for any labile complexes, data from three series of experiments are required[3]. In the first series of experiments complex formation by the central atom M with the ligand L should be studied in the presence of the most inert anions and cations, in the second series of experiments the reaction of the outer-sphere ion with the ligand or with the central ion should be studied, and in the third series of experiments the influence of the outer-sphere ions on the degree of complex formation by the central ion should be studied. The second series of experiments becomes unnecessary if almost no interaction between the outer-sphere ions and the central ion and ligands takes place due to specific features or because of the conditions used.

A procedure has been described[28,33,37] for calculating the association constants for relatively unstable anionic complexes with alkali and alkaline earth metal cations. In this procedure no allowance is made for the interaction of the outer-sphere cations with the ligand, but this simplification is unimportant. When interaction between the outer-sphere ions and the ligand takes place, the calculations by this procedure must be carried out with the equilibrium concentrations of outer-sphere ions B and ligands L. The values of [B] and [L] can be determined experimentally[3] or calculated using the formation constants of BL_n or $B(H_2O)_xL$.

The procedure for calculating outer-sphere association constants given in papers by Mironov and others[3,28,33,37,39] is suitable for calculating the constants for the association of anionic complexes with outer-sphere cations and of cationic complexes with outer-sphere anions. The chief assumption of this procedure is that the activity coefficients of the reacting ions and resulting complexes remain constant in all experiments whose results are used in the calculations.

Complex formation in the absence of outer-sphere association, that is in a medium of the most inert anions and cations, is represented in simplest form by the equilibrium

$$M + nL \rightleftarrows ML_n \qquad (3)$$

and is characterised by the stability constants of the ions ML_n:

$$\beta_n = [ML_n] \cdot [M]^{-1} \cdot [L]^{-n}, \qquad (4)$$

where $n = 1, 2, \ldots N$, and N is the maximum coordination number of M with respect to L under the conditions of the experiment.

Outer-sphere association is represented[3] in simple form by the equilibrium

$$yB + ML_n \rightleftarrows B_yML_n \quad (5)$$

and is characterised by the outer-sphere association constants

$$\gamma_{n,y} = [B_yML_n]\cdot[B]^{-y}\cdot[ML_n]^{-1}, \quad (6)$$

where $y = 1, 2, \ldots Y$, and Y is the maximum number of outer-sphere ions attached to ML_n.

When ionic complexes ML_n are formed, the total concentration of the central ion M (C_M) is defined by the equation

$$C_M = \sum_{n=0}^{n=N} [ML_n]. \quad (7)$$

With allowance for outer-sphere complexes, C_M is given[3,30,32,37] by the equation

$$C_M = \sum_{n=0}^{n=N} [ML_n] + \sum_{y=1}^{y=Y}\sum_{n=1}^{n=N} [B_yML_n]. \quad (8)$$

By expressing the concentrations of ionic and outer-sphere complexes in terms of the stability constants and dividing the right-hand and left-hand sides of Eqns. (7) and (8) by the equilibrium concentration of the central ion, we obtain the equations

$$C_M[M]^{-1} = \Phi = 1 + \sum_{n=1}^{n=N} \beta_n [L]^n \quad (9)$$

and

$$C_M[M]^{-1} = \Phi^{total} = 1 + \sum_{n=1}^{n=N} \beta_n [L]^n + \sum_{n=1}^{n=N}\sum_{Y=1}^{y=Y} \beta_n\gamma_{n,y}[B]^y[L]^n, \quad (10)$$

where Φ is the degree of complex formation by M with L to give ML_n, and Φ^{total} the degree of complex formation by M with L and B to give ML_n and B_yML_n.

Subtraction of Eqn. (9) from Eqn. (10) gives

$$\Delta\Phi = \Phi^{total} - \Phi = \sum_{n=1}^{n=N}\sum_{y=1}^{y=Y} \beta_n\gamma_{n,y}[B]^y[L]^n, \quad (11)$$

where $\Delta\Phi$ is the change in the degree of complex formation by M resulting from the outer-sphere association of ML_n with B.

The unknown quantities in Eqn. (11) are the values of y and $\gamma_{n,y}$, for the values of β_n and n are determined by familiar methods[14] from Φ–[L] data by solving Eqn. (9). To find the numerical values of y and $\gamma_{n,y}$, it is sufficient to measure the dependence of $\Delta\Phi$ on the concentration of outer-sphere ions at several ligand concentrations and then to compile and solve a system of several equations of the same type as Eqn. (11).

Outer-sphere association constants in different systems are calculated[3,8,9,30-34,36,37] using particular forms of Eqn. (11). In practice, the most frequently encountered systems are those in which one complex ion ML_N reacts with one outer-sphere ion[9,53] or in which, of two complex ions ML_N and ML_{N-1} present, the first reacts with two outer-sphere ions and the second with one outer-sphere ion[37,38]. When only BML_N is formed, Eqn. (11) acquires the simpler form

$$\Delta\Phi = \gamma_{N,1}[B]\beta_N[L]^N \quad (12)$$

and when BML_N, BML_{N-1}, and B_2ML_N are formed Eqn. (11) becomes

$$\Delta\Phi = \gamma_{N,1}[B]\beta_N[L]^N + \gamma_{N-1,1}\beta_{N-1}[B][L]^{N-1} + \gamma_{N,2}\beta_N[B]^2[L]^N. \quad (13)$$

A complete analysis of the characteristic features and methods of solution for Eqn. (11) has been published[3,39]. In practice up to the present no studies have been made of systems in which the outer-sphere interaction is described by a more complex form of Eqn. (11) than Eqn. (13). The latter is conveniently solved by a graphical method similar to Leden's method[14,54].

The first stage in the solution of Eqn. (13) involves the construction of the graphical dependence of the function F_1 on the concentration of B ions. The function F_1 is defined by the equation

$$F_1 = \Delta\Phi[B]^{-1}[L]^{-N}\beta_N^{-1} = \gamma_{N,1} + \gamma_{N-1,1}\beta_{N-1}\beta_N^{-1}[L]^{-1} + \gamma_{N,2}[B]. \quad (14)$$

Graphical extrapolation is used to find $\lim F_1$ as $[B] \to 0$

$$\lim_{[B]\to 0} F_1 = \gamma_{N,1} + \gamma_{-N1,1}\beta_{N-1}\beta_N^{-1}[L]^{-1}. \quad (15)$$

In a number of systems studied[3]

$$\gamma_{N,1} \gg \gamma_{N-1,1}\beta_{N-1}\beta_N^{-1}[L]^{-1} \quad (16)$$

and in these cases $\lim F_{1[B]\to 0} = \gamma_{N,1}$. If the two terms on the right-hand side of Eqn. (15) are commensurate, it is necessary in the determination of the values of $\gamma_{N,1}$ and $\gamma_{N-1,1}$ to determine F_1 at not less than two ligand concentrations and then to compile and solve a system of two equations of the same type as Eqn. (15). The solution of this system gives the values of $\gamma_{N,1}$ and $\gamma_{N-1,1}$. It is often impossible to measure the values of the function F_1 at several ligand concentrations even in cases where the two terms on the right-hand side of Eqn. (15) are commensurate. This was the situation, for example, in a study of the outer-sphere associated species formed by bromo-complexes of zinc[37,40] or chloro-complexes of lead(II) with heavy alkali metal cations[38,39]. These complexes were also studied in 4 M $Li(ClO_4$, L) solutions but it was necessary to study the outer-sphere association in 4 M (Li, B)L solutions, since the simultaneous presence of K^+, Rb^+, or Cs^+ cations and perchlorate anions in 4 M (Li, B)(ClO_4, L) solutions is impossible due to the low solubility of the perchlorates of the heavy alkali metals. In these cases[3,37-40] the values of F_1 were determined for 3 M and 4 M (Li, B)L solutions. The values of F_1 for 3.1 M and 3.9 M (Li, B)L solutions were found by making use of the linear dependence of F_1 on the ionic strength of the solution[55,56]. Systems of two equations of type (15) were then compiled. One system was compiled from data for 3.0 M and 3.1 M (Li, B)L solutions and the other from data for 3.9 M and 4.0 M (Li, B)L solutions. Solution of these systems gave the values of γ_N and γ_{N-1} for 3.0 M and 4.0 M (Li, B)L solutions. This method of finding γ_N and γ_{N-1} is based on the assumption that the outer-sphere association constants remain constant when the ionic strength of the solutions is changed from 3.0 to 3.1 and from 4.0 to 4.1. Experimental data confirmed that it is possible to make this assumption[3].

