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THE ROLE OF THE PERCHLORATE ION AS LIGAND IN SOLUTION

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CONTENTS

A. INTRODUCTION

Reports on perchlorate complex formation in solution are rapidly accumulating[1]. A closer examination, however, reveals many controversies, not only on the strengths of the complexes but often on their very existence.

While most workers, using the "constant ionic medium principle", are aware of the possibility that the medium ions react to some degree with the species under study, few have given the consequences of such reactions more than a passing thought. Equations pertinent to complex formation with the medium anion have been given occasionally (e.g. refs. 2–5). It is more commonly argued as follows. In aqueous $NaClO_4$, for instance, the so-called free metal ion concentration is actually the sum

$$\sum_p \sum_q \sum_r [M(H_2O)_p(Na^+)_q(ClO_4^-)_r]$$

As the medium is constant, this sum cannot be separated into its parts. Stability constants, valid in the particular medium, can be calculated. This reasoning is, however, an oversimplification. Particularly when we study weak complexes, we actually change the medium, e.g. by substituting ligand for ClO_4^-. Then the proportions between the terms in the sum are no longer constant. As a consequence, different experimental methods may give different results. This is a conclusion which does not seem to have been emphasized in the literature of solution chemistry. A thorough examination of the consequences of perchlorate association as well as a critical literature review thus seem relevant. As the perchlorate ion is by far the most commonly employed medium anion, this review will be restricted to this ion. The equations deduced, however, naturally apply to any (monovalent) medium anion.

It is sometimes maintained[6,7] that perchlorate association should be important only when outer-sphere complexes are studied. This view is not tenable, since ClO_4^- may a priori form complexes with a cation, whether this is a labile aquated metal ion or an inert complex ion. The perchlorate complexes are probably mainly outer-sphere, also for labile cations, but this is also irrelevant. It is the strength of the complexes studied, relative to the perchlorate complexes, that is important. Thus, when weak complexes are studied, the possibility of competition from the perchlorate ion should always be considered.

The question whether perchlorate complexes are inner- or outer-sphere will not be further discussed, and nor will the type of bonding in these complexes. No specific meanings will be ascribed to the terms "complex formation" or "association"; these will be used synonymously.

B. CONSEQUENCES OF PERCHLORATE ASSOCIATION

(i) Notation

M	metal ion
L	ligand ion
A	medium anion (perchlorate ion)
[ ]	actual concentration
C	total concentration
$\beta_{m,n}$	stability constant of the complex MA_mL_n:

$$\beta_{m,n} = [MA_mL_n]/([M][A]^m[L]^n)$$

$0 \leqslant m \leqslant M;\quad 0 \leqslant n \leqslant N$ (hence $\beta_{0,0} \equiv 1$).

Apparent constants or functions, resulting from the neglect of perchlorate complexes, are printed in **bold** type.

(ii) Constant ionic medium principle

When ionic equilibria are studied, it is customary to maintain a high and constant ionic medium in order to reduce the variations in activity coefficients[8]. A perchlorate is almost exclusively used as "supporting electrolyte", e.g. sodium, lithium or ammonium perchlorate, or perchloric acid. Ideally, the electrolyte used should not introduce any impurities to the solutions and should not react with the species under study. The medium should keep the activity coefficients effectively constant.

Several authors have devised methods to reduce the impurity level of perchlorate solutions (see, for example, refs 9–11).

The medium ions may react with the ions under study in various ways. The perchlorate ion has, as well as associating tendencies, oxidizing properties, but the rate of reaction is normally negligibly small. The medium cation is, of course, also a potential complexing agent. The limitations in the use of H^+ and NH_4^+ are obvious[12]. However, the tendencies of the alkali ions to associate with other ions are probably small, and have as a rule been neglected. They will also be neglected here.

Several authors have shown [8,13–15] that activity coefficients do change despite a constant medium, e.g. when a substantial amount of the medium cation is substituted by hydrogen ion, or the perchlorate ion by a halide ion. Occasionally, an improvement is seen when another cation is chosen for the supporting electrolyte. For perchlorate there is, however, often no alternative.

When very weak complexes, including perchlorate complexes, are studied, it is important to realize that in the end there always remains some uncertainty about the changes in activity coefficient. As the observed effect, i.e. the activity change, becomes small, it becomes increasingly difficult to assess the degree to which this change is due to a change in the activity coefficient (specific medium effect) or to a change in concentration (chemical reaction, formation of a new species). It should perhaps be emphasized that the fact that the experimental data fit a given model is no proof that the model is correct. Thus, although a model assuming constant activity coefficients and a weak perchlorate complex formation, for example, may explain data obtained with some experimental method, this is often not sufficient to prove the existence of the proposed complexes. Additional support is required, e.g. spectral evidence, or the fact that data from independent experiments fit the same model.

No definite answer can be given to the question of how, exactly, the concept "constant ionic medium" should be defined. There is no theoretical foundation for the use of a constant *ionic strength*, as defined by Lewis and Randall, except at low electrolyte concentrations. In more concentrated solutions it has often proved satisfactory and convenient to keep the total concentration of ionic charges constant. The present author has thus in a number of studies of halide complexes of polyvalent cations [5,16,17] kept the sum of the halide and the perchlorate ion concentrations constant.

$$I = [\mathrm{L}] + [\mathrm{A}] \tag{1}$$

A more general expression is of course

$$I = |z|\,[\mathrm{L}] + [\mathrm{A}] \tag{2}$$

where z is the ionic charge of the ligand. Equation (2) also covers the case of a neutral ligand, such as NH_3. However, in the following deductions it is assumed for simplicity that [L] and [A] are related by eqn. (1). I will, somewhat loosely, be called the "ionic strength". Naturally, if perchlorate association is to be considered for situations where (2) or any other relation between [L] and [A] is valid, equations corresponding to those given in the following can be readily derived using the proper expression in place of eqn. (1).

It is assumed, in this section, that activity coefficients are constant.

