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 *j*th 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 *j*th 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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(1) R. Osterberg, *Acta Chem. Scand.*, **14**, 471 (1960).
(2) B. Sarkar and T. P. A. Kruck, *Can. J. Chem.*, **51**, 3541 (1973).
(3) W. A. E. McBryde, *Can. J. Chem.*, **55**, 4211 (1977).
(4) R. Guevremond and D. L. Rabenstein, *Can. J. Chem.*, **55**, 4211 (1977).
(5) T. B. Field and W. A. E. McBryde, *Can. J. Chem.*, **56**, 1202 (1978).
(6) A. Avdeef and K. N. Raymond, *Inorg. Chem.*, **18**, 1605–1611 (1979).
(7) B. Hedstrom, *Acta Chem. Scand.*, **9**, 613 (1955).
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(9) K. Vadasdi, *J. Phys. Chem.*, **78**, 816–820 (1974).
(10) H. B. Jonassen, R. E. Reeves, and L. Sogal, *J. Am. Chem. Soc.*, **77**, 2748 (1955).
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Table I. Experimental Data for Copper(II) Ethylenediamine Potentiometric Titrations[a]

set no.	M, mM	L, mM	A,[b] mM	I,[c] mM	no. of pts	pH range	
1	0.0	5.20	18.57	167.9	74	1.8–12.5	
2	0.0	6.88	18.95	162.7	78	1.8–12.5	
3	0.0	8.61	18.74	158.0	76	1.8–12.5	
4	0.89	8.66	18.65	136.9	58	2.5–11.5	metal variation series
5	1.78	8.66	19.54	143.7	58	2.5–11.5	
6[d]	2.67	8.66	20.48	140.1	59	2.5–11.5	
7	3.55	8.66	21.42	136.7	58	2.5–11.5	
8	2.67	5.54	20.19	153.0	53	2.5–11.5	ligand variation series
9	2.67	6.93	20.25	151.1	57	2.5–11.5	
10[d]	2.67	8.66	20.28	140.2	57	2.5–11.5	
11	2.67	12.12	20.23	127.5	58	2.5–11.5	
12	2.67	15.58	20.34	115.1	58	2.5–11.5	

[a] At 25 °C; ionic strength adjusted to 0.2 M with KNO_3. [b] Initial HNO_3 concentration in titration solution. [c] Actual initial concentration of KNO_3. [d] "Common point" sets (see text).

gested an excellent opportunity to demonstrate the new approach.

The EVM algorithm is presently coded in Fortran and is a subset of the extensive library of routines, STBLTY,[6,12–14] dealing with equilibrium analysis of potentiometric data.

Methodology

Variation Method (VM). In order to introduce the EVM algorithm, we first need to briefly describe the VM experiments and the pM and pL derivations. Although the current presentation focuses on just three kinds of reactants (that is, metal, ligand, and hydrogen), the method is in principle extendable to any number of reactants, in addition to hydrogen ions. Within the ternary class of possible compounds, one can consider polynuclear metal complexes.

In the VM algorithm one needs to collect two series of pH titrations at mutually constant ionic strength, one for the metal and one for the ligand variation. Each series must contain at least two, and preferably more, data sets (pH, $H)_{M,L}$, where M, L, and H are the total concentrations of the metal, ligand, and hydrogen reagents, respectively, with

$$H = A - B + N'_{h}L \tag{1}$$

where $A - B$ is the difference between the total mineral acid and base concentrations added to the titration solution and N'_{h} is the number of dissociable protons associated with the ligand in its original analytical form. Each data set is acquired by titrating with a mineral acid or base a solution containing a fixed amount of total metal and ligand. In the metal-variation series, the total ligand concentration is kept fixed at one value, L_0, and one may have the data sets

$$(\mathrm{pH}, H)_{M_a,L_0}, (\mathrm{pH}, H)_{M_b,L_0}, (\mathrm{pH}, H)_{M_c,L_0}, \ldots$$

The other series is conversely constructed, with the total metal concentration kept fixed at M_0 (M_0 *must* be one of the values M_a, M_b, M_c, ...) and the total ligand varied:

$$(\mathrm{pH}, H)_{M_0,L_a}, (\mathrm{pH}, H)_{M_0,L_b}, (\mathrm{pH}, H)_{M_0,L_c}, \ldots$$

One of the varied ligand concentrations must be the same as L_0 in the first series. The consequence of the necessary restrictions[6] is that the two series must have one data set in common, (pH, $H)_{M_0,L_0}$. This has been referred to as the "common point"[6] (sets 6 and 10 in Table I).

