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PROBLEMS CONCERNING THE DETERMINATION OF SMALL STABILITY CONSTANTS OF ANIONO COMPLEXES IN AQUEOUS SOLUTIONS

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CONTENTS

A. INTRODUCTION

In order to determine the stability constants in an equilibrium mixture with many species, such as a complex system where a metal ion successively forms complexes with ligand ions, one has to consider several possibilities. In dilute electrolytic solutions with several equilibrium constants, it is not easy or recommendable to apply electrolyte theory because of the approximate character of the Debye–Hückel law for the activity coefficients of ions in electrolyte solutions. It is, therefore, an obvious possibility to study complex formation under conditions where the activity coefficients are

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approximately constant so that the classical concentration mass action law can be applied.

B. THE CONSTANT SALT MEDIUM

That Guldberg and Waage's concentration mass action law is valid for ion equilibria in the presence of a strong electrolyte in a dominating concentration was shown by Brønsted [1] in 1919, and N. Bjerrum [2] had in reality used this principle several years before when determining the first hydrolysis constant of the hexaaquachromium(III) ion in 0.1 and 0.2 M KCl in order to diminish the variation in the estimated values for the constant. Bjerrum in his studies of metal ammine formation in 1931 [3] and in the following years [4] also used ammonium nitrate media both for having defined ammonium ion concentrations and for maintaining a constant salt medium. After the second world war the constant medium principle was generally accepted and used by many authors, as is apparent from the collections of stability constants [5].

C. THE IONIC STRENGTH PRINCIPLE

According to Arrhenius' idea of isohydric solutions [6], the classical degree of dissociation is unchanged when equimolar solutions of uni-univalent salts with a common ion are mixed. This principle was often used in the early days of the electrolyte theory, among others by Grossmann [7] who studied complex formation in the mercury(II) thiocyanate system, and, influenced by Bodländer, used mixtures of equimolar solutions of KNO_3 and KSCN in order to keep the "degree of dissociation" constant. In the beginning of the new era of electrolyte theory, after N. Bjerrum [8] had presented his theory of complete dissociation of strong electrolytes, Lewis and Randall [9], even before the Debye–Hückel theory (1923), empirically introduced the term ionic strength $I = 1/2\Sigma m_i z_i^2$ as the determining factor for the size of the activity coefficients of the ions in mixtures of electrolytes at not too high ion concentrations. In the same year, Brønsted [10] had noticed, from solubility studies with cobalt(III) ammine salts in S.M. Jørgensen's collections, that ions are uniformly influenced by ions of their own sign, contrary to ions of opposite sign (Brønsted's principle of specific interaction of ions).

D. HARNED'S RULE

This theory was carefully tested by Harned [11] as well as by Güntelberg [12] by EMF measurements of cells without diffusion potential. Both investigators measured the activity coefficient of hydrochloric acid in binary mixtures with alkali metal chlorides and were able to show that there was a linear dependence of log γ_{HCl} on the concentration of the components at constant ion molarity. The changes in log γ_{HCl} are dependent on the hydration of the other electrolyte and are, according to Harned, approximately proportional to the total electrolyte concentration. The change Δ is small in solutions with LiCl but considerable in solutions with KCl where log γ_{HCl} increases by as much as 0.30 when going from 5 M HCl to 5 M KCl [13].

A similar rule is to be expected for the variation of stability constants in mixed salt solutions. Ellilä [14] has confirmed that such a linear relationship exists for the dissociation exponent pK_{HAc} of acetic acid in mixtures of 1 : 1 salts as well as in mixtures of 1 : 2 salts. According to Ellilä the linear relationship is also valid for some mixtures of 1 : 1 electrolytes without a common ion, e.g. KBr–NaCl and NaCl–$LiNO_3$ mixtures. The changes are on the whole considerable. Thus pK_{HAc} was found to have the following values in 2.7 M solutions of the pure salts: $LiNO_3$ 4.55, NaCl 4.75, NaBr 4.87 and KBr 4.94. It can be estimated from these figures that even changes of the order of 10% in the salt medium give measurable effects.