After the determination of $\lim F_1$ as $[B] \to 0$, Eqn. (11) is transformed to

$$F_2 = (\Delta\Phi - \lim_{[B]\to 0} F_1)[B]^{-1} = \gamma_{N,2} \quad (17)$$

and the values of $\gamma_{N,2}$ are calculated. In a number of systems studied with this method of calculating $\gamma_{N,2}$ it was found[3] that the values of the function F_2 depend on the

concentration of B; in this case $\lim F_2$ as [B] → 0 was determined and $\gamma_{N,2}$ was calculated in the same way as $\gamma_{N,1}$.

4. THE MOST WIDELY-USED METHODS FOR DETERMINING OUTER-SPHERE ASSOCIATION CONSTANTS

In recent years a large amount of information has been published[8,9,30-34,37-46] on constants for the association of labile anionic complexes with alkali and alkaline earth metal cations. Most of these data were obtained potentiometrically. Measurements are usually made of the e.m.f. of cells of the type

$$M(Hg)\,|\,S_{LiClO_4}\,|\,3 \quad \text{or} \quad 4\ M\ LiClO_4\,|\,S_x\,|\,M(Hg), \qquad (18)$$

$$M(Hg)\,|\,S_{LiL}\,|\,3 \quad \text{or} \quad 4\ M\ LiL\,|\,S_y\,|\,M(Hg), \qquad (19)$$

where M represents thallium, lead, bismuth, zinc, cadmium, etc., and L represents chloride, bromide, thiocyanate, iodide, nitrate, or other anions. The solutions S_{LiClO_4} consisted of 0.0001–0.05 M perchlorate of the cation M in 3 M or 4 M lithium perchlorate and the solutions S_{LiL} consisted of 0.0001–0.05 M L_j in 3 M or 4 M LiL. The solutions S_x were prepared by mixing the solutions S_{LiClO_4} and S_{LiL}, and the solutions S_y by mixing the solutions S_{LiL} and S_{BL}. The latter contained 0.0001–0.05 M L_j in 3 M or 4 M BL solution. To suppress the hydrolysis of M, all the solutions studied had a constant acidity, which varied in the range 0.001–1.0 g-ion H^+ litre^{-1}, depending on the stability of the hydroxo-complexes of M.

Other versions of the potentiometric method for determining outer-sphere association constants have been described[3,30] but they are comparatively little used.

Outer-sphere association constants have been determined by polarographic methods[3,30], based on the study of the dependence of the displacements of the half-wave potential of the central M ion on the concentration of L in solutions with compositions analogous to that of solution S_x in cell (18) and also the dependence of these displacements on the concentration of B cations in solutions with compositions analogous to that of solution S_y in cell (19).

The chief disadvantage of these versions of the potentiometric and polarographic methods for studying the interaction in S_x and S_y solutions is that they involve the measurement of the total e.m.f. or displacements of the half-wave potential due to association and diffusion. Thermodynamics does not make it possible to separate the effect of diffusion (the diffusion potential) from the effect of change in the activity coefficients[57]. In practice measurements are made of nominal diffusion potentials, including diffusion and change in the activity coefficients[51].

To increase the accuracy of the potentiometric and polarographic methods for studying association in cells (18) and (19), the diffusion potentials have been determined[3,58] by the flowing junction method[59-61,122].

The solubility of salts of the type ML_j or B_yML_n makes it possible to determine outer-sphere association constants from data obtained by the solubility method[39,62-65].

A large number of papers describe measurements of the solubilities of the halides and thiocyanates of thallium(I)[9,35,66-68], lead(II)[36,39,69], and silver[70], and other sparingly soluble salts with various compositions[40,64,65], usually in solutions with constant ionic strengths. These data have been used to calculate outer-sphere association contants[9,32,36,39,40,53,66,67,70].

Accurate values for the solubility products of sparingly soluble compounds are necessary for calculating the stability constants of ionic complexes and outer-sphere association constants from data obtained by the solubility method[14,16]. In most systems where outer-sphere association constants have been calculated from data obtained by the solubility method, the solubility products were determined potentiometrically[35,36,39,69].

A method has been described[44,45] for calculating the outer-sphere association constants for the anions Br_3^- and $Fe(SCN)_n^{3-n}$, where $n = 4-6$, from the distribution of Br_2 or $H[Fe(SCN)_4]$ between carbon tetrachloride or ethyl ether and 3 M (Li, H, B)L solutions. The extraction method for determining outer-sphere association constants is based on measurement of the distribution constants of Br_2 and Fe^{3+} at different concentrations of the outer-sphere cations[40,44,45].

The spectrophotometric method cannot be used to study relatively unstable outer-sphere complexes, since the latter are ion pairs, whose formation is not accompanied by a significant change in the absorption spectra of the simple ions or ionic complexes[3,40,44,71]. The spectrophotometric and electrical-conductivity methods are the most widely used procedures for studying stable outer-sphere associated species formed by highly-charged, extremely stable, or extremely inert ionic complexes[22].

The spectrophotometric method has been used many times to study the association of cationic complexes with outer-sphere anions, since their interaction is usually accompanied by a change in the spectrum of ML_n.[72-76]

The study of outer-sphere association by an ion-exchange method using cation and anion exchange resins has been described[77].

Data obtained by direct calorimetric measurements[3,40] and the temperature dependence of outer-sphere association constants[9,30,39,41] have been used to calculate enthalpy changes during outer-sphere interaction.

5. OUTER-SPHERE ASSOCIATION AND THE LAW OF MASS ACTION

The change in the stability constants of ionic complexes on going from one salt medium to another is attributed[14,16] to the change in the activity coefficients of M, L, and ML_n, since

$$\beta_n^0 = \beta_n \cdot f_{ML_n} \cdot f_M^{-1} \cdot f_L^{-n} \qquad (20)$$

where β_n^0 represents the stability constants relating to the solution with zero ionic strength, β_n the stability constants relating to the solution with a definite salt medium, and f with different subscripts represents the activity coefficients of the species denoted by the subscripts. This explanation of the influence of the salt medium on complex formation in solutions is purely formal, however, since it neglects the fact that any significant changes in activity coefficients are unavoidably associated with definite chemical processes.

The activity coefficients of ions are influenced little by ions of the same sign but are influenced appreciably by ions of the opposite sign[51]. This is explained by the structure of electrolyte solutions[57], in which each ion is surrounded by an atmosphere of ions of the opposite sign. Any ions with charges of different sign naturally attract one another in accordance with Coulomb's law, to form associated species of different types. The formation of any associated species, usually described in the case of strong

electrolyte solutions by the activity coefficients, can be characterised by the constants of the law of mass action[3], if the type of species formed is known and the influence of side processes is excluded. Izmailov[78] emphasised that "the properties of any electrolyte in non-aqueous and even in aqueous solutions must be described on the basis of a process obeying the law of mass action".

It is often possible to isolate the contribution of a definite association process to the influence of the ionic medium on complex formation in solutions[3,30]. The behaviour of certain systems[79] has been described by some workers in terms of formal values of the activity coefficients and by other workers in terms of the constants of the law of mass action.

Before the publication of papers by Mironov and co-workers[32,33], the influence of the salt medium on the stability constants of relatively unstable ionic complexes was always characterised by the changes in the activity coefficients. Experiments and calculations[3,30,32,39] showed that the values of the outer-sphere association constants, calculated from data on the influence of the salt medium on complex formation in solutions in accordance with the procedure described above and measured by various methods, remain almost constant when the concentration of the reacting components is changed by factors of several hundred. This is confirmed by the data in Table 1.

Various methods (Table 1) have been used to determine outer-sphere association constants in systems which might be expected to show a maximum change in these constants[3], for example as a result of a change in the activity coefficients, as a result of the very low stability of ionic complexes, or as a result of the influence of various side-processes. The errors of the determination of the outer-sphere association constants given in Table 1 amount to not less than ±5–40%.[3] In all the systems studied (with the exception of the Na^+–$PbBr_4^{2-}$ system), change in the concentration of ML_n by a factor of 10–500 changed the values of the constants by not more than 10%. The scatter in the values of the constants found by the potentiometric and polarographic methods and by solubility measurements rarely exceeds ±10%.