(iii) Central ion measurements

In a mixture of the central ion M and the ligand L in a medium containing A as anion, we assume that mononuclear complexes of the general composition $\mathrm{MA}_m\mathrm{L}_n$ are formed. The total concentration of M is then given by

$$C_{\mathrm{M}} = \sum_{n=0}^{N} \sum_{m=0}^{M} [\mathrm{MA}_m\mathrm{L}_n] \tag{3}$$

Introducing the stability constants $\beta_{m,n}$ and the condition (1) we obtain

$$C_{\mathrm{M}} = [\mathrm{M}] \sum_{n=0}^{N} \left(\sum_{m=0}^{M} \beta_{m,n} (I - [\mathrm{L}])^m \right) [\mathrm{L}]^n \tag{4}$$

Since

$$(I - [\mathrm{L}])^m = \sum_{j=0}^{m} (-1)^j \binom{m}{j} I^{m-j} [\mathrm{L}]^j \tag{5}$$

we may write

$$C_{\mathrm{M}} = [\mathrm{M}] \sum_{k=0}^{M+N} A_k [\mathrm{L}]^k \tag{6}$$

where A_k are constants.

$$A_k = \sum_{n} (-1)^{k-n} \left(\sum_{m=k-n}^{M} \binom{m}{k-n} I^{m+n-k} \beta_{m,n} \right) \tag{7,k}$$

The summation limits for n are $\max(0, k - M) \leqslant n \leqslant \min(k, N)$.
For instance,

$$A_0 = \beta_{0,0} + \beta_{1,0} I + \beta_{2,0} I^2 + \ldots \qquad (\beta_{0,0} \equiv 1) \tag{7,0}$$

$$A_1 = (\beta_{0,1} - \beta_{1,0}) + (\beta_{1,1} - 2\beta_{2,0}) I + \ldots \tag{7,1}$$

In a large variety of experimental methods some quantity Q, proportional to [M], is measured more or less directly.

$$Q = q\,[\mathrm{M}] = qC_\mathrm{M}/(\sum_k A_k\,[\mathrm{L}]^k) \tag{8}$$

Thus, in EMF measurements, if

$$E = E^0 + \frac{RT}{nF} \ln\,[\mathrm{M}] \tag{9}$$

then $\exp(EnF/RT)$ is proportional to [M]. In solubility measurements, in their simplest form[18], a solubility product is valid.

$$K_s = [\mathrm{M}]\;[\mathrm{L}]^\nu \tag{10}$$

Hence, $[\mathrm{L}]^{-\nu}$ is proportional to [M]. Solvent extraction methods are analogous. All these methods can be termed central ion measurements. It is important to realize that in no normal case is the proportionality constant, q, known a priori in the medium employed. In order to eliminate q, we also measure Q in ligand-free solutions (or extrapolate Q to $[\mathrm{L}] = 0$)

$$Q\,([\mathrm{L}] = 0) = q\;[\mathrm{M}]\;([\mathrm{L}] = 0) \tag{11}$$

If complexes involving A were absent

$$[\mathrm{M}]\;([\mathrm{L}] = 0) = C_\mathrm{M} \tag{12}$$

and q could readily be calculated. However, here

$$[\mathrm{M}]\;([\mathrm{L}] = 0) = C_\mathrm{M}/A_0 \tag{13}$$

according to eqn. (6), and

$$\mathrm{X} = \frac{Q([\mathrm{L}] = 0)}{Q} = \sum_k \frac{A_k}{A_0}\,[\mathrm{L}]^k \tag{14}$$

Thus, provided [L] is known (if, say, C_{M} is so low that $[\mathrm{L}] \approx C_{\mathrm{L}}$), the coefficients A_k/A_0 can be determined. As a rule **X** is interpreted as

$$\mathbf{X} = \sum_k \boldsymbol{\beta}_k \, [\mathrm{L}]^k \tag{15}$$

It may be concluded that when the medium anion is involved in the complex formation, central ion measurements give the apparent constants

$$\boldsymbol{\beta}_k = A_k/A_0 \tag{16}$$

If the simple (but quite plausible) situation that MA and the various ML_n are the only complexes formed is considered, then

$$\boldsymbol{\beta}_1 = \frac{\beta_{0,1} - \beta_{1,0}}{1 + \beta_{1,0} I} \tag{17,1}$$

and

$$\boldsymbol{\beta}_k = \frac{\beta_{0,k}}{1 + \beta_{1,0} I} \qquad k > 1 \tag{17,k}$$

In measurements of the type described, C_{M} can as a rule be kept low, so that the condition (1) is effectively valid. Small deviations will give rise to only small corrections in the above equations.

(iv) Ligand measurements

For the ligand concentration the following equation applies.

$$C_{\mathrm{L}} = [\mathrm{L}] + \sum_{n=1}^{N} \left(n \sum_{m=0}^{M} [\mathrm{MA}_m \mathrm{L}_n] \right) \tag{18}$$

By analogy with eqn. (6) we may then write

$$C_{\mathrm{L}} - [\mathrm{L}] = [\mathrm{M}] \sum_{k=1}^{N+M} B_k \, [\mathrm{L}]^k \tag{19}$$

where

$$B_k = \sum_n n(-1)^{k-n} \left(\sum_m \binom{m}{k-n} \beta_{m,n} \, I^{m+n-k} \right) \tag{20}$$

When C_M is high enough, the complex formation causes a significant difference between C_L and [L], and it becomes meaningful to perform *ligand measurements.* Some quantity proportional to [L] is then measured. For instance, if L is the anion of a weak acid, an electrode sensitive to $[H^+]$ may be used. Halides may be studied by the aid of silver–silver halide electrodes. The solubility of a sparingly soluble salt $M'L_y(s)$, where M′ is a cation other than M, is often used as a sensitive measure of [L].