E. ESTIMATION OF SMALL STABILITY CONSTANTS AT CONSTANT IONIC STRENGTH

(i) Suitable experimental methods

The potentiometric methods used so much to determine either the free metal ion concentration or the ligand ion concentration for ligands with basic properties by pH measurements have limited value in the case of weak complex formation. The study of weak aniono complexes necessitates a high and varying ligand ion concentration so that it is impossible to maintain a constant salt medium. Furthermore, the determination of the free ligand concentration is not very informative in a concentration range where $C_L \approx [L]$. Weak complex formation has been studied mainly by spectrophotometric methods but also by solubility and ion exchange methods often at a high ionic strength in mixtures with an inert electrolyte such as $NaClO_4$. Thus weak copper(II) chloride complex formation has been studied recently [15,16] in 5 M Na(Cl, ClO_4) solutions. It was therefore of some interest to estimate the systematic uncertainties in the stability constants obtained under these conditions. Such calculations have been made by Mønsted [17] in this laboratory.

(ii) Mønsted's uncertainty calculations

For simplicity, Mønsted considers only a system where, besides 1 : 1, only 1 : 2 complex formation occurs, and his starting point is the expression for the molar absorbance of the solution:

$$\epsilon = \alpha_0\epsilon_0 + \alpha_1\epsilon_1 + \alpha_2\epsilon_2$$

where α_0, α_1 and α_2 are the mole fractions of the species M, MA and MA_2, and ϵ_0, ϵ_1 and ϵ_2 the molar absorbances of these species at a specific wavelength.

Introducing the stability constants K_1 and $\beta_2 = K_1K_2$ in this expression, and if $C_M \ll C_L$, then

$$\epsilon = \frac{\epsilon_0 + \epsilon_1 K_1[\mathrm{L}] + \epsilon_2\beta_2[\mathrm{L}]^2}{1 + K_1[\mathrm{L}] + \beta_2[\mathrm{L}]^2}$$

Double differentiation of this expression, for $C_L = 0$, gives

$$\epsilon' = \frac{\mathrm{d}\epsilon}{\mathrm{d}[\mathrm{L}]} = K_1(\epsilon_1 - \epsilon_0)$$

$$\epsilon'' = \frac{\mathrm{d}^2\epsilon}{\mathrm{d}[\mathrm{L}]^2} = 2K_1^2(\epsilon_0 - \epsilon_1) + 2\beta_2(\epsilon_2 - \epsilon_0)$$

From these expressions it follows that

$$K_1 = -\frac{\epsilon''}{2\epsilon'}$$

when only 1 : 1 complex formation takes place. If, however, K_1 is determined neglecting the presence of a 1 : 2 complex, the experimentally determined constant K_1', for example obtained graphically by a Hildebrand [18] plot and with some approximation is given by

$$K_1' \approx \frac{\epsilon''}{2\epsilon'} = K_1 - K_2\frac{\epsilon_2 - \epsilon_0}{\epsilon_1 - \epsilon_0}$$

These approximate formulae were verified by interpretation of computer-generated data covering large metal and ligand concentration ranges [17]. The formula shows directly that the variation in K_1' determined at different wavelengths can provide evidence for higher complex formation. When using other experimental methods, such as, for example, ion exchange, one does not have the same possibility to vary an independent parameter. It is therefore a priori impossible to distinguish between a medium effect and the formation of higher complexes.

Assuming that only one complex ML is formed and that the medium dependence follows Harned's rule, the experimentally determined constant K_1' is given by the expression

$$K_1' \approx K_1^0 - \ln 10\Delta$$

where K_1^0 is the true association constant for $C_L = 0$. It will be noted from this expression that the systematic error is strongly dependent on the size of the constants. From the existing experimental data, it is reasonable to assume that $\Delta \lesssim |0.2|$ in the concentration range from 3 to 5 M. It is therefore evident that consecutive stability constants of the order of 0.01 l mol^{-1} (ln 10 = 2.3) are completely undefined. This is actually recognized in a recent paper by Mønsted et al. [19]. Constants of the order of 1 l mol^{-1} (free from experimental errors) are in reality only defined with an uncertainty of about 100%. However, constants as high as 100 l mol^{-1} have only an uncertainty of about 1%.