The values obtained are independent of the method of determination and the concentrations of the reacting substances only for the constants for the association of ionic complexes with the first ion of the outer-sphere. In calculations of the second and third outer-sphere association constants, change in the concentration of ML_n and, more particularly, change in the method of measuring $\Delta\Phi$ changed $\gamma_{n,y}$ by more than 20–80%.[3]

TABLE 1. Outer-sphere association constants for ML_n in 4 M (Li, B)L solutions at 25°.

Outer-sphere cations	Anionic complexes	Outer-sphere association constants, calculated from data obtained by			References
		potentiometric method	polarographic method	solubility method	
Na^+	$TlCl_2^-$	0.10	—	0.08	32
K^+	$TlCl_2^-$	0.14	0.15	0.15	30,32
Cs^+	$TlCl_2^-$	0.22	—	0.25	3,32
Na^+	$PbCl_4^{2-}$	0.73	0.73	0.52*	3,36
Na^+	$PbBr_4^{2-}$	0.11	0.15	0.16	3,30
Na^+	$CdCl_4^{2-}$	0.50	0.51	—	3,33
Na^+	$Pb(NO_3)_4^{2-}$	0.47	0.51	—	3,8
K^+	$PbCl_4^{2-}$	2.1	1.9	2.0	3,30
K^+	$Tl(SCN)_4^{3-}$	0.70	0.70	0.80	3,53
K^+	$PbBr_4^{2-}$	1.0	—	0.95	3,32

* This figure relates to 3 M (Li, B)Cl solutions.

Different methods for studying complex formation in solutions are sensitive to different extents to changes in the activity coefficients of the reactant and product ions[48], so that for the calculation of outer-sphere association constants [according to Eqn. (11) or modifications of this equation] the degree of complex formation by M with L and the degree of complex formation by M with L and B must be measured by the same method. This rule must be obeyed in the study of the stability of outer-sphere complex ion associated species with $\beta_1 < 100$, since in these systems it is necessary to replace more than 20% of the inert ions by ligands[39]. In the calculation of outer-sphere association constants, use is made of the stability constants of the most extensively coordinated ionic complexes, that is, the constants for ML_N, ML_{N-1}, etc. The value of β_N shows its maximum dependence on the changes in the activity coefficients when the composition of an ionic medium with constant ionic strength is varied[39,69,80]. Thus the values of the stability constants of $PbCl_n^{2-n}$ with $n = 1-3$ remain constant in 3 M solutions of a mixture of lithium perchlorate and chloride, but the stability constant of $PbCl_4^{2-}$ is 52 ± 12 according to solubility data[36] and 11 ± 2 according to potentiometric data[80]. This is due to the fact that the $PbCl_4^{2-}$ ion is formed in 3 M Li(ClO_4, Cl) solutions at a chloride ion concentration greater than 0.6 M, that is, in the range of chloride ion concentrations in which the replacement of ClO_4^- by Cl^- changes the activity coefficient of the doubly-charged lead cation[36]. Thus the stability constant of $PbCl_4^{2-}$ ions, determined for 3 M Li(ClO_4, Cl) solutions, includes both the effect of the interaction of the lead cation with four chloride ions and the change in the activity coefficients. If the effect of change in the latter is not to influence the value of the outer-sphere association constants for $PbCl_4^{2-}$, it must be eliminated by using the values of β_N calculated from data obtained using the same method as in the determination of $\Delta\Phi$.

An interesting feature is that the potentiometric and polarographic methods for determining the stability constants of ionic complexes in 3 M and 4 M Li(ClO_4, L) solutions apparently reflect to equal extents the changes in the activity coefficients resulting from the change in the composition of an ionic medium with constant ionic strength[3].

The values of the second outer-sphere association constants calculated using Eqn. (13) are determined by the slope of the linear plot of F_1 against [B]. The replacement of more than 20% of the lithium cations by the cations of other metals in 3–4 M (Li, B)L solutions may lead to a change in the activity coefficients of the reaction ions[35,39]. Thus the slope of the linear plot of F_1 against [B] and hence $\gamma_{n,2}$ may change with change in the method of measuring $\Delta\Phi$ and with change in the concentration of ML_n.

At high concentrations of B in (Li, B)L solutions, an appreciable quantity of BML_n complexes is formed. The statistical mean charge of ML_n is greater than the charge of BML_n, so that the complex BML_n has a greater tendency to add on an additional ligand ion than the free ML_n ion. It may be assumed[3] that the greater part of the change in the activity coefficients of M, L, and ML_n in 3–4 M (Li, B)L solutions with [B] greater than 0.5–2.0 M is due to the conversion of BML_n into BML_{n+1}. The correctness of this explanation is confirmed by a large quantity of

published data[3] which indicate an increase of n in ML_n with increase in the ability of the outer-sphere ions to undergo association with ionic complexes.

6. SOME RULES OF OUTER-SPHERE ASSOCIATION

In the formulation of the rules of outer-sphere association, only the first association constants are used[3], since the values of $\gamma_{n,y}$ for $y > 1$ are arbitrary[14].

The first constants for the outer-sphere association of anionic complexes with alkali and alkaline earth metal cations depend on the dimensions of the outer-sphere cations, being related to the radii of the latter by the equation

$$\gamma_{n,1} = A(r_B - C) \qquad (21)$$

where A and C are constants whose values change with change in M, L, or the charge of ML_n, and r_B the Goldschmidt radii of the outer-sphere cations (in Å). The correctness of Eqn. (21) and of the postulates of the present section is confirmed by the data in Tables 2–4.

The outer-sphere association constants for most labile, relatively unstable chloro-complexes vary according to Eqn. (21) with $C = 0.78$, which is numerically equal to the crystallographic radius of the Li^+ cation. The association constants of bromo-, nitrato-, thiocyanato-, and certain other types of anionic complexes[3,40] are characterised by Eqn. (21) with values of C in the range 0.7–1.1 (Table 2).

The constants for the outer-sphere association of cyanoferrate(III) and other inert highly stable anionic complexes with alkali and alkaline earth metal cations are given by the equation

$$\log \gamma_{n,1} = Ar_B - C, \qquad (22)$$

although within the limits of error of their determination the constants are also described by Eqn. (21) [40,65] (Table 3).

The constants for the outer-sphere association of anionic complexes of low stability with caesium cations (Table 2) are sometimes found to be greater or less than those calculated from Eqn. (21). High values of $\gamma_{n,1}$ are attributed[34] to the inclusion, in the value of the constant, of the increase in the degree of complex formation by M resulting from the increase of n in $CsML_n$. This is apparently the case for the constants for the outer-sphere association of the $ZnCl_3^-$ ion with the Cs^+ cation (Table 2). In general, the possibility that the effect of inner-sphere interaction is included in the value of the first outer-sphere association constant increases with decrease in the stability of the M–L bonds and with increase in the stability of the B–ML_n bonds[3]. From this, it is to be expected that at very low values of β_n and high values of $\gamma_{n,1}$ the values of the latter will depend on the concentration of ML_n and on the method used to determine the outer-sphere association constants.

Low values of $\gamma_{n,1}$ relative to those calculated from Eqn. (21) are attributed to a significant difference between the total and equilibrium concentrations of ligand when C_L is used in the calculations. In the series of alkali metal cations, the stability of the ion pairs $B(H_2O)_xL$ increases from lithium to caesium[82] for $L = Cl^-$, Br^-, I^-, NO_3^-, SCN^-, etc., with the exception of OH^-, CH_3COO^-, etc.[32] Thus the maximum differences between C_L and [L] in the systems whose characteristics are given in Table 2 might be observed for $B = Cs^+$.

TABLE 2. Outer-sphere association constants for anionic complexes at 25°.