Whatever technique is used in ligand measurement, a calibration must be performed. For this purpose measurements are performed in solutions free of the central ion [M]. Here, C_L = [L], since none of the complexes considered can be formed. Thus, the calibration is "correct" and a correct value of [L] is readily assessed also when $C_M > 0$. The quantity

$$\bar{n} = (C_L - [L])/C_M \tag{21}$$

may then be computed. From eqns. (19) and (6)

$$\bar{n} = \left(\sum_{k=1}^{M+N} B_k\,[L]^k\right)\Big/\left(\sum_{k=0}^{M+N} A_k\,[L]^k\right) \tag{22}$$

Since, generally, $B_k \neq kA_k$, a model

$$\bar{n} = \left(\sum_{k=1} k\beta_k\,[L]^k\right)\Big/\left(\sum_{k=0} \beta_k\,[L]^k\right) \tag{23}$$

cannot always be forced onto the experimentally determined $\bar{n}$. However, often only a part of the $\bar{n}$ curve is known, or the perchlorate association does not interfere in the whole range studied. The experimental data may then fit to the model (23). Identification of eqns. (22) and (23) yields

$$\beta_1 = B_1/A_0 \tag{24,1}$$

$$\beta_2 = (B_1(B_1 - A_1) + B_2A_0)/2A_0^2 \tag{24,2}$$

and so forth.

If we again consider the simple situation only where MA and the various ML_n are formed $B_1 = \beta_{0,1}$ according to eqn. (20), and thus, for example,

$$\beta_1 = \frac{\beta_{0,1}}{1 + \beta_{1,0}\,I} \tag{25,1}$$

$$\beta_2 = \frac{\beta_{0,2}}{1 + \beta_{1,0}\,I} + \frac{\beta_{0,1}\,\beta_{1,0}}{(1 + \beta_{1,0}\,I)^2} \tag{25,2}$$

(Compare eqn. (17)).

If, when C_M is high, a significant amount of A is consumed, so that eqn. (1) is no longer fulfilled, it should nevertheless be possible to obtain a correct value of $\bar{n}$ by extrapolating to $C_M = 0$.

The ligand number, $\bar{n}$, can often be obtained when other methods, not ligand measurements in the sense defined here, are used. For example, potentiometric central ion measurements may yield $\bar{n}$ by the Bodländer equation. In solubility measurements, the slope of the solubility curve yields $\bar{n}$, as does the slope of the partition curve in solvent extraction measurements. In these cases, the ligand number determination is based on the equation[19]

$$\bar{n} = \mathrm{d}\log X/\mathrm{d}\log\,[\mathrm{L}] \tag{26}$$

If we actually have the apparent X defined by eqn. (14), then

$$\mathrm{d}\log X/\mathrm{d}\log\,[\mathrm{L}] = \left(\sum_k k\frac{A_k}{A_0}\,[\mathrm{L}]^k\right)\Big/\left(\sum_k \frac{A_k}{A_0}\,[\mathrm{L}]^k\right) \tag{27}$$

No constants other than those given by eqn. (16) can be extracted from this function.

(v) Measurement of some intensive property

Often, stability constants are evaluated from measurements of some intensive property, F', that is the sum of contributions from several of the species in the solution

$$F' = d\left(\sum_{m,n} \varphi_{m,n}\,[\mathrm{MA}_m\mathrm{L}_n] + \varphi_\mathrm{L}\,[\mathrm{L}]\right) \tag{28}$$

where d is a known constant, and φ are constant factors, often unknown. It is assumed for simplicity that ions from the medium do not contribute to F'.

The intensive property most commonly studied is optical absorbance. In this case d is the length of the light path through the solution and φ are the individual absorption coefficients.

If φ_L is obtained from measurements in solutions where $[\mathrm{L}] = C_\mathrm{L} = I$, a new function, F, can be calculated

$$F = F'/d - \varphi_\mathrm{L} C_\mathrm{L} \tag{29}$$

Then (eqns. (28) and (18))

$$F = \sum_{m,n} (\varphi_{m,n} - n\varphi_\mathrm{L})\,[\mathrm{MA}_m\mathrm{L}_n] \tag{30}$$

As before, stability constants and eqn. (1) are introduced, [M] is eliminated, and eqn. (30) may be written

$$F/C_M = \left(\sum_{k=0}^{M+N} F_k\,[\mathrm{L}]^k\right) \Big/ \left(\sum_{k=1}^{M+N} A_k\,[\mathrm{L}]^k\right) \tag{31}$$

where (cf. eqn. (7))

$$F_k = \sum_n (-1)^{k-n} \left(\sum_m \binom{m}{k-n} l^{m+n-k} (\varphi_{m,n} - n\varphi_L)\beta_{m,n}\right) \tag{32}$$

and A_k are given by eqn. (7). Any attempt to fit eqn. (31) to a model

$$F/C_M \left(\sum_{k=0} (\varphi_k - k\varphi_L)\,\beta_k\,[\mathrm{L}]^k\right) \Big/ \left(\sum_{k=0} \beta_k\,[\mathrm{L}]^k\right) \tag{33}$$

will yield the same apparent constants as those given by eqns. (16) or (17). For absorbance measurements, the L method, or numerical methods of computation, are such "identification" methods[20]. Although eqns. (31) and (33) can always be identified, unreasonable (e.g. negative) absorption coefficient values may well be the apparent result of the ClO_4^- association. The errors that may occur when higher complexes are neglected, especially if the L method is used, have been discussed elsewhere[20].

The direct identification requires [L] to be known; normally C_M is kept low so that $[\mathrm{L}] \approx C_L$. There are, however, alternative ways of employing intensive property data that require [L] to be significantly different from C_L.

In the method of corresponding solutions[19], it is recognized (eqn. (31)) that F/C_M is a function of [L] only. Thus, when F/C_M is constant, [L] is also constant, as is $\bar{n}$ (eqn. (22)). From measurements of F vs. C_L and C_M the connection between C_L and C_M at constant F/C_M is assessed. This connection is, as described (eqn. (21)), linear.

$$C_L = [\mathrm{L}] + \bar{n}\,C_M \tag{34}$$

The line yields [L] and $\bar{n}$, and from the function $\bar{n}$ vs. [L] the constants given by eqns. (24) or (25) are computed.