From the above discussion, it follows that the stability constants of very weak complexes cannot with any certainty be determined in mixtures of an inert electrolyte and the complex-forming electrolyte. For this reason, a treatment different from that involving a constant ionic strength was used by the author. Weak complex formation in solutions of $CuCl_2$ [20–23], $CoCl_2$ [24] and $FeCl_3$ [25] was studied at small concentrations of the complex-forming metal chloride in solutions with up to the highest possible concentrations of highly soluble chlorides such as HCl, LiCl or $CaCl_2$.

F. ESTIMATION OF SMALL STABILITY CONSTANTS IN THE PRESENCE OF ONLY THE COMPLEX-FORMING ELECTROLYTE

The chloro complexes studied were all coloured with characteristic spectra in the UV and visible and complex formation could in all cases be followed spectrophotometrically to nearly completion at high concentrations of HCl, LiCl or $CaCl_2$.

(i) Activity coefficients in strong salt solutions

The behaviour of strong electrolytes in concentrated solutions is simpler than in the Debye–Hückel range where the activity coefficients are strongly influenced by the interionic forces. The influence of the interionic forces is much smaller at higher ion concentrations. Log $\gamma^{(c)}$ passes through a minimum in solutions of concentration about 1 M and for concentrations higher than 3 M increases nearly linearly with the salt concentration. Thermodynamically, the activity of the non-hydrated ions is measured, and the increase in log γ is mainly due to the fact that the concentration of the non-hydrated ions increases with the decreasing water activity of the solution. This increase becomes more pronounced the higher the hydration of the salt [26].

This seems to be a general rule, and according to the latest isopiestic determinations [27,28] of the activity coefficients of HCl, LiCl and $CaCl_2$, the following formulae are valid, with good approximations for chloride concentrations in the range from 3 M up to 10 M or more.

$$\begin{aligned} \log \gamma^{(c)}_{HCl} &= -0.45 + 0.187[Cl^-] \\ \log \gamma^{(c)}_{LiCl} &= -0.53 + 0.190[Cl^-] \\ \log \gamma^{(c)}_{CaCl_2} &= -0.90 + 0.22[Cl^-] \end{aligned} \tag{1}$$

(ii) Assumptions about the activity coefficients

In a system with coordination number four, the consecutive stability constants K_1, K_2, K_3 and K_4 for the complexes are defined by the following expressions:

$$\begin{aligned} \frac{[ML]}{[M][L]} &= K_1 \frac{f_M f_L}{f_{ML}} \qquad \frac{[ML_2]}{[ML][L]} = K_2 \frac{f_{ML} f_L}{f_{ML_2}} \\ \frac{[ML_3]}{[ML_2][L]} &= K_3 \frac{f_{ML_2} f_L}{f_{ML_3}} \qquad \frac{[ML_4]}{[ML_3][L]} = K_4 \frac{f_{ML_3} f_L}{f_{ML_4}} \end{aligned} \tag{2}$$

where M is the metal ion, L the ligand anion and f_X the activity coefficient of the molecule or ion X. This looks a priori rather complicated, and in order to describe the system by a single mean activity coefficient F, defined as

$$\log F = A + B[L] \tag{3}$$

where A and B are constants, it is necessary to assume that the four activity coefficient expressions are not very different, so that

$$F \approx \frac{f_M f_L}{f_{ML}} \approx \frac{f_{ML} f_L}{f_{ML_2}} \approx \frac{f_{ML_2} f_L}{f_{ML_3}} \approx \frac{f_{ML_3} f_L}{f_{ML_4}} \tag{4}$$