Anionic complexes	Constants for association with the cations of: sodium	potassium	rubidium	caesium	ammonium	Method of determination*	Medium	References
$TlCl_2^-$	0.10	0.14	0.20**	0.22	—	E	4 M (Li, B)Cl	32
$PbCl_4^{2-}$	0.73	2.1	2.8	3.4	—	E	ditto	3,38
$PbCl_4^{2-}$	0.72	2.1	2.6	3.1	1.0	E	3 M (Li, B)Cl	38,39
$PbCl_4^{2-}$	0.14	0.23	—	1.0	0.9	E	3 M (Li, H, B)Cl with $[H^+] = 1$	3,39
$BiCl_6^{3-}$	0.55	1.5	2.0	2.5	1.3	E	ditto	31
$ZnCl_4^{2-}$	0.40	>1.0	—	—	—	E	4 M (Li, B)Cl	3
$CdCl_4^{2-}$	0.50	1.35	1.8	2.25	0.80	E	ditto	33
$HgCl_4^{2-}$	0.78	1.5	2.0	—	—	E	0.1 M $B_2[HgCl_4]$	3
$ZnCl_3^-$	0.15	0.52	0.70	1.2	—	E	4 M (Li, B)Cl	3
$SnCl_3^-$	0.10	0.50	—	—	—	E	ditto	3
$PbCl_3^-$	0.12	0.53	0.71	0.88	—	E	»	38,39
$PbCl_3^-$	0.09	0.49	0.62	0.82	—	E	3 M (Li, B)Cl	38,39
$ZnBr_4^{2-}$	0.39	1.4	1.6	1.6	1.2	E	3 M (Li, B)Br	37,41
$ZnBr_4^{2-}$	0.46	1.2	1.5	2.4	1.4	E	4 M (Li, B)Br	37,41
$PbBr_4^{2-}$	0.11	1.0	1.4	1.8	—	E	ditto	3,32
$CdBr_4^{2-}$	0.05	0.15	0.22	0.35	—	E	»	3,31
$Pb(NO_3)_4^{2-}$	0.47	1.4	—	—	—	E	4 M (Li, B)NO_3	8
$Zn(SCN)_4^{2-}$	0.052	0.17	0.23	0.72	0.23	E	4 M (Li, B)SCN	40,46
$Zn(SCN)_3^-$	0.013	0.042	0.057	0.18	0.057	E	ditto	40,46
$Pb(SCN)_3^-$	0.015	0.040	0.058	0.074	—	E	»	3,43
$Tl(SCN)_2^-$	0.30	0.80	—	—	—	S	»	3,53
$Fe(SCN)_4^-$	0.009	0.060	0.090	0.13	0.082	Ex	3 M (Li, B)SCN	40,46
$Fe(SCN)_5^{2-}$	0.036	0.24	0.36	0.50	0.33	Ex	ditto	40,46
$Fe(SCN)_6^{3-}$	0.081	0.55	0.81	1.13	0.74	Ex	»	40,46
$Fe(CN)_6^{3-}$	0.17	0.38	—	0.55	—	S	3 M (Li, B)Cl	40,65
$Fe(CN)_6^{3-}$	0.41	—	—	—	—	S	3 M (Li, B)NO_3	40,65
TlI_4^{3-}	0.05	0.20	—	—	—	S	4 M (Li, B)I***	3
ZnI_4^{2-}	—	0.25	—	—	—	E	ditto	4
ZnI_3^-	—	0.06	—	—	—	E	»	40
Br_3^-	0.02	0.30	—	0.80	—	Ex	3 M (Li, B)Br	48
$ZnBr_3^-$	0.10	0.30	0.40	0.50	0.30	E	4 M (Li, B)Br	37,40
$ZnBr_3^-$	0.14	0.29	0.43	0.86	0.43	E	3 M (Li, B)Br	37,40
Cl^-	0.2	0.4	0.6	0.8	—	****	****	82

* E denotes potentiometric method, S solubility method, and Ex extraction method.

** Calculated from solubility data.

*** Calculations carried out using the stability constants of the TlI_4^{3-} ion found for 4 M $Na(ClO_4, I)$ solutions and not for 4 M $Li(ClO_4, I)$ solutions.

**** The constants relate to a solution with zero ionic strength and were calculated using the Fuoss–Onsager equation[82]. The same method[82] gave for the stability constants of $Na^+(H_2O)_xBr^-$, $K^+(H_2O)_xBr^-$, $Na^+(H_2O)_xI^-$, and $K^+(H_2O)_xI^-$ the values 0.2, 0.4, 0, and 0.3 respectively.

Decrease in the charge and decrease in the dimensions of hydrated anionic complexes leads to a decrease in the outer-sphere association constants (Table 2). In the series of anionic complexes $TlCl_2^-$, $PbCl_4^{2-}$, $BiCl_6^{3-}$, $ZnBr_3^-$, $ZnBr_4^{2-}$, $PbCl_3^-$, and $PbCl_4^{2-}$,[3,40] the outer-sphere association constants change according to the equation

$$\gamma_{n,1} = \gamma \cdot Z^2 \qquad (23)$$

where Z is the charge of the anionic complex, and γ without subscript denotes the outer-sphere association constant for the singly-charged anionic complex. In some systems[44,46] this equation has been used to calculate γ_N

TABLE 3. Stability constants of $B^{z+}[Fe(CN)_6]^{3-}$ complexes at 25°.

B	Medium	Stability constants	Method of determination*	References
K^+	0**	16.6	El	82
K^+	3 M (Li, K) Cl	0.38	S	40,65
Mg^{2+}	0	610	El	83
Mg^{2+}	3 N (Li, Mg) Cl***	0.094	S	40,65
Sr^{2+}	0	710	El	83
Sr^{2+}	3 N (Li, Sr) Cl	0.17	S	40,65
Ba^{2+}	0	760	El	83
Ba^{2+}	3 N (Li, Ba)Cl	0.25	S	40,65

* El denotes electrical conductivity method and S solubility method.

** 0 — solutions with zero ionic strength.

*** (Li, Mg)Cl — mixtures of lithium and magnesium chlorides.

and γ_{N-1} from $\lim F_1$ as [B] → 0 [see Eqn. (15)]. For example, this method was used to calculate the constants for the outer-sphere association of $Fe(SCN)_n^{3-n}$ ions (n = = 4–6) with alkali metal and ammonium cations[44] (Table 2).

Eqn. (23) is applicable to outer-sphere association constants relating to the same standard state. This equation is not applicable to the outer-sphere association constants found for $PbCl_4^{2-}$ ions in 3 M (Li, B)Cl solutions or to the outer-sphere association constants found for $BiCl_6^{3-}$ anions in 3 M (Li, H, B)Cl solutions with $[H^+]$ = 1 M (Table 2), since an appreciable proportion of the $BiCl_6^{3-}$ ions in solutions with $[H^+]$ = 1 M are bound in $[HBiCl_6]^{2-}$ complexes, which also associate with alkali metal cations. $TiCl_2^-$ anions undergo almost no association with H^+, so that the constants for the formation of the outer-sphere complexes $BTlCl_2$ are little influenced by the replacement of Li^+ by H^+ in 4 M (Li, B)Cl solutions[3] or by the change from 4 M to 3 M (Li, B)Cl solutions.

In the series of anionic complexes $ZnCl_4^{2-}$, $CdCl_4^{2-}$, $HgCl_4^{2-}$, and $PbCl_4^{2-}$, the constants for association with alkali metal cations (Table 2) are inversely proportional to the crystallographic radii of the central ions[3]. The tendency to undergo hydration increases in the opposite sequence of central ions but the dimensions of the hydrated MCl_4^{2-} anions apparently decreases in the sequence given above.

The nature of the central ion has no influence on the outer-sphere association constants for singly-charged anionic complexes (Table 2). The anionic complexes $ZnCl_3^-$, $PbCl_3^-$, and $SnCl_3^-$ have identical constants for association with Na^+, K^+, and Rb^+ cations. The values of the outer-sphere association constants for the singly-charged $TlCl_2^-$ anions differ from those for MCl_3^- ions. This is due to the difference in the dimensions of the hydrated $TlCl_2^-$ and MCl_3^- anions and possibly to a number of other factors[3].

The outer-sphere association constants for MBr_4^{2-} anions decrease in the sequence Zn, Pb, Cd (Table 2); this distinguishes the dependence of the outer-sphere association constants for bromo-complexes on the nature of the central ion from the analogous dependence for the chloro--complexes MCl_4^{2-}. The high values of the outer-sphere association constants for $B^+ZnBr_n^{2-n}$ have been attributed[40] to the low stability of $ZnBr_n^{2-n}$ and the contribution to the value of $\gamma_{n,1}$ due to the increase of n in $ZnBr_n^{2-n}$. This explanation is not convincing, however[3]. Unfortunately, the outer-sphere association constants for $ZnBr_4^{2-}$ anions were determined only by the potentiometric method[40].