There is, however, an important difference between this method and the ligand measurements, where [L] is unequivocally determined by direct measurement. Here, even a small deviation from eqn. (1) may distort eqn. (34) appreciably. An erroneous value of [L] then results, more so the longer the extrapolation to $C_M = 0$. Rather long extrapolations are often unavoidable, as the precision of F decreases rapidly with decreasing C_M. Therefore, the method of corresponding solutions should be used with caution, when adverse effects of ClO_4^- association cannot safely be ruled out.

Another alternative is the M method[20], best known from the work of Evans and Nancollas[21]. Absorbance, or any other intensive property, is measured at small ligand concentrations only, $C_L \ll C_M$. Complexes with more than one ligand need not be considered. For very small [L], eqn. (31) may be written

$$F/C_M = F(C_L = 0)/C_M + \frac{1}{\Phi}[L] \tag{35}$$

where Φ is a constant. Moreover, according to eqns. (19) and (6)

$$C_L = [L]\,(1 + [M]B_1) \tag{36}$$

and

$$C_M = [M]A_0 \tag{37}$$

Hence

$$C_L C_M/(F - F(C_L = 0)) = \Phi(1 + \frac{B_1}{A_0}C_M) \tag{38}$$

When the quantity on the left is plotted vs. C_M, the constant B_1/A_0 is obtained as slope/intercept (cf. eqn. (24,1)). If the assumptions used here are not justified, corrections add to eqn. (38). This method is less sensitive to slight deviations from eqn. (1). On the other hand, it is strictly limited to the region of very low ligand concentrations.

(vi) Further aspects

We now concentrate on $\boldsymbol{\beta}_1$, and moreover consider only the simple situation where no other complexes than ML_n and MA are formed. The preceding deductions may then be summarized as follows.

In the first place, ClO_4^- association may not immediately become apparent in an experimental study since the pertinent equations normally retain their form. However, instead of the "true" constants, apparent constants result.

Secondly, the various methods of measurement divide into two classes.

(1) Central ion measurements, direct intensive property measurements, and equivalent methods.

(2) Ligand measurements, method of corresponding solutions, M method, and equivalent methods.

The two classes give, as long as eqn. (1) is valid, the apparent constants

$$\boldsymbol{\beta}_1(1) = \frac{\beta_{0,1} - \beta_{1,0}}{1 + \beta_{1,0}I} \tag{39}$$

$$\boldsymbol{\beta}_1(2) = \frac{\beta_{0,1}}{1 + \beta_{1,0}I} \tag{40}$$

Thus, if two different methods are applied to the same system, different values of $\boldsymbol{\beta}_1$ may result. Moreover, when this is the case, values of the "true" constants $\beta_{0,1}$ and $\beta_{1,0}$ may readily be calculated.

When is this possibility feasible? In the first place, the perchlorate complex is always weak. Therefore, for strong L complexes, no difference between $\boldsymbol{\beta}_1$ (1) and $\boldsymbol{\beta}_1$ (2) can be detected. Further, it is to be noted that

$$\boldsymbol{\beta}_1(1) - \boldsymbol{\beta}_1(2) = \frac{\beta_{1,0}}{1 + \beta_{1,0} I} \leqslant \frac{1}{I} \tag{41}$$

The chances that the difference is significant decrease with increasing ionic strength. This is amplified by the fact that the constants normally decrease with increasing I, up to $I \sim 1M$.

While it is true that for strong systems different methods give the same results, it should be emphasized that the constants observed, $\boldsymbol{\beta}_1$, still differ from the "true" $\beta_{0,1}$ by a factor $(1 + \beta_{1,0} I)$, regardless of the strength of the M–L complexes. The same is true for $\beta_{0,n}$, $n > 1$.

For weak systems there are other possible ways of assessing the true constants, but as these are probably mainly hypothetical, they will not be described here. Further aspects of this question will be discussed in connection with iron (III) perchlorate complexes (p. 256).

C. LITERATURE SURVEY

In the following, the more important reports on perchlorate complex formation will be surveyed, with interest focussed primarily on aqueous solutions. Quantitative data are given in terms of stability constants even though other constants, e.g. instability constants, may be given in the original papers. The data are valid at or near 25 °C.

A few systems, or groups of systems, of particular interest, viz. outer-sphere systems, the iron (III) system and the thallium(I) system, will be discussed separately. Perchlorate association to other metal ions will be discussed more briefly thereafter.

Evidence for perchlorate association has frequently been obtained indirectly in the course of other studies, often from considerations similar to those discussed in the previous section. Unfortunately, such evidence is more often than not reported only in passing, and the risk that valuable information may have escaped notice is evident.

More direct evidence for perchlorate association has been obtained with methods such as activity and conductance measurements, and spectroscopic methods. Some broad studies of this type deserve mention. Masterton and Berka[22] calculated stability constants of several systems from osmotic coefficient data. The conductivity of alkali perchlorates was studied by Bury et al.[23] and by D'Aprano[24]. Jones et al.[25] and Hester and Plane[26] studied Raman spectra of several perchlorates. Only for a few systems was any interaction observed. Klanberg et al.[27] studied several NMR spectra with similar results.

If the spectrum of any kind of metal ion is affected by perchlorate ion, or vice versa, it is usually taken as strong evidence for complex formation, although some workers have called for caution, at least in the case of optical spectra[28,29]. On the other hand, the absence of an interaction is of course no proof of the absence of complex formation, as perchlorate complexes are often of the outer-sphere type, likely to leave spectra unaffected. This has been pointed out, normally, but claims to the contrary are not infrequent. It should also be noted that when the spectra are affected, the complex formed is not necessarily exclusively inner-sphere. Closer examinations (of systems with ligands other than ClO_4^-) have shown that the complexes may be predominantly outer-sphere[30–32].