This approximation corresponds to the assumption that, for example, $f_{CuCl_n^{2-n}}$ changes smoothly from $f_{Cu^{2+}}$ to $f_{CuCl_4^{2-}}$ and this is quite reasonable in the case of concentrated solutions for which the chemical similarity between the ions, rather than their charges, determines the activity coefficients. The determining activity coefficient F can be estimated from the measurements themselves in cases where a determination of the concentrations of at least one of the complexes can be made over a large ligand concentration interval. If this is not possible, the mass action law for the *n*th consecutive stability constant, in the lack of a better approximation, can be used in the simplified form:

$$K_n = \frac{[\mathrm{ML}_n]}{[\mathrm{ML}_{n-1}][\mathrm{L}]\gamma_{\pm}^{(c)}} \tag{5}$$

where $\gamma_{\pm}^{(c)}$ is the mean activity coefficient of the complex-forming electrolyte and $a_{\mathrm{L}} = [\mathrm{L}]\gamma_{\pm}^{(c)}$ the effective ligand activity in the terminology of Marcus [29].

G. THE COPPER(II) CHLORIDE SYSTEM

Weak complex formation in the copper(II) chloride system has been studied by many authors with rather different results (cf. Table 1 in ref. 21). Most investigators give only values for the first or the first two stability constants. Kahn and Schwing-Weill [15] and Ramette and Fan [16] estimate all four stability constants at constant ionic strength in 5 M Na(Cl, ClO_4), but their values for the third and fourth constant are too small to be defined according to Mønsted's calculations. However, their values for K_1 and K_2 are of the right order of magnitude [23]. Bjerrum [20] has estimated the four stability constants by assuming that the tetrachloro complex is the only complex which absorbs in the blue wavelength range. This appears indirectly from the fact that the molar absorbance at 436 nm, according to the literature [30,31], increases with nearly the fourth power of the chloride concentration for small values of $\bar{n}$. On the basis of this fact and with the assumption made in eqns. (3) and (4) about the activity coefficients, the following relationship was derived [20] for chloride concentrations higher than 3 M:

$$\frac{\mathrm{d}\log \epsilon_{436}}{\mathrm{d}\log[\mathrm{Cl}^-]} = \left(\frac{0.4343}{[\mathrm{Cl}^-]} + B\right)(4-\bar{n}) \tag{6}$$

In eqn. (6), $\bar{n}$ is the average ligand number, $[\mathrm{Cl}^-] \approx C_{\mathrm{Cl}^-}$ is the free ligand concentration and B the constant in the activity expression in eqn. (3). Applying eqn. (6) to data [20] for log ϵ_{436} as a function of $[\mathrm{Cl}^-]$, values for B and $\bar{n}$ were calculated for several highly soluble chlorides. B was estimated [20] to have the following values: HCl, 0.20; LiCl, 0.23; $MgCl_2$, 0.18; $CaCl_2$, 0.21. The value for the constant A, which disappears by differentiation of expression (3), was left open but in later papers [21–23] was taken to be -0.5 with reference to the expressions (1) for log $\gamma_{\mathrm{HCl}}^{(c)}$ and log $\gamma_{\mathrm{LiCl}}^{(c)}$. The newest value [27] for A in the expression for $\gamma_{\mathrm{CaCl}_2}^{(c)}$ is -0.9; but from values