The stability of the outer-sphere associated species formed by anionic complexes ML_n^- and ML_n^{2-} decreases with increase in the dimensions of the ligand (Table 2). For example, the constants for the formation of outer--sphere complexes $BPbL_4$, where B represents Na^+ and K^+ cations and L represents chloride, bromide, and nitrate anions, and also the constants for the formation of complexes $BZnL_3$, where L represents chloride, bromide, and iodide anions, decrease in direct proportion to the crystallographic radii of the ligands[40]. The values of $\gamma_{n,1}$ apparently always decrease in the same sense as the dimensions of the ligand, if the values of the outer-sphere association constants are determined with a sufficient degree of reliability[3].

The outer-sphere association constants of thiocyanato--complexes are very low compared with those for halogeno--complexes (Table 2). It may be suggested[3] that the ion pairs $B^+(H_2O)_x(SCN)^-$ are more stable than the analogous compounds with chloride and bromide anions, so that in the calculation of the outer-sphere association constants for thiocyanato-complexes in 3–4 M (Li, B)SCN solutions it is necessary to make allowance for the difference between the total and equilibrium concentrations of thiocyanate ions, since this difference is much larger than in systems containing halogeno-complexes.

The ionic strength of the solutions has little influence on the outer-sphere association constants in the ionic strength range three to four (Table 2).[3] Change in the ionic strength of the solutions from zero to four leads to an appreciable decrease in outer-sphere association constants[40], as in the case of the constants for inner-sphere interaction[3]. A noteworthy feature (Table 3) is that the decrease in the constants for the outer-sphere association of anionic complexes with alkali metal cations on going from solutions with zero ionic strength to solutions with an ionic strength equal to three is much less than that for the analogous characteristics for alkaline earth metal cations. In solutions with an ionic strength equal to three, the constants for outer-sphere association, for example of cyanoferrate(III) anions with alkali and alkaline earth metal cations, are almost identical, but in solutions with zero ionic strength the constants for the attachment of alkaline earth metal cations are several dozen times greater than the constants for the attachment of alkali metal cations (Table 3).

The decrease in the differences between the constants for the attachment of alkali and alkaline earth metal cations on going from solutions with zero ionic strength to solutions with an ionic strength equal to three is attributed[3] (Table 3) to the increase in the interaction of the alkaline earth metal cations with the ligand anions or anions of the salt medium with increase in the ionic strength of the solution[84]. Alkali metal cations also undergo association with ligands or anions of the salt medium, like the alkaline earth metal cations, but this interaction does not have a significant influence on the outer-sphere association constants, if $[ML_n] \ll [B]$. In solutions with equal ratios $[ML_n]/[B]$ and $[L]/[B]$, the $B(H_2O)_xL$‡ complexes are more

‡ The stability constants of $B^+(H_2O)_xCl^-$ in 3–4 M (Li, B)Cl solutions for B = Na^+, K^+, Rb^+, and Cs^+ are 0.4, 0.8, 1.2, and 1.6 respectively[86] if the change from solutions with I = 0 to solutions with I = 3–4 doubles the stability constants.

stable than the $B(H_2O)_xML_n$ complexes, if the charges of L and ML_n are equal. The correctness of this last statement is confirmed by study of electrical conductivity in 3 *N* solutions of mixtures of cadmium chloride with alkali metal chlorides at equal concentrations of $CdCl_2$ and BCl [3,85] and also by potentiometric studies of the stability of the chloro-complexes of cadmium at C_{Cd} = 0.001–0.01 M and high concentrations (up to 5 M) of alkali metal chlorides [41,87]. Data obtained by the electrical conductivity method indicate that the degree of complex formation by cadmium increases in the sequence caesium chloride–lithium chloride, but potentiometric data indicate that the degree of complex formation by cadmium increases in the sequence lithium chloride–caesium chloride. Thus [32] in solutions with equal concentrations of cadmium and alkali metal chlorides the behaviour of the system is determined by the formation of $B^+(H_2O)_xCl^-$ while in solutions with low cadmium concentrations it is determined by the formation of $B^+(H_2O)_xCdCl_3^-$, since the stability of the complexes of both types increases from lithium to caesium.

The stability of the outer-sphere complexes of ML_n with alkali and alkaline earth metal cations increases in inverse or direct proportion to the dimensions of the latter [3]. For association without breakdown of the hydration sheaths of the alkali and alkaline earth metal cations, the stability of the outer-sphere complexes increases in the sequences lithium–caesium and magnesium–barium, but for interaction with breakdown of the hydration sheaths the stability increases in the opposite sequences. From this, it follows that all the complexes whose stability constants are given in Tables 2 and 3 are formed without complete breakdown of the hydration sheaths of the outer-sphere cations; however, the outer-sphere association constants are linear functions of the crystallographic radii of the outer-sphere ions. Under the conditions studied (3–4 M solutions of inert salts) the radii of the hydrated alkali metal cations are apparently inversely proportional to the crystallographic radii of these cations [3]; this explains why the outer-sphere association constants are given by Eqns. (21) and (22).

The enthalpy and entropy changes accompanying outer-sphere association have been determined [3,9,31,32,40,41,81]. The numerical data in Table 4, collected from various papers, show that the interaction of singly-, doubly-, and triply-charged anionic complexes with alkali and alkaline earth metal cations is accompanied by appreciable enthalpy and entropy changes. The decrease in entropy again indicates interaction without complete breakdown of the hydration sheaths of the alkali metal cations [88].

The outer-sphere interaction of quadruply-, quintuply-, and some triply-charged anions is accompanied by an increase in entropy [24], as is the interaction of singly-, doubly-, and triply-charged anionic complexes with outer-sphere cations with low degree of hydration or high charge (greater than three) [89–91].

Increase in the charge or decrease in the dimensions of the anionic complex or outer-sphere cation leads to a smaller decrease in entropy during outer-sphere association (Table 4). The identical decrease in entropy for the association of $PbCl_4^{2-}$ and $BiCl_6^{3-}$ anions with alkali metal cations is attributed to the high acidity of the solutions§ in

TABLE 4. Entropy change accompanying the formation of BML_n at 25°.

Anionic complexes	Entropy change (e.u.) for association with the cations of				Medium	References
	sodium	potassium	rubidium	caesium		
$TlCl_2^-$	—22	—21	—21	—20	4 M (Li, B)Cl	3,9
$PbCl_4$	—	—4	—4	—4	3 M (Li, B)Cl	39
$BiCl_6^{3-}$	—5.0	—3.2	—3.2	—2.9	3 M (Li, H, B)Cl at $[H^+] = 1$	31
$CdCl_4^{2-}$	—26	—23	—22	—20	4 M (Li, B)Cl	41
$CdBr_4^{2-}$	—	—29	—27	—23	4 M (Li, B)Br	81
$PbBr_4^{2-}$	—17	—17	—15	—14	4 M (Li, B)Br	3,32

which the outer-sphere associated species of the chloro-complexes of bismuth were studied (Table 4). In the presence of hydrogen ions even the doubly-charged $PbCl_4^{2-}$ anions react according to the equation

$$H^+ + PbCl_4^{2-} \rightleftarrows HPbCl_4^- \qquad (25)$$

with equilibrium constant equal to five.[3]

The entropy change accompanying the outer-sphere association of one anionic complex with various alkali metal cations is described by the equation [9,31,39,41]

$$\Delta S = 0.1Q_B + A \qquad (26)$$

where Q_B is the heat of hydration of the alkali metal cations and *A* is a constant. The low accuracy of the determination of the entropy change, however, makes necessary repeated verification of the correctness of this statement [3]. These doubts are also raised by the fact that an equation of type (26) characterises the entropy change in substitution processes but not in addition processes [16].

A direct calorimetric method was recently used to measure the enthalpy changes accompanying the association of alkali and alkaline earth metal cations with cyanoferrate(III) anions [40,65]. This increased the accuracy of the determination of the entropy changes. The accurate data [65] showed that the association of $Fe(CN)_6^{3-}$ ions with sodium, potassium, magnesium, and barium cations in 3 *N* solutions of mixtures of lithium chloride with the chlorides of the metals studied is accompanied by a decrease in entropy by 15–17 e.u., the value of ΔS being apparently independent of the nature of the outer-sphere cation.