(i) Outer-sphere systems

Numerous workers have studied outer-sphere complexes formed between inert complex cations of the cobaltammine type, and a variety of ligands[6]. Typically, such complexes are weak, and as electrostatic attraction is an important factor in the bonding, the risk that ClO_4^- will compete as ligand is evident.

Direct evidence for ClO_4^- association has been obtained by a variety of methods. Archer et al.[33] inferred from solubility studies that $Co(NH_3)_5Cl^{2+}$ and ClO_4^- form a complex, the stability constant at zero ionic strength being $\approx 15M^{-1}$. Of the several other ligand ions investigated, nitrate, chloride, acetate and azide gave weaker association than perchlorate. Katayama and Tamamushi[34] studied the conductivity of several hexaamminecobalt salts, including perchlorate. The stability of the ClO_4^- complex was comparable to that of I^-, while the other ions investigated (NO_3^-, Cl^-, Br^-, SO_4^{2-}, $C_2O_4^{2-}$) show stronger association. The constants were estimated from the deviations from the Onsager limiting equation, a method not without objections[8,35]. The authors[34] also point out that their quantitative results should be regarded with caution. This view is strengthened by the comparison with other studies of the hexaamminecobalt iodide and bromide systems[16,17]. On the other hand, there cannot be any doubt about the qualitative conclusion, that ClO_4^- is associated to hexaamminecobalt to some degree.

Burnett[36] interpreted earlier conductance[37] and activity coefficient measurements (refs. 37–40) in terms of association. A significant perchlorate association to $Co(en)_3^{3+}$, $Co(pn)_3^{3+}$ $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5Cl^{2+}$ was inferred.

Direct evidence of perchlorate association with various complex cations of a more qualitative kind has been reported by Mazzei and Lederer[41] and by Yoneda et al.[42] from electrophoresis measurements.

Nyman and Plane[43] studied the absorption spectra of $Pt(en)_3^{4+}$ salts, including the perchlorate. Their interpretation is that the association between $Pt(en)_3^{4+}$ and ClO_4^- is negligible. This result may seem surprising, in view of the high charge of the cation, but is questionable also for other reasons. It is in part based on the fact that ClO_4^- does not affect the absorption of $Pt(en)_3^{4+}$, which, as admitted[43], does not preclude that a complex is nevertheless formed. Secondly, the authors studied $Pt(en)_3^{4+} - Cl^-$ complexes using the spectrophotometric L method[20], which is not reliable in a case like this, where higher complexes, ML_2 etc., are quite likely to be formed. Therefore[20], the constant estimated for, say, $Pt(en)_3Cl^{3+}$, is probably too low, and the absorption coefficient of the same species too high. As can readily be shown, this will result in a trend in the direction found[43], in the measurements in $Cl^- - ClO_4^-$ mixtures of constant ionic strength. This trend may well obscure an opposite trend caused by ClO_4^- association. Thus, this experiment is no proof of lack of association between $Pt(en)_3^{4+}$ and ClO_4^-.

It may be mentioned that ClO_4^- has no effect on the circular dichroism spectrum[44,45] of $Co(en)_3^{3+}$.

Evidence for perchlorate association of a more indirect kind has been produced by several workers. Typically, perchlorate association is put forward as a hypothesis to explain some apparent inadequacy in the measurements. The hypothesis is not always subjected to verifying (or disproving) tests. Larsson[4], in a study of *trans*-$(Co(en)_2(SCN)_2)^+ - SCN^-$ complexes found a discrepancy between measurements (solubility and distribution) in the presence and absence of perchlorate ions, which could be accounted for by assuming ClO_4^- complexes to be formed. An equation corresponding to eqn. (14) was derived. An experiment aimed at the direct proof of perchlorate association was inconclusive.

Mironov et al.[46-49] studied hexaamminecobalt halide complexes and similarly found a much lower β_1 value (chloride system) in 1 M perchlorate[46] than in chloride solutions of varying ionic strength[47]. Later[48], the difference was ascribed to perchlorate association. In further studies[49] on the same systems at lower ionic strengths (0.1 – 0.2M), concordant values of the halide stability constants recalculated to zero ionic strength were secured by postulating suitable degrees of perchlorate association. While the halide stability constants thus obtained compare well with those found by others[1,16,17], the degrees of perchlorate association implied seem unreasonably high, for reasons not immediately evident. All in all, however, the data[46-49] indicate some interaction between $Co(NH_3)_6^{3+}$ and ClO_4^-.

In a number of papers,[7,50,51] Heck has produced qualitative evidence for association between $Co(NH_3)_6^{3+}$ and ClO_4^-. It was thus shown that the solubility product of $Co(NH_3)_6(ClO_4)_3(s)$ increases[7], and the apparent stability constant of $Co(NH_3)_6I^{2+}$ decreases[50] when $[ClO_4^-]$ is increased at constant ionic strength. The light absorption of hexaamminecobalt bromide solutions is affected by perchlorate ions[51]. Heck also cited[50,51] certain low values[52,53,46] for the stability constant for $Co(NH_3)_6Cl^{2+}$ as evidence of perchlorate association. As pointed out elsewhere[20], the main reason why low values have been obtained is the choice of an unreliable method.

Secondly, Heck[7,50,51] also attempted to assess the degree of perchlorate association more quantitatively. As both perchlorate ($\beta_{1,0}$) and halide ($\beta_{0,1}$) constants are given, at different ionic strengths ($\leqslant 0.15\ M$), it seems rational to discuss the ratio, $\beta_{1,0}/\beta_{0,1}$. This ratio should be roughly independent of the ionic strength. In the first paper[7], $\beta_{1,0} \approx 22$ ($I = 0$) is given, i.e. $\beta_{1,0}/\beta_{0,1} \approx 0.37$. From the data on iodide solutions[50], the present author has estimated $\beta_{1,0}/\beta_{0,1} \approx 0.43$. The value preferred by Heck is, however, that estimated from light absorption measurements in hexaamminecobalt bromide solutions[51], $\beta_{1,0}/\beta_{0,1} \approx 1.0$. No obvious reason can be seen why this experiment should be preferred to the others. It must also be said that the numerous studies on the hexaamminecobalt halide systems[1,16,17] under conditions where eqn. (1) is valid, strongly support a value $\beta_{1,0}/\beta_{0,1} < 1$ (cf. eqn. (17,1) at high ionic strengths.

