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Experimental Determination of the Complexity Sum in Investigating Metal Ion Complex Formation

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From measurement of the pH, it is possible to calculate the free-ligand concentration in the study of metal ion complexes, without any assumption about the model, by using an extension of the Hedström–McKay relation as has been presented by Osterberg and others. In this study a similar technique is described, which allows the calculation of the complexity sum, i.e., the total concentration of the metal ion complexes, and the free-ligand concentration from experimental pH and pM values.

Introduction

The complexity sum S, introduced by Sillén,[1] can in its most general form be represented by eq 1. M, L, and H denote

$$S = \sum_i [\mathrm{M}_{p_i}\mathrm{L}_{q_i}\mathrm{H}_{r_i}] \qquad (1)$$

the metal ion, the ligand, and the hydrogen ion, respectively. The summation in eq 1 is over all complexes which are present in the solution. p_i and q_i can be any positive integer different from zero, and r_i can be any integer, including zero (a negative value of r_i means a hydroxide). S can be useful in the analysis of experimental data, describing metal ion complex equilibria, especially in determining the composition of the formed complexes, a main problem when polymeric, protonated, or hydroxo complexes are present. $\bar{p}$, the mean amount of complexed metal ion, $\bar{q}$, the mean amount of complexed ligand, and $\bar{r}$, the mean amount of complexed hydrogen ion, can be calculated from S, when the values of [M], [L], and [H] are known, by using the eq 2–4. Charges are omitted for the sake

$$\bar{p} = [C_\mathrm{M} - [\mathrm{M}] - \sum_j p_j \beta_{p_j 0 r_j} [\mathrm{M}]^{p_j} [\mathrm{H}]^{r_j}]/S \qquad (2)$$

$$\bar{q} = [C_\mathrm{L} - [\mathrm{L}] - \sum_k q_k \beta_{0 q_k r_k} [\mathrm{L}]^{q_k} [\mathrm{H}]^{r_k}]/S \qquad (3)$$

$$\bar{r} = [C_\mathrm{H} - [\mathrm{H}] + [\mathrm{OH}] - \sum_j r_j \beta_{p_j 0 r_j} [\mathrm{M}]^{p_j} [\mathrm{H}]^{r_j} - \sum_k r_k \beta_{0 q_k r_k} [\mathrm{L}]^{q_k} [\mathrm{H}]^{r_k}]/S \qquad (4)$$

of simplicity. $\bar{p}$, $\bar{q}$, and $\bar{r}$ have also been introduced by Sillén.[1] C_M, C_L, and C_H are the total concentration of metal ion, ligand, and titrable hydrogen ion, respectively. β_{pqr} is defined by eq 5. The $\beta_{p_j 0 r_j}$'s are the stability constants which describe the

$$\beta_{pqr} = [\mathrm{M}_p\mathrm{L}_q\mathrm{H}_r]/[\mathrm{M}]^p[\mathrm{L}]^q[\mathrm{H}]^r \qquad (5)$$

hydrolysis of the metal ion, and the $\beta_{0 q_k r_k}$'s are those stability constants which describe the acid–base equilibria of the ligand.

In this paper it will be shown that S can be calculated from pH measurements in a way analogous to the methods published by Osterberg,[2] Sarkar and Kruck,[3] and Avdeef and Raymond[4] for the calculation of the concentration of free ligand and free metal ion by the use of pH measurements alone, no assumptions being needed about the type of the complexes. Furthermore it will be shown that, when the values for pH and pM are known, the free-ligand concentration can also be calculated without any assumption about the formed complexes.

Gibbs and Gibbs–Duhem–Margules Equations and Metal Ion Complex Equilibria

As discussed by Gokcen[5] either the equation for the change of the Gibbs free energy or the Gibbs–Duhem–Margules equation can be used to calculate the partial molar properties of a multicomponent system provided that experimental data on the partial molar properties of one component is available. For this purpose two methods can be used. Darken[6] obtained the desired property by an integration of the Gibbs–Duhem–Margules equation followed by differentiation. Wagner,[7] McKay,[8] and Schumann[9] reversed the operations and obtained the desired molar property by integrating a cross-differentiation relation. Using this principle, McKay[10] reported a method for calculating [M] from measurements of [L] for a mononuclear system. It was the first time that a relation of that kind was published. A similar equation was found by Hedström[11] in a completely different way. Lefebvre[12] gave for the first time a series of relationships applicable to general systems, including a clear statement of the integration and differentiation conditions, but with unusual symbols, as has been remarked by Sillén,[1] and a rather unconvincing derivation. He followed the method proposed by Darken.[6] A method for determining the number of solute particles was given earlier by Byé.[13] One of the present authors has also given some relations.[14–16]