Association with a decrease in the number of species by unity is accompanied by an entropy decrease of ~17 e.u. [20,92]. This quantity is almost independent of the nature of the interacting species. This result, together with experimental data [40,65], shows that the association of cyanoferrate(III) ions with alkali and alkaline earth metal cations takes place without breakdown of the hydration sheaths of the interacting ions. Spectrophotometric study [65] confirms this conclusion but indicates breakdown of the hydration sheaths in the association of K^+ with $Fe(CN)_6^{4-}$ in 3 M (Li, K)Cl solutions.

The interaction of anionic complexes with highly charged cations ($Z > 2$), weakly hydrated cations, or cations with a tendency to form covalent bonds is usually accompanied by an increase in entropy and a change in the ultraviolet range of the spectrum of ML_n and B. [22,87,89,90] These facts indicate the formation of direct bonds (without the presence of intervening solvent species along the $B–ML_n$ link) between the anionic complexes and outer-sphere cations of these types.

§ In strongly acidic solutions the $BiCl_6^{3-}$ ion is converted into $HBiCl_6^{2-}$, which reacts to form $B^+(H_2O)_xHBiCl_6^{2-}$ with higher positive values of ΔS than $BiCl_6^{3-}$.

Nitrate, sulphate, phosphate, and similar ions are complex anions which do not dissociate in aqueous solutions. The association of these anions with various cations may involve complex formation or outer-sphere association, depending on the nature of the interacting ions. For example, in 3 N Li(ClO_4, L) solutions, Tl^+ forms only ion pairs $Tl^+(H_2O)_xNO_3^-$ with nitrate ions but gives typical complexes with pyrophosphate anions[15]. An intermediate position is occupied by associated species comprising sulphate and thallium[93]. Highly charged cations and cations with a tendency to form stable hybrid bonds form typical ionic complexes with pyrophosphate and sulphate anions and also with nitrate anions[22]. The clearly-defined stepwise nature of their formation distinguishes inner-sphere complexes from outer-sphere complexes. The rules governing the interaction of undissociated complex anions with cations have been examined repeatedly[5,16].

There is as yet no information about the association of labile and relatively unstable cationic complexes with outer-sphere anions, but the outer-sphere association of inert and stable cationic complexes has been studied by many workers[22]. The outer-sphere complexes of the $Co(NH_3)_6^{3+}$ ion have been studied most completely and most frequently, but the data on the stability constants of these complexes are extremely contradictory[3] and are the subject of discussion[62,74]. The values obtained by various workers for the formation constant of the complex $Co(NH_3)_6^{3+}.Cl^-$ lie in the range 0.2–390.[63] Verification of the values of this constant[3] showed that the results of all earlier work[22,74] are correct and that the values of the constants for the formation of the luteochloride complex depend to a marked extent on the concentration and composition of the salt medium in which the studies are carried out[63]. Change in the composition of the salt medium changes the thermodynamic characteristics of the luteochloride complex by factors of several hundred and even changes their sign. Thus the complexes with composition $Co(NH_3)_6^{3+}.Cl^-$ at 25° are formed with $\gamma_{6,1} = 15.3$, $\Delta H = -5.8$ kcal mole^{-1}, and $\Delta S = -11$ e.u. in 0.1–0.5 M sodium chloride solutions but with $\gamma_{6,1} = 0.49$, $\Delta H = 5.6$ kcal × × mole^{-1}, and $\Delta S = 18$ e.u. in a 1 M solution of a mixture of sodium perchlorate and chloride[62]. This sharp change in the thermodynamic characteristics of the luteochloride complex is attributed to a change in the type of association on going from one salt medium to the other. In 0.1–0.5 M NaCl solutions the association of the $Co(NH_3)_6^{3+}$ and Cl^- ions takes place with the formation of a direct bond between the ionic complex and the outer-sphere ion. This is indicated by the decrease in entropy and by the agreement between the values of the outer-sphere association constant determined by solubility and spectrophotometric methods[3]. In 1 M sodium perchlorate solution the luteo-ion forms $\{[Co(NH_3)_6^{3+}].(ClO_4)_x\}^{3-x}$ complexes which are less stable than the complexes with other anions. The replacement of perchlorate ions by chloride ions in 1 M $NaClO_4$ solution leads to conversion of the luteoperchlorate complexes into luteochloride complexes; this process is accompanied by a bathochromic displacement of the absorption band of the luteo-ion in the ultraviolet range of the spectrum and is characterised by an increase in entropy, like the usual process of complex formation in aqueous solutions[5].

The marked influence of the composition and concentration of the salt medium on the thermodynamic characteristics of the ion pairs formed by cationic complexes makes it difficult to compare these characteristics and to recalculate them for solutions with zero ionic strength. Semi-quantitative comparison of a large amount of published data[22] shows that the $Co(NH_3)_6^{3+}$ ion and apparently the ions $Coen_3^{3+}$, $Copn_3^{3+}$, $Pten_3^{4+}$, $Cuen_2^{2+}$, etc., where en represents ethylenediamine and pn propylenediamine, form outer-sphere complexes with various anions, the stability of these complexes (with composition $ML_n.B$) increasing in the order

$$SCN^-,\ OH^-,\ I^-,\ N_3^-,\ Br^-,\ Cl^-,\ S_2O_3^{2-},\ SO_4^{2-},\ P_3O_9^{3-},\ P_4O_{12}^{4-} \qquad (27)$$

Increase in the dimensions of the cationic complex decreases the outer-sphere association constants; for example, the stability of the outer-sphere complexes formed by $Co(NH_3)_6^{3+}$, $Coen_3^{3+}$, and $Copn_3^{3+}$ with chloride, sulphate, and other anions decreases with increase in the molecular weight of the amine in the inner sphere[22].

According to modern theories, the stability of the outer-sphere complexes is determined by the charges and dimensions of the ionic complex and outer-sphere ion[94], but the values of the outer-sphere association constants are influenced by the structure of the ionic complex and also, apparently, by the structure of the outer-sphere ion. The *cis*-isomer of $CoCl_2en_2^+$ forms outer-sphere complexes with chloride and acetate anions in aqueous alcohol solutions but the analogous *trans*-isomer does not[49,95]. This can be attributed to the presence of a dipole moment in the *cis*-isomer and its absence in the *trans*-isomer.

The $Cr(H_2O)_6^{3+}$ ion forms less stable outer-sphere complexes with outer-sphere anions than the $Co(NH_3)_6^{3+}$ ion[22]. This difference has been related[94,96] to the higher positive charge of the $Co(NH_3)_6^{3+}$ ion, which has six protons more than the $Cr(H_2O)_6^{3+}$ ion. Increase in the number of protons in cationic complexes of the type $M(RH_n)_6^{3+}$, where RH_n represents molecules containing protons, increases the positive character of the peripheral charge of these complexes[94].

Most ion pairs of cationic complexes are formed by endothermic reactions involving an appreciable increase in entropy[3] and a change in the charge-transfer spectra[72,97]. Linhard[97] showed that the ultraviolet absorption spectrum of the luteo-ion exhibits a bathochromic shift when halide ions are added to a solution of the luteoperchlorate. The magnitude of the bathochromic shift changes in the same sense as the dimensions of the halide ion[72]. The charge transfer in the process

$$[Co(NH_3)_6]^{3+} + I^- \xrightarrow{h\nu} [Co(NH_3)_6]^{2+}.I^0$$

is responsible for the bathochromic shift in the spectrum of the luteo-ion when iodide ions are added to the solution[97].

The outer-sphere association of cationic complexes whose charge exceeds two usually takes place with breakdown of the hydration sheaths of the interacting ions and is accompanied by the formation of direct bonds between the ionic complexes and outer-sphere ions[3] but the nature of this bond has been little studied.

CN^- ions are joined to central cations via the carbon atom[97]. From this, it may be assumed that interaction takes place via the nitrogen atom in the outer-sphere complexes $B[Fe(CN)_6]$. The structures of outer-sphere complexes of the Prussian Blue type are apparently analogous to those of organo-derivatives of gold cyanide. The same is approximately true of the bonds in thiocyanato super-complexes[3]¶.

¶ The term "super-complex compound" is synonymous with the term "outer-sphere complex".