To derive pM and pL values by the VM technique, one starts with the three mass balance equations (2)–(4). NSP

$$M = m + \sum_{j=1}^{\mathrm{NSP}} e_{mj}C_j \tag{2}$$

$$L = l + \sum e_{lj}C_j \tag{3}$$

$$H = h - K'_{w}/h + \sum e_{hj}C_j \tag{4}$$

is the number of associated species in the system. We have already defined e_{kj} (k = m, l, h). K'_{w} is the ionization constant of water, on the concentration scale. C_j is the concentration of the jth associated species and can be defined in terms of the three free-reactant concentrations m, l, and h and the overall formation constant for the jth species, β_j, as

$$C_j = m^{e_{mj}}l^{e_{lj}}h^{e_{hj}}\beta_j \tag{5}$$

From the differential properties[1–8] of the mass balance expressions, one can derive pM and pL values *independent* of the knowledge of β_j and e_{kj} terms from relations 6 and 7.

$$\left(\frac{\partial \ln m}{\partial \ln h}\right)_{M,L} = -\left(\frac{\partial H}{\partial M}\right)_{L,h} \tag{6}$$

$$\left(\frac{\partial \ln l}{\partial \ln h}\right)_{M,L} = -\left(\frac{\partial H}{\partial L}\right)_{M,h} \tag{7}$$

The slopes $(\partial H/\partial M)_{L,h}$ and $(\partial H/\partial L)_{M,h}$ can be experimentally obtained from isohydric (constant pH) intersections of the two series of titration curves (pH, $H)_M$ and (pH, $H)_L$, a procedure already adequately discussed. We will need these slopes in the EVM algorithm. The function formed by these slopes, when integrated over pH, *at the common point values of M* and *L*, yields values of pM and pL, as has been covered elsewhere.[1–6]

The Extended Variation Method (EVM): Derivation of the Overall Average Stoichiometric Coefficients, e_k. Sillen[8] defined the average stoichiometric coefficients in terms of the complexity sum

$$S = \sum_{j=1}^{\mathrm{NSP}} C_j \tag{8}$$

as in (9)–(11). From the mass balance expressions (2)–(4),

$$\bar{e}_m = \sum_{j=1}^{\mathrm{NSP}} e_{mj}C_j \Big/ \sum_{j=1}^{\mathrm{NSP}} C_j \tag{9}$$

$$\bar{e}_l = \sum e_{lj}C_j / \sum C_j \tag{10}$$

$$\bar{e}_h = \sum e_{hj}C_j / \sum C_j \tag{11}$$

we obtain (12)–(14).

$$\bar{e}_m = (M - m)/S \tag{12}$$

$$\bar{e}_l = (L - l)/S \tag{13}$$

$$\bar{e}_h = (H - h + K'_{w}/h)/S \tag{14}$$

Since the VM procedure produces m and l values for the common point set (pH, $H)_{M_0,L_0}$, we need only to determine values of S in order to deduce the average stoichiometric coefficients of (12)–(14). Essentially the EVM step accomplishes just that.

Since S is a function of the variables m, l, and h, we can express its differential as

$$\mathrm{d}S = \left(\frac{\partial S}{\partial \ln m}\right)_{l,h} \mathrm{d} \ln m + \left(\frac{\partial S}{\partial \ln l}\right)_{m,h} \mathrm{d} \ln l + \left(\frac{\partial S}{\partial \ln h}\right)_{m,l} \mathrm{d} \ln h \tag{15}$$

From (2)–(5) and (8) we can simplify the expression further.[8]

$$\mathrm{d}S = (M - m)\,\mathrm{d} \ln m + (L - l)\,\mathrm{d} \ln l + (H - h + K'_{w}/h)\,\mathrm{d} \ln h \tag{16}$$

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(12) A. Avdeef, to be submitted for publication.
(13) A. Avdeef, S. R. Sofen, T. L. Brigante and K. N. Raymond, *J. Am. Chem. Soc.*, **100**, 5362–5370 (1978).
(14) A. Avdeef and J. J. Bucher, *Anal. Chem.*, **50**, 2137–2142 (1978).