Most of the systems containing metal ion complexes can be considered as quaternary systems, composed of m mol of metal ion, l mol of ligand, h mol of hydrogen ion, and w mol of water. The change of the Gibbs free energy at constant temperature and pressure is given by eq 6, and the Gibbs–Duhem–Margules

$$\mathrm{d}G = \mu_\mathrm{M}\mathrm{d}m + \mu_\mathrm{L}\mathrm{d}l + \mu_\mathrm{H}\mathrm{d}h + \mu_\mathrm{w}\mathrm{d}w \qquad (6)$$

relation can be expressed as eq 7. In eq 6 and 7 μ_X denotes

$$m\mathrm{d}\mu_\mathrm{M} + l\mathrm{d}\mu_\mathrm{L} + h\mathrm{d}\mu_\mathrm{H} + w\mathrm{d}\mu_\mathrm{w} = 0 \qquad (7)$$

the chemical potential of the component X. The derivation of eq 6 and 7 is described in a condensed form in the Appendix.

Metal ion complexes in aqueous solution are usually studied under such conditions that the activity coefficients are approximately constant; therefore, eq 8 can be written for each

$$\mathrm{d}\mu_\mathrm{X} = 2.303RT\ \mathrm{d}\log[\mathrm{X}] \qquad (8)$$

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solute. For the solvent, eq 9 holds at a constant value for the

$$d\mu_w = RT \, d \ln x_w \tag{9}$$

activity coefficient. The mole fraction of water, x_w, can be expressed as eq 10, where n_w is the actual number of moles

$$x_w = \frac{n_w}{n_w + \sum_i n_i} = \frac{1}{1 + \sum_i n_i/n_w} \tag{10}$$

of water and $\sum_i n_i$ is the total number of moles of solutes. Since for a dilute solution $\sum_i n_i/n_w \ll 1$, eq 10 can be written as eq 11. The volume of a dilute solution is directly proportional

$$d\mu_w = RT d(\sum_i n_i/n_w) \tag{11}$$

to the amount of solvent, and, if the difference between n_w and w is negligibly small, then

$$n_w = w = kV \tag{12}$$

where k is a proportionality factor. With eq 6–12 a number of equations can be derived. For example, cross-differentiation of (6) yields $[\partial \log [L]/\partial h]_{m,l,w} = [\partial \log [H]/\partial l]_{m,h,w}$. Holding w constant is keeping V constant, and by putting $V = 1$ dm^3, this equation can be transformed into eq 13. As has been

$$\left[\frac{\partial \log [L]}{\partial C_H}\right]_{C_M,C_L} = \left[\frac{\partial \log [H]}{\partial C_L}\right]_{C_M,C_H} \tag{13}$$

demonstrated by Avdeef and Raymond,[4] the Osterberg equation can be derived from (13) by using a Jacobian transformation.

The analogous equation to the Osterberg equation can be obtained by using the method of Darken.[6] For this purpose eq 7 is, after some transformations, integrated from μ_H' to μ_H at constant values of m, l, and w (eq 14). Equation 14 is then

$$\left[\int_{\mu_H'}^{\mu_H} h \, d\mu_H\right]_{m,l,w} = -m(\mu_M - \mu_M') - l(\mu_L - \mu_L') - w(\mu_w - \mu_w') \tag{14}$$

differentiated for l at constant values of m, [H], and w. This gives, taking into account the Gibbs–Duhem–Margules equation at constant [H], eq 15. With the use of preceding

$$\mu_L - \mu_L' = -\left(\frac{\partial}{\partial l}\left[\int_{\mu_H'}^{\mu_H} h \, d\mu_H\right]_{m,l,w}\right)_{m,[H],w} \tag{15}$$

remarks, eq 15 may be written as eq 16. This equation differs

$$\log \frac{[L]}{[L]'} = -\left(\frac{\partial}{\partial C_L}\left[\int_{\log [H]}^{\log [H]'} C_H \, d \log [H]\right]_{C_M,C_L}\right)_{C_M,[H]} \tag{16}$$

from the Osterberg equation in the reversion of the operations. Sarkar and Kruck[3] have given a somewhat similar treatment, but the integration and differentiation conditions are not clearly specified.