The stability of the bond formed by the first halide anions with the luteo-cation increases with decrease in the atomic weight of the outer-sphere ion, but the stability of the anionic super-complexes $\{[Co(NH_3)_6].Hal_x\}^{-x+3}$, where Hal represents halide anions, changes in the opposite sense. This is indicated by chromatographic studies[77] and by study of the solubility of the luteoperchlorate in aqueous solutions of lithium and sodium chlorides and bromides. The increase in the stability of the anionic super-complexes $\{[Co(NH_3)_6].Hal_x\}^{-x+3}$ with increase in the atomic weight of the outer-sphere ion is attributed[77] to the formation of a covalent bond by $Co(NH_3)_6^{3+}$ with halide ions as a result of the donor properties of the latter. This explanation is confirmed[3] by the fact that the values of the stability constants of the luteohalide outer-sphere complexes, calculated from solubility and spectrophotometric data, are identical.

Outer-sphere association has a significant influence on the kinetics of chemical reactions[93,99-101] since outer-sphere complexes of the ion-pair type are more reactive than the free ionic complexes. It cannot be assumed that this is applicable to all systems[3] but up to the present no systems are known[94] in which outer-sphere interaction leads to a significant decrease in the rate of chemical reactions.

The catalysis of a number of redox processes is based on the formation of outer-sphere complexes[99], the catalytic effect increasing in the same sense as the stability of the outer-sphere complexes.

7. PREDICTION OF THE CONSTANTS FOR THE ASSOCIATION OF ANIONIC COMPLEXES WITH ALKALI METAL CATIONS

The results of studies which have been partly summarised in Table 2 and a number of other papers[3,39,40] show that the dependence of $\gamma_{N,1}$ on r_B, r_M, r_L, and Z^2 is linear for most systems studied. These relationships can be used to predict association constants in systems which have not been studied or have been little studied. Experimental verification has confirmed that such prediction is possible[3]. Some predicted outer-sphere association constants[3,40] are given in Table 5. The verification of the numerical data in this Table is of interest.

The dependence of the e.m.f. of cell (19) on the concentration of Na^+ in S_y solutions is linear for all systems studied[3,39], so that for the calculation of the constant for the outer-sphere association of ML_n with Na^+ it is sufficient to measure the e.m.f. of cell (19) at a single Na^+ concentration in the S_y solution. The constants for the association of ML_n with the other alkali metal cations are then most conveniently determined from the plot of $\gamma_{N,1}$ against r_B or the plot of $\log\gamma_{N,1}$ against r_B, knowing that the value of r_B at which $\gamma_{N,1} = 0$ is determined by the nature of the ligand[3] (see section 6).

8. COMPARISON OF OUTER-SPHERE AND INNER-SPHERE ASSOCIATION CONSTANTS

There is a large amount of published information[22] on the composition and stability constants of acido-complexes, determined without allowance for the association of anionic complexes with outer-sphere cations. As a result of such studies, it was found[35,66,67,102-104] that a given central ion forms, for example, a smaller number of ionic complexes and less stable ionic complexes with the halides of light alkali metals than with the halides of heavy alkali metals. An analogous result was observed in the study of nitrato-,[105] thiocyanato-,[68] and other[3] complexes. On the other hand, in a study of hydroxo-complexes[106] it was found that the degree of complex formation by central ions with hydroxide ions increases in the sequence CsOH–LiOH. Calculations of the composition and stability constants of ML_n from data obtained by different methods showed that the values of n and β_n depend on the method of determination[35] and also led to anomalously low or anomalously high values for stepwise stability constants and to the detection of ionic complexes which in fact do not exist in solution[3]. All this was observed when no allowance was made for outer-sphere interaction[3], but these contradictions disappeared in many systems formed by ionic complexes when allowance was made for the formation of outer-sphere complexes, and the constants for the formation of the latter did not depend on the method of determination or the concentration of the reacting substances[32,39].

The need to make allowance for outer-sphere interactions can be seen by comparing the data in Tables 2 and 6, which show that the constants for the attachment of the N-th ligands to ML_{N-1} are less than the constants for the outer-sphere association of ML_N with alkali metal cations for the chloro-complexes of thallium(I), lead(II), zinc, cadmium, and even bismuth(III).[31]

In the formation of nitrato-complexes of lead(II), only the first nitrate anion is joined to Pb^{2+} by a more stable bond than that joining the K^+ cation to the $Pb(NO_3)_4^{2-}$ anion.

TABLE 5. Predicted[3] values of the stability constants of the ion pairs $B(H_2O)_xML_n$ at 25° in 4 M (Li, B)L solutions.

Anionic complexes	Constants for outer-sphere association with the cations of			
	sodium	potassium	rubidium	caesium
$PtCl_4^{2-}$	0.5	1.2	1.6	1.8
$CuCl_2^-$	0.1	0.2	—	—
$AgCl_2^-$	0.1	0.2	—	—
$AgBr_2^-$	—	0.03	0.06	0.08
$SnCl_4^{2-}$	0.6	1.9	2.6	3.0

TABLE 6. Stability constants of ML_n ions in 4 M $Li(ClO_4, L)$ solutions at 25°, calculated from potentiometric data.

M	L	Stepwise stability constants of ML_n with n equal to				References
		1	2	3	4	
Tl^+	Cl^-	0.80	0.14	—	—	35
Pb^{2+}	Cl^-	17	3.1	2.3	0.18	80
Zn^{2+}	Cl^-	2.0	0.50	10	0.01	34
Zn^{2+}	Br^-	1.16	0.13	12.7	0.18	37
Zn^{2+}	I^-	0.34	0.03	18	0.31	40
Cd^{2+}	Cl^-	58	6.9	3.7	0.29	33
Pb^{2+}	NO_3^-	3.0	1.2	0.37	0.19	3

Heavy alkali metal cations are joined by a more stable bond to $PbCl_3^-$ and $ZnCl_3^-$ anions than to the four-coordinated chloro-anions. This explains the fact that when Na, K, Rb, or Cs chlorides are added to a solution containing Pb^{2+}, Zn^{2+}, and, apparently, Cd^{2+} cations, the formation of MCl_3^- ions is followed by the formation of $BMCl_3$ outer-sphere complexes, to which the fourth chloride ion is attached. The alkali metal cations are joined to the MCl_3^- anions via a layer of water molecules, but the fourth chloride ion is joined by a direct bond to the central metal ion[3]. This indicates that the outer-sphere interaction without direct bonding between MCl_3^- and alkali metal cations leads to an increase in the coordination sphere of the central ion or, more accurately, increases the probability of the replacement of water in the inner sphere of $[MCl_3(H_2O)]^-$ by a Cl^- anion.

The data in Tables 2 and 6 show that in many systems which have been studied repeatedly the effect of outer-sphere interaction is much greater than the effect of attachment of the last ligands in ML_N, so that the data on the composition and stability constants obtained for these ionic complexes without allowance for outer-sphere interaction[22] require correction†.

9. COMPLEX FORMATION WITH ALLOWANCE FOR ASSOCIATIVE INTERACTION WITH THE IONS OF THE SALT MEDIUM

The composition of the medium, that is the nature and concentration of the solvent and any ions present in the solution, influences complex-formation equilibria. The salt medium may produce either an increase or a decrease in the degree of complex formation by the central ion[3]. A decrease in the degree of complex formation by M with L often takes place when these components form new structural units[15] with the influencing ions, and an increase in the degree of complex formation is observed when outer-sphere complexes are formed by the ionic complexes with the influencing ions. The decrease in the degree of complex formation by M with L under the influence of ions which form new structural units with M or L has been used many times[14] to study complex formation in solution. The increase in the degree of complex formation under the influence of the ions of the salt medium was first taken into account after a series of studies had been carried out in solutions with high and constant ionic strengths, maintained using inert salts[17], but up to the present the allowance made for this effect has been purely qualitative. It is often considered[107] that secondary reasons for the influence of the ions of the salt medium, involving a change in the activity of the solvent, a change in the activity coefficients of the reactant and product ions, a change in the structure of the solution, etc. exert an influence which cannot be distinguished from chemical interaction in systems with labile and relatively unstable complexes. The contents of the preceding sections of the present review refute this suggestion. At present, however, there is little information on outer-sphere interaction or on the dissociation of the alkali and alkaline earth metal salts whose anions are used as ligands in the study of complex formation in aqueous solutions with high and constant ionic strengths.

† The coordination number of the super-Werner sphere is equal to 12; less frequently it amounts to 6 for octahedral complexes and 4 for tetrahedral complexes. The centres of the edges or faces of the tetrahedra and octahedra are used in super-Werner coordination[123].