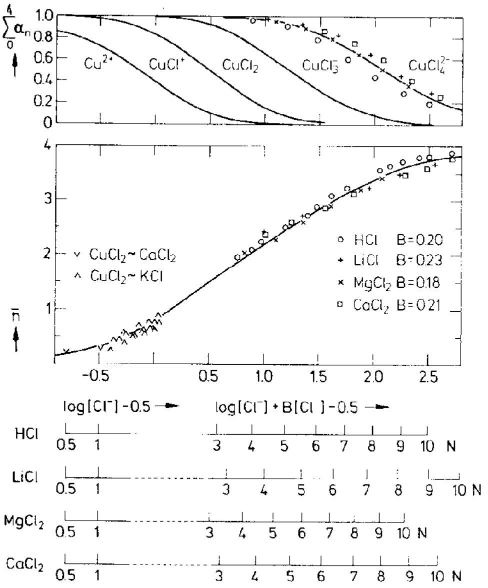

Fig. 1. Survey of the results obtained in the copper(II) chloride system. The main graph shows the formation function $\bar{n}$ as a function of $-\log a_{\text{Cl}^-}$, i.e. $\log[\text{Cl}^-]-0.5$ for 0.5 M $\leq[\text{Cl}^-]\leq 2$ M, and $\log[\text{Cl}^-]-0.5+B[\text{Cl}^-]$ for $[\text{Cl}^-]>3$ M. The upper part of the figure, with the sum of fractions α_n plotted vs. the same abscissa, shows the distribution of the copper on the four chloro complexes. Finally, a number of concentration scales corresponding to each of the chlorides used are plotted below.

in the Landolt–Börnstein Tables the value was earlier [20] estimated to be -0.55.

For chloride concentrations between 0.5 and 2 M the activity coefficients have their minimum values ($\log \gamma^{(c)} \approx -0.4$). The classical mass action law is approximately valid in this concentration range and the rather small values for $\bar{n}$ were estimated by means of the principle of corresponding solutions [32] by use of data for $CuCl_2$ in KCl [30] and $CaCl_2$ [33] solutions.

The stability constants were calculated by analysis of the formation curve [4] with the estimated values for $\bar{n}$ plotted vs. $\log a_{\text{Cl}} \approx \log[\text{Cl}^-]+B[\text{Cl}^-]-0.5$. The following consecutive activity constants were obtained: $K_1 \approx 1$ l mol^{-1}, $K_2 = 0.4$ l mol^{-1}, $K_3 = 0.06$ l mol^{-1} and $K_4 = 0.01$ l mol^{-1}, and a survey of the results calculated using these constants for all the used chloride salts is shown in Fig. 1.

The assumption that the absorption of $CuCl_4^{2-}$ alone accounts for the light absorption at 436 nm was confirmed in a recent paper [23] by analysis of the isosbestic mixture of $CuCl_3^-$ and $CuCl_4^{2-}$ in hydrochloric acid solutions between 8 and 12 M; the value for K_4 was confirmed to be 0.010 l mol^{-1}. The stability constants in the same paper [23] were used to calculate the absorption spectra of the four copper(II) chloro complexes in UV, visible and near-IR.

II. THE COBALT(II) CHLORIDE SYSTEM

Strongly coloured cobalt(II) chloride solutions have been the subject of numerous studies, and it is now generally recognized that the red octahedral hexaaquacobalt(II) ion in chloride solutions is more or less converted into the blue tetrahedral tetrachloro complex [34–36]. The transformation to the tetrachloro complex is complete in 11 M HCl and in concentrated solutions of LiCl and $CaCl_2$. Bjerrum et al. [24] have shown that the tetrachloro complex alone is responsible for the five absorption bands between 600 and 700 nm for chloride concentrations higher than 5 M. The mole fraction of the tetrachloro complex can therefore be given by the expression $\alpha_4 = \epsilon/\epsilon_4$, which is obeyed well in the wavelength range considered for $\alpha_4 \gtrsim 0.05$.

The stability constants were calculated by use of eqn. (7):

$$\alpha_4 = \beta_4 a_{\mathrm{Cl}^-}{}^4 / \sum_0^4 \beta_n a_{\mathrm{Cl}^-}{}^n \tag{7}$$

where $\beta_n = K_1 K_2 \ldots K_n$ and the chloride activity is defined by $a_{\mathrm{Cl}^-} = [\mathrm{Cl}^-] \times 10^{B[\mathrm{Cl}^-]-0.5}$. Most of the determinations of α_4 were made in LiCl solutions, and these measurements were used in the calculation. Applying preliminary estimated stability constants as starting values, eqn. (7) was minimized as a function of the four stability constants:

$$\frac{\left[\alpha_4(\mathrm{calc})_i - \alpha_4(\mathrm{obs})_i\right]^2}{\sigma_i^2}$$

where σ_i are the tentatively assumed uncertainties in the α_4 values. The following values for the consecutive stabilities were obtained with $B = 0.170 \pm 0.005$: $\log K_1 = -1.05 \pm 0.38$, $\log K_2 = -2.69 \pm 0.90$, $\log K_3 = -1.54 \pm 0.89$, $\log K_4 = -1.34 \pm 0.13$ and $\log \beta_4 = -6.62 \pm 0.24$. In Fig. 2 a graphical picture of the distribution of the cobalt(II) chloro complexes is presented and shows the very small range of existence of the dichloro and trichloro complexes.

Of the many investigators of the cobalt(II) chloride system only Zeltmann et al. [35] have given results which are suitable for comparison with those of Bjerrum et al. [24]. Their values for α_4 in hydrochloric acid solutions obtained from NMR measurements with oxygen-17 and chlorine-35 are also shown in Fig. 2.

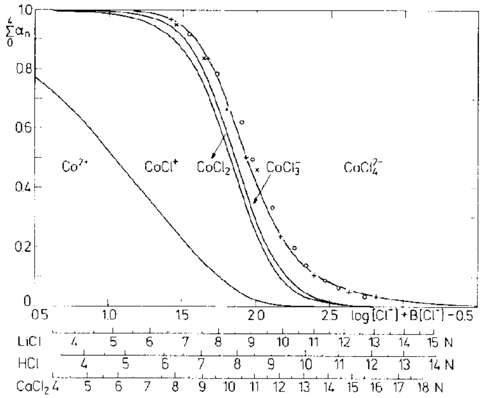

Fig. 2. Survey of the results obtained in the cobalt(II) chloride system. Plots of the fractions α_n of the various complexes $CoCl_n{}^{2-n}$ vs. the logarithm of the chloride ion activity function, $a_{Cl^-} = [Cl^-] \times 10^{B[Cl^-]-0.5}$. The full curves show graphically the distribution of the complexes calculated using the stability constants valid for LiCl solutions with the parameter $B = 0.170$. The experimental values shown for α_n(HCl (+); $CaCl_2$ (×)) are plotted vs. log a_{Cl^-} calculated using the values for B (HCl, 0.185; $CaCl_2$, 0.132) which give the best fit to the full curve for LiCl. Below the activity scale are given scales for the molar chloride concentrations which correspond to the stated values for the B parameter. For comparison purposes, related values for α_4 and C_{HCl} from the paper by Zeltmann et al. [35] (converted from molal to molar concentrations) are indicated by open circles (○) in the figure.

Skibsted and Bjerrum [37] have also studied cobalt(II) chloro complex formation in 10 M H(Cl, ClO_4). Owing to the low water activity in 10 M $HClO_4$, which is about 4% of that in pure water, the stability constants are much larger than in dilute aqueous solutions. For the concentration stability constants in 10 M H(Cl, ClO_4) it was found that $K_1 = 10^{1.34}$ l mol^{-1} and $\beta_4 = 10^{2.57}$ l^4 mol^{-4} with negligibly small ranges of existence for the dichloro and trichloro complexes. Comparing the stability constants in 10 M $HClO_4$ with those found in dilute aqueous solutions, it is calculated, using the β_4 values in the two media, $(10^{2.57}/10^{-6.62})^{1/4} = 10^{2.30}$, that the chloride ion activity is about 200 times larger in 10 M $HClO_4$ than in the aqueous medium, and it is satisfying that a similar estimate using the values for K_1 $(10^{1.34}/10^{-1.05} = 10^{2.39})$ leads to a value of the same order of magnitude.