Determination of the Complexity Sum

When metal ion complex equilibria are described, mostly three independent variables are used: C_M, C_L, and C_H. However from eq 6, 7, and 12 it follows that four independent variables can be considered: m, l, h, and V. Up to now V was held constant. It will be shown that, by varying V in a conditional way, it is possible to determine C, the total concentration of the solutes. From eq 11 and 12 it follows that

$$d\mu_w = RT \, d\frac{C}{k} \tag{17}$$

Since dG is a total differential, eq 18 can be obtained from

$$\left(\frac{\partial \mu_w}{\partial h}\right)_{m,l,w} = \left(\frac{\partial \mu_H}{\partial w}\right)_{m,l,h} \tag{18}$$

eq 6. With eq 9, 11, and 12, eq 18 can also be written as eq 19. Integration of eq 19 gives eq 20. Equation 20 can be

$$\left(\frac{\partial C}{\partial h}\right)_{m,l,V} = -2.303\left(\frac{\partial \log [H]}{\partial V}\right)_{m,l,h} \tag{19}$$

$$C - C_0 = -2.303\left[\int_{h_0}^{h}\left(\frac{\partial \log [H]}{\partial V}\right)_{m,l,h} dh\right]_{m,l,V} \tag{20}$$

considered as an extension of the equation given by Byé[13] for a binary system. This equation is in fact equivalent with the method of Lefebvre[12] as will be shown later.

From $C - C_0$ the value for S, the complexity sum, can be calculated on the condition that [M], [L], [H], and C_0 are known. [H] is determined experimentally. [M] and [L] can be derived from experimental data by using, for example, the Osterberg equation. In most cases [M] can also be determined experimentally, and C_0 can be calculated from mass-balance equations provided that the value of [H] is sufficiently high to prevent complex formation. [L] can also be obtained from the experimental data, used for the calculation of $C - C_0$ by means of eq 20, on the condition that [M] can be determined experimentally. Consider therefore the Gibbs–Duhem–Margules equation (7) transformed by eq 8, 11, and 12:

$$C_M \, d \ln [M] + C_L \, d \ln [L] + C_H \, d \ln [H] - dC = 0 \tag{21}$$

Note that eq 21 is equivalent with Sillén's[1] equation (17). Integration of eq 21 at constant values for C_L and C_M yields eq 22. The third term, the integral, can be evaluated by using

$$C_M \ln \frac{[M]}{[M]_0} + C_L \ln \frac{[L]}{[L]_0} + \int_{C_{H_0}}^{C_H} C_H \, d \ln [H] - (C - C_0) = 0 \tag{22}$$

the same experimental data as used for the calculation of $C - C_0$ from eq 20. The possibility of the determination of $C - C_0$, provided [L] is known, as an alternative for the proposed method will be discussed later in this paper. Lefebvre[12] found eq 23 which is analogous to eq 20 and which can be considered as an extension of Byé's[13] formula.

$$C - C_0 = \left(\frac{\partial}{\partial V}\left[\int_{h_0}^{h} \log [H] \, dh\right]_{m,l,V}\right)_{m,l,h} \tag{23}$$

Equations 4 and 7 of Levebvre[12] have been transformed in our notations; furthermore, h_0 can take on any value, in contrast with the original formulations. Equations 20 and 23 are theoretically equivalent.

Since in many cases [M] can also be determined experimentally, it can be useful to derive equations analogous to those given before, by starting from log [M] instead of log [H].

Validity of the Method

For evaluation of eq 20 the following procedure is proposed. A solution containing m mol of metal ion, l mol of ligand, h mol of titrable protons, and w mol of solvent is diluted with pure solvent. After addition of each portion of the solvent, the pH is measured. In reality the solvent will not be pure water, but it will be an aqueous solution of an indifferent electrolyte. This dilution process is repeated a number of times in such a way that each starting solution contains the same amount of metal ions and ligand, but the amount of hydrogen ions is varied from one dilution process to another.

In this way several pH vs. V curves are obtained. The derivative $(\partial \log [H]/\partial V)_{m,l,h}$ can now be evaluated at each point of each curve. A series of integrations is then performed. In each integration series the values for the derivative are used at the same V value, as is imposed by eq 20.