The replacement of water by aqueous solutions of inert salts smoothes out the difference in the extents to which the dissociation of strong and weak electrolytes obeys the law of mass action[108], so that the interaction of a central ion with ligands and the ions of a salt medium, like the dissociation of all alkali and alkaline earth metal salts, can be characterised by the constants for the formation of definite complexes[3].

Formulae (1) and (2) characterise the composition of the simple ions and ionic complexes formed in concentrated solutions of inert salts. The replacement of any ions of the salt medium influences the composition and structure of the complexes (1) and (2). Increase in the tendency of the ions of the inert salt to react with the central ion decreases the experimentally measured degree of complex formation with the ligand. Thus in the study of the formation of bromo-complexes of lead in solutions with constant ionic strengths, maintained with sodium perchlorate, nitrate, and chloride, it was found[55] that the degree of complex formation of Pb^{2+} in solutions with equal bromide ion concentrations decreases with change in the ions of the salt medium in the sequence ClO_4^-, NO_3^-, Cl^-. This is attributed to the fact that these anions themselves form complexes with the bivalent lead cation, and complex formation with bromide ions involves the replacement, by bromide ions, of the above anions in the inner sphere of the lead cation. The stabilities of the Pb^{2+} complexes increase in the sequence $Pb(ClO_4)_n^{2-n}$, $Pb(NO_3)_n^{2-n}$, $PbCl_n^{2-n}$.[56]

The Li^+ cation forms the least stable outer-sphere complexes with the great majority of anionic complexes with charges less than three[3]. Perchlorate anions rarely form anionic complexes with central ions[22,109] and, more particularly, do not form anionic complexes with charges exceeding three. Thus the stability of complexes of type (1) will be smaller in the presence of Li^+ than in the presence of other cations which do not form stable compounds with the ligand. This explains why, in the interaction of central ions with alkali and alkaline earth metal salts, the highest degree of complex formation by the central ion is observed in a medium containing of lithium salts[110]. This result is not affected by the increase in the stability of the outer-sphere complexes B_yML_n in the sequence lithium–caesium and magnesium–barium[3], since the relative increase in the degree of complex formation by M as a result of the outer-sphere interaction increases with decrease in the stability of the M–L or M–ClO_4^- bonds[103,117].

The stability of the ion pairs $B(H_2O)_xL$, the outer-sphere complexes B_yML_n, and the complexes

$$\sum_{n=0}^{n=N}\sum_{x=0}^{x=X}\sum_{y=0}^{y=Y}\sum_{z=0}^{z=Z} ML_n(H_2O)_xA_yB_z, \qquad (28)$$

by which we mean[14,15,17,54] ionic complexes ML_n in concentrated solutions of inert salts with cation B and anion A, increases from lithium to caesium and from magnesium to barium for different A and L = Cl^-, Br^-, I^-, NO_3^-, SCN^-, SO_4^{2-}, etc.[35,102,103,111], but changes in the opposite sequence for L = OH^-, CH_3COO^-, etc.[3,106] Usually, the stability of the B–ML_n and $B(H_2O)_x$–L bonds changes in the same sequence of cations B, and increase in the strength of these bonds leads to an increase in the degree to which M is bound in complex (28). The anions A, like the cations B, increase the extent to which M is bound in complex (28) with increase in the stability of the M–A bond[3]. Some published data[55,56] contradict this result, due to the fact that the salt medium

was regarded as an inert solvent for M, L, and ML_n, and not as a component of the equilibrium for the dissociation of complex (28).

The cations of the salt medium have little influence on the stability constants of cationic complexes and neutral molecules[63,102,112] if complexes BL_n are not formed. The influence of alkali and alkaline earth metal cations involves chiefly a change in the structure of the cationic complexes, and hence a change in ΔH and ΔS for formation of the latter[20]. The replacement of alkali metal cations in the sequence lithium, sodium, and potassium[113] displaces the equilibrium

$$CdNO_3^+ + xH_2O \rightleftarrows Cd^{2+}(H_2O)_xNO_3^- \quad (29)$$

to the right, since the tendency of these cations to bring about the dehydration of the Cd^{2+} cation decreases in the above sequence.

The influence of the cations of inert salts on the formation of neutral molecules, for example of the type ML_2, is due to their influence[39,43,46,110] on the equilibria

$$2ML_2 \rightleftarrows ML^+ + ML_3^- \quad (30)$$

and

$$3ML_2 \rightleftarrows 2ML^+ + ML_4^{2-} \quad (31)$$

which are often established in stepwise complex formation[3], but which have unfortunately been little studied as yet.

Increase in the tendency of the cations of the salt medium to form outer-sphere complexes with ML_3^- and ML_4^{2-} anions displaces equilibria (30) and (31) to the right and leads to a decrease in the stability constants of ML_2.[43]

The most direct method for investigating complex formation in solutions is by studying the Raman spectra[17,109]. Data obtained by this method are influenced to the minimum extent by the effect of the medium on complex formation and give information about the concentration of individual ionic complexes and also about the nature of the bonds M–L, B–ML_n, and ML–A.[114]

The intensity of the characteristic bands of the Raman spectra is proportional to the concentration of the complex formed and can be used as the chief parameter for the quantitative representation of processes taking place in solutions[114]. Clear-cut measurement of the intensity of the characteristic bands in Raman spectra is possible, however, only for the ionic complexes predominating in the ML, $ML_2 \ldots ML_n \ldots ML_N$ system[115]. The predominating ions are usually ML and ML_N.

Raman spectra are extremely useful for demonstrating the differences between outer-sphere and inner-sphere complexes[109]. The formation of outer-sphere complexes is not reflected in the Raman spectra[116].

The low sensitivity of present-day apparatus unfortunately makes it impossible to use Raman spectra to study complex formation in solutions with reactant concentrations less than 0.5 M.[3] Increase in the sensitivity of the apparatus by several orders of magnitude may make this method the most suitable for studying various types of complex in solution in any salt medium[17].

Despite the low sensitivity of the method, the use of Raman spectra has proved the existence of inner-sphere nitrato-complexes of Ca^{2+}, Ce^{4+}, Th^{4+}, Cu^{2+}, Ag^+, Zn^{2+}, Hg^{2+}, Al^{3+}, and In^{3+} [117,118] and has completely refuted, for almost all elements of the Periodic System, the suggestion that perchlorato-complexes are inner-sphere complexes[109].

The influence of the salt medium on complex formation in solutions often involves the formation of various types of ionic molecules[78] for which allowance is not made in the interpretation of the experimental data[3]. The low energies of formation of ionic molecules points to the possibility of detecting these complexes by means of the vibrational and rotational spectra.

Unfortunately, there is almost no published information on the use of infrared spectra to study the association of ions and the influence of the salt medium on complex formation.

Water absorbs over a wide range of the infrared spectrum. Only the use of thin-layer (5–10 μm) cells or surface reflectance spectra makes it possible to study association in aqueous solutions by infrared spectroscopy and even then only for a limited number of anions.

The sulphato-,[119] thiocyanato-,[120] and cyano-complexes[121] of various metals in aqueous solutions have been studied by infrared spectroscopy. The separate detection of outer-sphere complex formation, usually attributed to the influence of the nature of the salt medium, and inner-sphere interaction showed[119] that the tendency to form inner-sphere monosulphato-complexes decreases in the sequence $Cd^{2+} \simeq Cu^{2+} > Ni^{2+} > Co^{2+} \simeq Zn^{2+} > Mn^{2+}$. The change from the monosulphato- to the disulphato-complexes decreases the contribution made by outer-sphere complex formation[119].

Mathematical treatment of the experimental infrared spectroscopic data sometimes makes it possible to estimate the constants for both inner-sphere and outer-sphere interaction[120].

Increase in the sensitivity and the more extensive use of physical methods for studying association in aqueous solutions should extend our knowledge in this field.

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ELECTRONIC ABSORPTION AND LUMINESCENCE SPECTRA OF AROMATIC POLYCYCLIC HYDROCARBONS

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1. ELECTRONIC STATES AND VIBRONIC SPECTRA OF POLYATOMIC MOLECULES

The complete electronic spectrum of a molecule arises from changes in electronic, vibrational, and rotational energy[1-7]. The energy of rotational quanta in polyatomic