I. THE IRON(III) CHLORIDE SYSTEM

Stability constants for the iron(III) chloride system have been studied by several authors. Of these, Rabinowitch and Stockmayer [38] have determined, from spectrophotometrical measurements, values for K_1, K_2 and K_3 in 1 M H(Cl, ClO_4). The first two of these constants are sufficiently large to be determined using the constant ionic strength principle, and by applying modern electrolyte theory, they estimate the activity constants at zero ionic strength to be $K_1 = 30$ l mol^{-1} and $K_2 = 4.5$ l mol^{-1}. Gamlen and Jordan [39] have determined K_4 spectrophotometrically by analysing isosbestic solutions in the range of high hydrochloric acid concentrations where only trichloro and tetrachloro complexes are present. They used the mass action law in the simplified form (eqn. (5)) and estimated K_4 to be 0.0105 l mol^{-1}. Bjerrum and Lukes [25] have repeated these measurements and found K_4 to be 0.0078 in HCl and 0.0068 in LiCl solutions. For the third consecutive constant, Bjerrum and Lukes [25] calculate the value of K_3 to be ca. 0.15 l mol^{-1}.

(i) Calculation of partition coefficients

Several authors [40,41] have analysed ether solutions of iron(III) extracted from hydrochloric acid solutions and found that the iron(III) is extracted as $HFeCl_4$, probably present as the ion pair $H_3O^+,FeCl_4^-$. In order to utilize the stability constants, Bjerrum and Lukes [25] have measured the partition coefficients

$$K_D = \frac{C_{Fe(III)}^{(org.)}}{C_{Fe(III)}^{(aq.)}}$$

for the extraction of $HFeCl_4$ with octan-2-ol and dibutylether from weakly acidic ($C_{HCl} = 0.10$ M) LiCl solutions and found that K_D obeys the expression

$$K_D = S\alpha_4 a_{LiCl} 10^{k_s C_{LiCl}}$$

where α_4 is the mole fraction of the tetrachloroferrate(III) in LiCl solutions, $a_{LiCl} = \gamma_{LiCl}^{(c)} C_{LiCl}$, k_s a salting-out coefficient and S a solubility constant. Figure 3 gives a survey of the results. The measured values for K_D are plotted vs. C_{LiCl}, and the figure shows good agreement between the experimental and calculated K_D values for the two organic liquids. It is also noteworthy that the estimated values for the salting-out coefficients, $k_s = 0.6$ for octan-2-ol and $k_s = 0.2$ for dibutylether, have the right order of magnitude [42]. A survey of the estimated spectra of the four iron(III) complexes is given in Fig. 4. The figure shows that the spectra of $HFeCl_4$ in octanol and dibutylether are rather similar to that of tetrachloroferrate(III) in hydrochloric acid solutions. Furthermore, it will be noticed that the spectrum of the tetrachloro complex is strongly perturbed in concentrated lithium and calcium chloride solutions. The estimated spectrum of the trichloro complex in aqueous hydrochloric acid looks rather anomalous compared with those

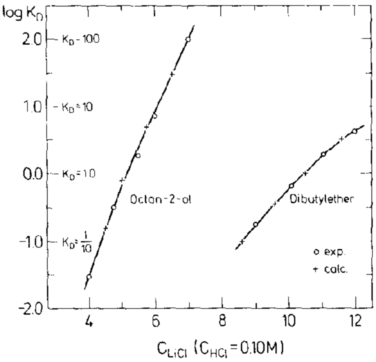

Fig. 3. The partition coefficients for extractions of iron(III) from weakly acidic LiCl solutions with octan-2-ol and dibutylether as a function of C_{LiCl}. The curves quantitatively follow the expressions

$$K_D(\text{oct.}) = 10^{-3.16}\alpha_4 a_{LiCl} 10^{0.6C_{LiCl}}$$

$$K_D(\text{dibu}) = 10^{-4.42}\alpha_4 a_{LiCl} 10^{0.2C_{LiCl}}$$

The salting-out coefficients, $k_s = 0.6$ for octanol and 0.2 for dibutylether, have the correct order of magnitude [42].