The validity of eq 20 was tested, by using computer-generated data for five different metal ion complex systems. For this purpose a computer program EQUIL, designed by Ting-Po and Nancollas,[17] was used. The five systems can be described as follows.

System 1. The ligand is a dibasic acid with acidity constants $\log \beta_{012} = 14.00$ and $\log \beta_{011} = 11.00$. Two complexes are formed: ML ($\log \beta_{110} = 4.00$) and MLOH ($\log \beta_{11\bar{1}} = 6.00$). Each solution contains $m = 0.0005$ mol and $l = 0.001$ mol; h is varied from 0.000 105 to 0.0021 mol in 20 equal steps, and V is varied from 0.1 to 0.5 dm^3 in 20 equal steps as well. In the other systems V and h are varied in the same way as in system 1. In each series $\log K_w = -14.00$.

System 2. The ligand is a dibasic acid ($\log \beta_{012} = 12.00$, $\log \beta_{011} = 8.00$) and forms the complexes ML ($\log \beta_{110} = 4.50$), M_2L_2 ($\log \beta_{220} = 12.00$), and ML_2 ($\log \beta_{120} = 7.00$). Each solution contains 0.005 mol of M and 0.0015 mol of L, and h is varied from 0.000 155 to 0.0031 mol.

System 3. The ligand is a dibasic acid ($\log \beta_{012} = 12.00$, $\log \beta_{011} = 8.00$) and forms the complexes M_2L_2 ($\log \beta_{220} = 12.00$) and ML_2 ($\log \beta_{120} = 7.00$); $m = 0.0005$ mol, $l = 0.0015$ mol, and h is varied from 0.000 155 to 0.0031 mol.

System 4. The ligand is a tribasic acid ($\log \beta_{013} = 18.00$, $\log \beta_{012} = 12.00$) and forms ML ($\log \beta_{110} = 4.00$) and ML_2 ($\log \beta_{120} = 7.00$); $m = 0.0003$ mol, $l = 0.001$ mol, and h is varied from 0.000 155 to 0.0031 mol.

System 5. The ligand is a tribasic acid ($\log \beta_{013} = 18.00$, $\log \beta_{012} = 15.00$, $\log \beta_{011} = 10.00$) and forms MHL ($\log \beta_{111} = 12.00$), ML ($\log \beta_{110} = 4.00$), ML_2 ($\log \beta_{120} = 7.00$), and MLOH ($\log \beta_{11\bar{1}} = -6.00$); $m = 0.0003$ mol, $l = 0.001$ mol, and h is varied from 0.000 155 to 0.0031 mol.

In total, the five systems represent 1700 experimental points. For each point C is calculated in two different ways; the results are called C_1 and C_2.

C_1 is calculated from eq 24.

$$C = [\mathrm{M}] + [\mathrm{L}] + [\mathrm{H}] + [\mathrm{OH}] + \sum_i^n \beta_{01i}[\mathrm{L}][\mathrm{H}]^i + \sum_i \beta_{p_iq_ir_i}[\mathrm{M}]^{p_i}[\mathrm{L}]^{q_i}[\mathrm{H}]^{r_i} \quad (24)$$

C_2 is obtained from the generated pH values and eq 20. Two standard IBM subroutines[18] were hereby used: DDTG2—the differentiation of a tabulated function using second-degree polynomial interpolation—and DQTG—a quadrature of a tabulated function by trapezoidal rule. For each integration series C_0 is calculated from the most acidic solution of the series by using eq 25.

$$C_0 = [\mathrm{M}] + [\mathrm{L}] + [\mathrm{H}] + [\mathrm{OH}] + \sum_i^n \beta_{01i}[\mathrm{L}][\mathrm{H}]^i \quad (25)$$

For each point the percentage in which C_2 differed from C_1 is calculated. For 86% of the points this difference is less than 1%, and for 17% of the points it is less then 0.1%. Most of the deviations higher then 1% are observed when data are used for the first point of each dilution process (highest concentration). The highest difference stated between C_1 and C_2 was about 4%. The highest values for the differences between calculated and theoretical values for C coincide in each integration series with the highest values for $(\partial^2 \log [\mathrm{H}]/\partial V^2)_{m,l,h}$. For reduction of these differences the number of dilution curves is increased in that concentration range. Thereby it is found that, when Δh, the difference in h values between two successive dilution curves, is halved, the 4% differences are reduced below 1%. On the other hand no substantial improvement is obtained by applying this procedure in the concentration range where the results are already acceptable.