The studies just cited[7,50,51] are based on the assumption that activity coefficients are constant once the formal ionic strength is constant, even if one solution is composed largely of 1 : 1 salts and another of a 3 : 1 salt. It is doubtful if this assumption is true unless the ionic strength is very small (for a detailed discussion, see ref. 8).

When the $Co(en)_3^{3+} - I^-$ system was studied[5] by solubility measurements and the spectrophotometric M method, slightly different values of $\boldsymbol{\beta}_1$ were obtained, $1.42 \pm 0.05M^{-1}$ and $1.73 \pm 0.15M^{-1}$, respectively ($I = 1M$). The difference could be rationalized by assuming slight association between $Co(en)_3^{3+}$ and ClO_4^-. Then, the two methods employed would give constants according to eqns. (39) and (40), respectively. The values $\beta_{0,1} = 2.5$ and $\beta_{1,0} = 0.45$ fit the data[5]. The result should be regarded with caution, since the observed difference in $\boldsymbol{\beta}_1$ is small, and especially since the spectrophotometric method is sensitive to experimental errors. On the other hand, in view of the other evidence for association between cobaltammines and ClO_4^- presented in this section, the result appears to be quite reasonable.

In summarizing, a substantial number of data support the view that ClO_4^- forms complexes with cobaltammines and other inert complex cations. Reliable and precise stability constants are lacking, however. As it is highly desirable to be able to investigate outer-sphere systems in constant media, quantitative data on the perchlorate association, preferably measured at high as well as at low ionic strengths, are much needed.

(ii) Iron (III) system

The question of whether ClO_4^- forms a complex with Fe^{3+} was raised early; it has been the subject of lively debate over the years and, as will be seen, cannot as yet be considered as definitely settled. The question was discussed by Rabinowitch and Stockmayer[54], and by Olerup[55]; both groups assumed from various lines of evidence that the association was negligible. Olson and Simonson[56] studied the hydrolysis of iron (III) in sodium, barium or lanthanum perchlorate solutions. In one series of experiments the perchlorate concentration was constant, in another the ionic strength. A difference in the degree of hydrolysis was observed between the two series. The authors[56] give as alternative (qualitative) explanations, either perchlorate complex formation or a kinetic salt effect. As perchlorate had no effect on the spectrum of Fe^{3+}, the authors were inclined to prefer the latter explanation.

Contrary to the earlier investigators, Sutton[57] found that ClO_4^- influenced the spectrum of Fe^{3+} by extending the measurements to shorter wavelengths ($\geqslant$ 220 nm) and/or higher perchloric acid concentrations ($1 - 7M$). A value of ~ 0.5 was assigned to the constant at zero ionic strength.

Sykes[58] showed that the data of Olson and Simonson[56] are compatible with the formation of $Fe(ClO_4)^{2+}$, and also presented independent evidence. As the calculations were later revised (see below), no details will be given here.

From earlier measurements on the Fe^{2+}/Fe^{3+} electron-exchange reaction, Horne[59] estimated the stability constant of $Fe(ClO_4)^{2+}$ to $0 \leqslant \beta_1 \leqslant 6$, at the ionic strength $I = 0.55M$. As pointed out[59], the data of Sykes[58] also fall within these limits. The estimate[59] is, however, based on a number of assumptions not subject to experimental verification.

The formation of $Fe(ClO_4)^{2+}$ was doubted by Coll et al.[28]. From spectrophotometric measurements, the stability constant of $FeCl^{2+}$ was determined for various $HClO_4$ concentrations in the range 2.5 to $9M$. The stability constant greatly increased with increasing $[HClO_4]$ (increasing ionic strength). This would, however, be expected from the well-known increase in activity factors at high ionic strengths. The effect of $Fe^{3+} - ClO_4^-$ complex formation would take the opposite direction, as pointed out[28], but would be of a much more modest magnitude. It would therefore be swamped by the much larger medium effect. The observed effect is thus not relevant to the question of $Fe^{3+} - ClO_4^-$ complex formation. The medium effect can of course be largely explained by hydration changes[28].

The data of Olson and Simonson[56] were analyzed in more detail in terms of $Fe^{3+} - ClO_4^-$ association by Sykes[3]. The stability constant was estimated to be $6.7M^{-1}$ and $3.7M^{-1}$ at $I = 0.024$ and $I = 0.044$, respectively. These values were shown to be compatible with Bjerrum's theory, if it was assumed that Fe^{3+} and ClO_4^- are separated by *two* water molecules. Later, Richards and Sykes[60], in connexion with a study of the hydrolysis of iron(III), estimated a value of the perchlorate constant in the range $0 - 5.5M^{-1}$ at $I = 0.15$. The values extracted from Olson and Simonson's data are consistent with this, with due regard to the differences in ionic strength[60]. Both estimates[3,60] are based on the assumption that activity factors are constant at constant ionic strength, irrespective of whether the medium is sodium or barium perchlorate, for instance.

The effect of various perchlorate salts on the ultraviolet spectrum of iron(III) was studied by Zagorets and Bulgakova[61]. When perchloric acid was added they observed, like Sutton[57], an effect at high concentrations ($> 3M$), which, according to the authors[61], may be ascribed to complex formation. However, when $[ClO_4^-]$ was kept constant ($5M$), the effect on the iron(III) spectrum was strongly dependent on the cation ($1\,MH^+ + 2\,M\,Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+}$ or Be^{2+} or $4\,M\,Na^+$ or Li^+). The effect varied in a simple manner with the ionic radius of the cation[61].