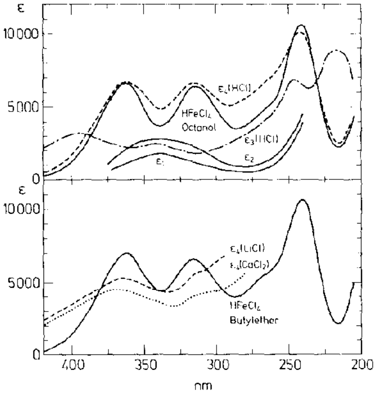

Fig. 4. Upper part: ϵ,λ-spectrum of tetrachloroiron(III) acid extracted with octan-2-ol from 0.10 M HCl, 7.00 M LiCl with $C_{Fe(III)} = 1.95 \times 10^{-3}$ M. The two broken curves are those of the tetrachloroferrate(III) ion and of the trichloroferrate(III) in strong hydrochloric acid. The full curves for ϵ_1 and ϵ_2 are estimated spectra for the monochloroiron(III) and dichloroiron(III) complexes in aqueous solution. Lower part: ϵ,λ-spectrum of tetrachloroiron(III) acid extracted with dibutylether from 0.10 M HCl, 12.0 M LiCl. The broken curve is the spectrum of the tetrachloroferrate(III) ion in strong LiCl and the dotted curve is that in strong CaCl$_2$ solutions.

of the aquachloro complexes of $FeCl^{2+}$ and $FeCl_2^+$ and to that of the anhydrous tetrachloro complex [43].

J. GENERAL REMARKS

The aquachloro complexes studied are well-defined coordination compounds and the small stability constants found for their chloro complex formation are a consequence of the low tendency of the aqua metal ions to exchange their water molecules for chloride ions in aqueous solution. As shown in this paper, it is possible, with reasonable certainty, to determine such small stability constants by following complex formation in hydrochloric acid solutions as well as in easily soluble chloride salts to the highest possible concentrations. In solutions with low water activity, as in the cobalt(II) chloride system in 10 M $HClO_4$ [37] or in solvents with a lesser tendency to solvate than water, such as acetonitrile [44] or acetic acid [45], the stability constants for copper(II) and cobalt(II) chloride complex formation have such high values that they can be determined according to the usual practice in a nearly constant salt medium.

The small ranges of existence of the intermediate complexes in the cobalt(II) chloride system are usually explained as being caused by the changes in configuration during complex formation from octahedral in the aqua ion to tetrahedral in the tetrachloro complex. But why have not the same changes in configuration in the iron(III) system [43] a similar influence on the ranges of existence of the intermediate complexes? However, the peculiar spectrum of the trichloro complex in Fig. 4 gives some evidence that this complex is present as a pentacoordinate transition form between the octahedral monochloroaqua and dichloroaqua complexes and the anhydrous tetrachloro complex. The copper(II) system, in which a hexaaqua ion with a tendency to square-planar configuration [46] is converted to a quasi-tetrahedral tetrachloro complex, has a rather normal distribution of the complexes. Contrary to the ligand-field bands studied in the cobalt(II) system, the UV spectra in the copper(II) and iron(III) systems are electron transfer bands and as such subject to a considerable perturbation of their bands as shown in Fig. 4 for LiCl and especially $CaCl_2$ solutions. However, this perturbation does not hinder their use in obtaining reasonable values for the stability constants.

K. CONCLUSIONS

The limitations inherent in the constant ionic medium principle were discussed with respect to the determination of weak stability constants for metal–anion complexes. It follows from Harned's rule that it is irrational and erroneous, as many authors believe, to determine very small stability constants of the order 1 l mol^{-1} or less at constant ionic strength in a mixed solvent of an inert electrolyte and the complex-forming electrolyte. More trustworthy results are obtained by determining the stability constants at small metal ion concentrations in the presence of only a single highly soluble salt of the complex-forming anion up to the highest possible concentrations.

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