Table I. Differences between Calculated and Theoretical Values for C

C_M, M	no. of points >10%	>5%	>2%	>1%	<0.1%
2.5–0.6	25	93	290	374	0
0.25–0.06	1	7	67	207	0
0.025–0.006	0	0	17	137	3
0.0025–0.0006	0	0	0	16	95
0.000 25–0.000 06	0	0	0	11	180

The same generated data are also treated according to eq 23, the method of Lefebvre.[12] No differences could be observed between the results of eq 20 and 23, indicating that the two equations are not only theoretically but also practically equivalent at least when the above cited subroutines are used.

With use of generated data, the validity of the method is tested as a function of the concentration. Therefore generated data are obtained by using the initial data of system 4 but with concentrations for C_L, C_M, and C_H differing by a constant factor. The results of this test are summarized in Table I. Each test contains 380 points. It must be remembered here that increasing the number of dilution curves by decreasing Δh, as explained before, will reduce considerably the number of points with a great difference between the theoretical and calculated values for C.

The validity of eq 22, used for the calculation of [L], has been tested in a number of cases. Both good and bad results are obtained. An analysis of the calculation reveals that for most points the third term of eq 22 is the dominating one. This term becomes in the integration process extremely inaccurate when ΔpH, the difference in pH between two successive points, is too high. For ΔpH values of 0.2–0.3, pL deviations of 0.001 are found; on the contrary, for ΔpH >0.5 deviations higher than 1 pL unit are observed.

An alternative to the proposed method, as it has already been mentioned, is the calculation of [L] from an equation such as the Osterberg equation, followed by the calculation of $C - C_0$ from eq 23 on the condition that [M] is known. E.g., the use of the Osterberg equation imposes the constancy of C_M, whereas in this method the ratio C_M/C_L must be a constant. That means that with a comparable number of experimental data a greater concentration range of C_M is covered by our method, a feature which is not unimportant in the study of polynuclear complexes.

Appendix

Consider a solution composed of m mol of metal ion M, l mol of ligand L, h mol of hydrogen ion H, and w mol of water. In this solution a number of reactions take place, and hereby the following substances are formed: a series of metal ion complexes $M_{p_i}L_{q_i}H_{r_i}(OH)_{s_i}$, represented by c_i, metal ion hydroxides $M_{p_k'}(OH)_{q_k'}$, represented by b_k, and protonated products of the ligand $H_{r_j'}L_{q_j'}$ represented by a_j. The change in the stoichiometric coefficients (s = number of OH's and r = number of H's) is required because in this derivation a clear distinction must be made between H^+ and OH^+ due to differences in their chemical potential (see, e.g., eq A10). The differential of the Gibbs function of such a solution at constant temperature and pressure is given by eq A1. The Gibbs–

$$\mathrm{d}G = \mu_M \mathrm{d}n_M + \mu_H \mathrm{d}n_H + \mu_L \mathrm{d}n_L + \mu_{OH} \mathrm{d}n_{OH} + \mu_w \mathrm{d}n_w + \sum_i \mu_{c_i} \mathrm{d}n_{c_i} + \sum_k \mu_{b_k} \mathrm{d}n_{b_k} + \sum_j \mu_{a_j} \mathrm{d}n_{a_j} \quad (A1)$$

Duhem–Margules relation is given by eq A2. Here n_X and

$$n_M \mathrm{d}\mu_M + n_H \mathrm{d}\mu_H + n_L \mathrm{d}\mu_L + n_{OH} \mathrm{d}\mu_{OH} + n_w \mathrm{d}\mu_w + \sum_i n_{c_i} \mathrm{d}\mu_{c_i} + \sum_k n_{b_k} \mathrm{d}\mu_{b_k} + \sum_j n_{a_j} \mathrm{d}\mu_{a_j} = 0 \quad (A2)$$