An attempt to determine the stability constant of $Fe(ClO_4)^{2+}$ was made by Fordham[62]. However, a number of objections can be raised to his treatment of the data. In the first place, the spectrophotometric L method[20] was used. For example, the absorbance of Fe(III) was measured with changing $[Cl^-]$ at 340 nm. Olerup[55] showed that at ~ 360 nm, the value of β_1 obtained in this way was only about half the correct value. The discrepancy is caused by $FeCl_2^+$ formation[20,55] and is independent of $[Cl^-]$.

Secondly, Fordham[62] attempted to solve a system of equations that are not independent. Thus, if OH^-, Cl^- and ClO_4^- are denoted by A, B, and C respectively, the measured quantities are (cf. eqn. (39))

$$a = \frac{\beta_A - \beta_B}{1 + \beta_B I} \tag{42,a}$$

$$b = \frac{\beta_A - \beta_C}{1 + \beta_C I} \tag{42,b}$$

$$c = \frac{\beta_B - \beta_C}{1 + \beta_C I} \tag{42,c}$$

In practice $\beta_A \gg (\beta_B, \beta_C)$, and it was moreover preferred to measure $^*a = a \cdot K_w$ and $^*b = b \cdot K_w$, where K_w is the ionic product of water, but this is of no consequence to the following considerations. In addition, the quantity

$$d = \frac{\beta_B}{1 + \beta_C I} \tag{42,d}$$

was also measured, a small variation in the ionic strength being allowed. The necessary extrapolation (Fig. 2 of ref. 62) is, however, quite spectacular, and it must be merely coincidental that a positive value of **d** was obtained. The value of **d** was not used in the subsequent calculations[62]. The three equations used are not independent; it is readily shown that

$$c = (b/a - 1)/I \equiv (^*b/^*a - 1)/I \tag{43}$$

The values of β_A, β_B and β_C suggested[62] must be artefacts, due to the experimental errors. Indeed, two sets of constants (one with the $FeClO_4^{2+}$ constant $\beta_C = 0$, one with $\beta_C > 0$) were both found[62] to give a good fit with the experimental data.

To sum up, the stability constant values for $Fe(ClO_4)^{2+}$ suggested[3,57–60] are small, decidedly smaller than those of trivalent cobaltammine ions under comparable conditions. It is then inherently difficult to distinguish between complex formation and other effects [56,61,63]. Moreover, none of the studies in favour of complex formation is free from experimentally unverified assumptions. It must also be pointed out that the complex of a "third-sphere" structure suggested[3] cannot reasonably be responsible for the spectral effects reported[57,61] at high perchloric acid concentrations. It must be concluded that before the question of $Fe^{3+} - ClO_4^-$ association can be regarded as settled, more experimental work of high quality is required.

(iii) Thallium(I) system

As indicated by eqns. (16) and (17), negative apparent stability constants may result if perchlorate forms stronger complexes than does the ligand studied. The thallium(I) fluoride system appears to behave in this way. However, the effects seen are very small, and great caution must be exercised in interpretation of the data. We first consider the more direct evidence for (or against) association between thallium(I) and perchlorate ions.

From the conductivity of $TlClO_4$ solutions, Robinson and Davies[64] estimated the stability constant at zero ionic strength as $\sim 1.0\,M^{-1}$. Jones et al.[25] recorded Raman spectra of perchlorate solutions of several metals, including thallium(I). A large number of very faint lines, not visible in the spectra of alkali metal perchlorate solutions, for example, strongly indicated some inner-sphere interaction between Tl^+ and ClO_4^-. Masterton and Berka[22] estimated the stability constants of several complexes from literature data on osmotic coefficients. For $TlClO_4$, a value $\beta_1 \approx 1.6\,M^{-1}$ was reported. Zagorets and Bulgakova[65] studied the absorption spectrum of Tl^+ in the range 210 – 250 nm. When the perchloric acid concentration (0.5 – 6 M) was increased, the absorption decreased quite significantly. According to the interpretation given[65], the complex formed, $TlClO_4$, does not absorb at all in this wavelength range. The stability constant was estimated at the various perchloric acid concentrations. For zero ionic strength, extrapolation[65] gave $\beta_1 \approx 0.6\,M^{-1}$.

The agreement between the stability constants reported[22,64,65] must be regarded as good, considering the wide differences in experimental approach. Moreover, in particular the effects of $TlClO_4$ on Raman and absorption spectra[25,65] show quite convincingly that a complex is formed. The facts that ClO_4^- has no effect on the NMR spectrum[66] or the apparent molar volume[67] of Tl^I of course do not invalidate this conclusion.

The thallium(I) fluoride system in perchlorate medium was first studied by Nilsson[68]. The potential of a thallium amalgam electrode indicated an increase of $[Tl^+]$ with increasing fluoride concentration. As correctly remarked[68], changing activity coefficients and thallium perchlorate complex formation are possible causes of this effect. No speculation as to the contribution of each factor was made. For $Tl^+ - F^-$, however, $\beta_{0,1} = 0$ was suggested, somewhat arbitrarily. If medium effects are assumed to be negligible, $\boldsymbol{\beta}_1 \approx -0.20 \pm 0.02 M^{-1}$ at 1 M ionic strength can be estimated from Nilsson's data (cf. eqn. (17,1)).

Bond[69] studied the same system by the polarographic method (a type of central ion measurement). As a consequence of the previous work[68], the $Tl^+ - ClO_4^-$ system was studied, fluoride being regarded as a medium ion. At $I = 1\,M$, a value $\boldsymbol{\beta}_1 = 0.32 \pm 0.04\,M^{-1}$ was obtained (eqn. (17,1)). The author[69] pointed out that liquid junction and activity coefficient changes could, at least in part, be responsible for the observed effect. Bond and O'Donnell[69,70] also studied the $Tl^+ - F^-$ system by a ligand measurement method; the free fluoride concentration was determined with a fluoride membrane electrode. In perchlorate[69] as well as in nitrate[70] medium, the electrode potential was constant, within the limits of error, when $[Tl^+]$ was increased from 0 to 0.1 M. Thus, $\beta_1 = \beta_{0,1} = 0$ (eqn. (25)), within the limits of error. The latter were, however, rather wide, $\pm 0.4\ M^{-1}$. Moreover, contrary to the opinion expressed in one of the papers[69], liquid junction potential and activity coefficient changes may also be significant when 0.1 M Tl^+ is substituted for 0.1 M Na^+.

Since activity coefficient changes generally have different effects for different methods, the present author has studied[71] the $Tl^+ - F^-$ system in perchlorate medium using different method from those used earlier[68–70]. The ionic strength 0.5 M was chosen to enhance the difference in β_1; cf. eqn. (41). The solubility of $TlIO_3(s)$ was measured as a function of $[F^-]$. As this is a type of central ion measurement, a negative apparent stability constant for TlF was obtained, $\beta_1 = -0.27 \pm 0.03\ M^{-1}$. Furthermore, the system was studied with a ligand method consisting of measuring the solubility of $BaF_2(s)$ in solutions of varying $[F^-]$ and $[Tl^+]$. Up to $[Tl^+] = 0.1\ M$, the solubility was independent of $[Tl^+]$, which gives an apparent constant $\beta_1 = 0.00\ (\pm)\ 0.05\ M^{-1}$ (errors refer to a 99% confidence level). In combination (eqns. (39) and (40)), the values of β_1 give $\beta_{0,1} = 0.00\ (\pm)\ 0.06\ M^{-1}$ for the formation of TlF, and $\beta_{1,0} = 0.32 \pm 0.07\ M^{-1}$ for the formation of $TlClO_4$.

Although activity coefficient changes might play a significant role in any of the various studies discussed[68–71], the good agreement obtained, for central ion measurements [68,69,71] as well as for ligand measurements[69–71], rather suggests that medium effects are of minor importance. Thus, it seems safe to conclude that Tl^+ forms a stronger complex with ClO_4^- than with F^-.

(iv) Other systems

There seems to be agreement[23,24,72] that, among the alkali metals, perchlorate association with lithium and sodium is negligible, while association with the heavier ions is small but significant.

For Hg^I, potentiometric measurements by Hietanen and Sillén[73] strongly indicated the formation of a complex $Hg_2(ClO_4)^+$ stronger than the corresponding $Hg^{II} - ClO_4^-$ complex. Kinetic data [74] also indicated a $Hg^I - ClO_4^-$ association.

Association between Zn^{2+} and ClO_4^- has been proposed[75,76], but other data[77,78] indicate this association to be negligible. $Cd^{2+} - ClO_4^-$ association has also been suggested[76,79].

Among the trivalent lanthanides, cerium(III) in particular has been subject to speculation on perchlorate complex formation. Thus, Heidt and Berestecki[80], and Sutcliffe and Weber[81], inferred from spectral changes that $Ce(ClO_4)^{2+}$ was formed. Values of the stability constant were estimated. These studies were, however, criticized by Krumholz[29], on the grounds of inconsistencies in the models proposed[80,81]. The spectrum of Nd^{III} in perchlorate media was interpreted[29] in terms of association at high $[ClO_4^-]$ and medium effects at low $[ClO_4^-]$. A slight association between La^{3+} and ClO_4^- was assumed by Sykes[3].

Association of trivalent americium with perchlorate was inferred by Baisden et al.[82] from solvent extraction data.

Jones and Bjerrum[83] studied the kinetics of the formation of inner-sphere $Cr(H_2O)_5(ClO_4)^{2+}$ and found that the data could be explained if it was assumed that inner-sphere complex formation was preceded by complete formation of the outer-sphere complex $Cr(H_2O)_6(ClO_4)^{2+}$.

Rogers and Waind[84], from spectrophotometric data, found evidence for a complex of thallium(III) with perchlorate at high perchlorate concentration.

Reports of perchlorate association with tetravalent metal ions are quite scarce. Smith and Getz[85] found that the effect of ClO_4^- on the oxidizing properties of Ce^{IV} can be best explained by assuming a perchlorate complex to be formed. Weak association of perchlorate with U^{IV} and Po^{IV} has been claimed[86,87]. The suggested formation[88] of $Zr(ClO_4)_6^{2-}$ must be in error.

D. CONCLUSIONS

When equilibria are studied in constant perchlorate media, perchlorate association may cause an error that can, as shown in Section B, be in principle eliminated. In the view of the present author it is natural that it also should be eliminated, when possible. It must be said immediately, however, that for relatively few central ions has perchlorate association been proven beyond doubt to be of a magnitude that necessitates significant corrections under normal circumstances.

Generally, inert complex ions, or at least cobaltammine ions, form relatively strong perchlorate complexes. These are strong enough, both in an absolute sense and relative to complexes of other ligands, to make corrections necessary (cf. eqns. (39) and (40)). Labile aquated metal ions show, as far as can be judged from the data on hand, a perchlorate association that is relatively weak, and probably negligible for some metal ions. The effect on the denominators of eqns. (39) and (40) is then modest. If strong complexes of these metal ions are studied, perchlorate association is therefore of minor consequence. On the other hand, it should be emphasized that when markedly weak complexes are studied, the competing perchlorate complex, although weak as well, may be *relatively* significant, having an effect on the numerator of eqn. (39). This is illustrated by the studies on the thallium(I) fluoride system cited above (p.257).

It is evident that although the metal ions investigated form weak perchlorate complexes only, this is not necessarily true for all of the several metal ions for which reliable data are largely lacking. It may also be noted here that the data on hand indicate no simple relation between the charge (or charge density) of an ion and its affinity to the perchlorate ion.

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