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μ_X are respectively the number of moles and the chemical potential of the component X. In this solution the mass-balance equations (A3)–(A6) hold. Equation A6 demonstrates

$$m = n_M + \sum_k p_k' n_{b_k} + \sum_i p_i n_{c_i} \qquad (A3)$$

$$l = n_L + \sum_j q_j' n_{a_j} + \sum_i q_i n_{c_i} \qquad (A4)$$

$$h = n_H - n_{OH} - \sum_k s_k' n_{b_k} - \sum_i s_i n_{c_i} + \sum_j r_j' n_{a_j} + \sum_i r_i n_{c_i} \qquad (A5)$$

$$w = n_w + n_{OH} + \sum_k s_k' n_{b_k} + \sum_i s_i n_{c_i} \qquad (A6)$$

the difference between w, the amount of water used by the preparation of the solution, and n_w, the actual amount of water. The equilibrium condition (A7) and the series of equilibrium

$$\mu_H + \mu_{OH} = \mu_w \qquad (A7)$$

conditions (A8)–(A10) can be considered. Substitution of eq

$$p_k' \mu_M + s_k' \mu_{OH} = \mu_{b_k} \qquad (A8)$$

$$q_j' \mu_L + r_j' \mu_H = \mu_{a_j} \qquad (A9)$$

$$p_i \mu_M + q_i \mu_L + r_i \mu_H + s_i \mu_{OH} = \mu_{c_i} \qquad (A10)$$

A7–A10 into eq A1 and A2 gives eq A11 and A12 because of eq A3–A6.

$$dG = \mu_M dm + \mu_H dh + \mu_L dl + \mu_w dw \qquad (A11)$$

$$m d\mu_M + h d\mu_H + l d\mu_L + n_w d\mu_w = 0 \qquad (A12)$$

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Composition of Ternary (Metal–Ligand–Hydrogen) Complexes Experimentally Determined from Titrations Using Only a pH Electrode

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In the studies of ternary metal–ligand–hydrogen complex equilibria in aqueous solutions the variation techniques presented by Osterberg, Sarkar, Kruck, and McBryde allow one to calculate free metal and free (unassociated) ligand concentrations from titration experiments using only a pH electrode. The method, which is completely model independent, is extended in the present study to the determination of the average stoichiometric coefficients of the species present in solution. The approach is valid in the cases of mononuclear as well as polynuclear metal-containing species. The method was successfully applied to the evaluation of potentiometric data of a series of copper(II) ethylenediamine titrations.

Introduction

Osterberg[1] introduced an extremely valuable technique for evaluating free (unassociated) ligand concentrations in complex metal–ligand equilibria. The method was subsequently extended to the determination of free metal concentrations by Sarkar and Kruck[2] and McBryde.[3] Later elaborations of the approach were presented by Guevremond and Rabenstein,[4] Field and McBryde,[5] and Avdeef and Raymond.[6] The method is quite remarkable in that one uses only a pH electrode to determine pM and pL values (pX = −log [X], where X = M, L, or H). One need not assume the identity of the species present in solution in order to apply the method, and in that sense the pM and pL values so derived are "model independent". The method applies to both mononuclear and polynuclear metal complexes.[4,6] The technique, called the *variation method* (VM)[6] since it requires several titrations where the total reactant concentrations are varied systematically, owes some of its origins to the earlier work of Hedstrom[7] and Sillen.[8] It appears to us to be a thoroughly valuable technique, and it surprises us that its use has not been more widespread.

In the present paper we append to the VM approach a general procedure for determining the average stoichiometric coefficients of the species which are present in solution. One needs no more data than those already required to determine the VM values of pM and pL. If a certain region in pH contains the jth metal–ligand–hydrogen complex $M_{e_{mj}}L_{e_{lj}}H_{e_{hj}}$, the *extended variation method* (EVM) can be used to determine the number of different kinds of reactants present in the complex. These are the metal, ligand, and hydrogen stoichiometric coefficients: e_{mj}, e_{lj}, and e_{hj}, respectively, of the jth associated species. If the region contains more than one complex, which is quite often the case in complicated equilibrium reactions, the EVM approach can be used to determine the average coefficients: $\bar{e}_m$, $\bar{e}_l$, and $\bar{e}_h$. Such information is often sufficient to identify most of the predominant species present in solution. However, in the analysis of complicated equilibrium systems, it is critically important to use data of the highest quality.[5,8] Recently this has been emphasized by Vadasdi,[9] who discussed a nonlinear least-squares method of composition analysis. The EVM technique we propose can be sensitive to experimental errors and in some adverse cases this may limit its application.

We applied the new algorithm to a series of potentiometric titrations of copper(II) ethylenediamine, with the total metal and ligand (abbreviated en) concentrations in the ranges 1–4 and 6–16 mM, respectively. The large uncertainties in the equilibrium constants[10,11] of the reported ternary complex $Cu(en)_2OH^+$ and the weakly formed $Cu(en)_3{}^{2+}$ species sug-

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