The partial derivative of S with respect to the natural log of h at fixed values of M and L becomes

$$\left(\frac{\partial S}{\partial \ln h}\right)_{M,L} = (M - m)\left(\frac{\partial \ln m}{\partial \ln h}\right)_{M,L} + (L - l)\left(\frac{\partial \ln l}{\partial \ln h}\right)_{M,L} + (H - h + K'_{\mathrm{w}}/h) \quad (17)$$

From the VM algorithm, we can use (6) and (7) to further reduce (17).

$$\left(\frac{\partial S}{\partial \ln h}\right)_{M,L} = -(M - m)\left(\frac{\partial H}{\partial M}\right)_{L,h} - (L - l)\left(\frac{\partial H}{\partial L}\right)_{M,h} + (H - h + K'_{\mathrm{w}}/h) \quad (18)$$

At the common point we can evaluate every term in (18). Using essentially the same approach as that used to calculate pM and pL by integration,[1–6] we can also deduce S at a given pH.

$$S = S_1 + 2.303 \int_{\mathrm{pH}_1}^{\mathrm{pH}} \left(\frac{\partial S}{\partial \ln h}\right)_{M,L} \mathrm{dpH} \quad (19)$$

Values of S_1, the integration constant, can be obtained in a manner analogous to the way initial pM and pL are obtained in the VM algorithm.[6] That is, one starts the variation series at a sufficiently low pH value so that no appreciable amount of metal–ligand complexation takes place. Under these conditions, S_1 can be defined readily from the knowledge of the ligand–proton dissociation constants. That is, $S_1 \approx L - l$. This poses little difficulty in practice.

Residual Composition Analysis. If many species are simultaneously present or if the ligand concentration greatly exceeds that of the metal, the identification of the species present in solution from knowledge of $\bar{e}_{\mathrm{k}}$ can be quite difficult. Sillen likened the use of the average stoichiometric coefficients to the use of the Patterson function in X-ray crystallography. All the information about the structure is present in the latter function but it is obscured by extraneous information.

One simplification we can make involves separating out contributions to S due to species whose formation constants are reliably known. This is again analogous to methods in X-ray crystallography. That is, one can more easily locate the positions of hydrogen atoms in a "difference Fourier" electron-density map when the contributions due to "heavy atoms" are subtracted.[15] In the present case one performs analogous subtractions from the Sillen sum as well as from the total concentrations, as illustrated below.

Subtracting Ligand–Proton Species. The ligand–proton constants can be very accurately determined by independent titrations in the absence of metal ions. For an N_{h}-proton ligand one can form the residual sums (20)–(23) where β_j^{H} =

$$M' = M \quad (20)$$

$$L' = L - l\sum_{j=1}^{N_{\mathrm{h}}} h^j\beta_j^{\mathrm{H}} \quad (21)$$

$$H' = H - l\sum_{j=1}^{N_{\mathrm{h}}} jh^j\beta_j^{\mathrm{H}} \quad (22)$$

$$S' = S - l\sum_{j=1}^{N_{\mathrm{h}}} h^j\beta_j^{\mathrm{H}} \quad (23)$$

$[\mathrm{H}_j\mathrm{L}]/[\mathrm{L}][\mathrm{H}]^j$. These sums are free of contributions due to protonated species of the ligand. Consequently, the revelation of the composition of metal-containing species is simplified by the residual coefficients (eq 24–26).

$$\bar{e}'_{\mathrm{m}} = (M' - m)/S' \quad (24)$$

$$\bar{e}'_{\mathrm{l}} = (L' - l)/S' \quad (25)$$

$$\bar{e}'_{\mathrm{h}} = (H' - h + K'_{\mathrm{w}}/h)/S' \quad (26)$$

Subtracting $\mathbf{M}_p\mathbf{(OH)}_q$ Hydrolysis Species. From the independent studies of metal hydrolysis reactions, in the absence of ligand molecules (other than OH^-), one can deduce constants which may be used to construct residual sums similar to (20)–(23) but which are free of the effects of species $\mathrm{M}_p(\mathrm{OH})_q$. Known constants of this sort are compiled critically by Baes and Mesmer.[16]

Subtracting Mononuclear $\mathbf{ML}_n$ Species. In order to focus on polynuclear metal–ligand complexes, one may construct residual sums which are free of contributions of mononuclear components. The constants for the mononuclear species may have been obtained from solutions so dilute in the metal ion that polynuclear species were unlikely components.

For example, suppose one were able to independently assess the constants for the ML_j (j = 1–N) complexes. The residual sums free of these species (as well as all forms of the metal-free protonated ligand) are given in (27)–(30) where β_j =

$$M'' = M' - m\sum_{j=1}^{N} l^j\beta_j \quad (27)$$

$$L'' = L' - m\sum_{j=1}^{N} jl^j\beta_j \quad (28)$$

$$H'' = H' \quad (29)$$

$$S'' = S' - m\sum_{j=1}^{N} l^j\beta_j \quad (30)$$

$[\mathrm{ML}_j]/[\mathrm{M}][\mathrm{L}]^j$. Thus the "difference" coefficients $\bar{e}''_{\mathrm{m}}$, $\bar{e}''_{\mathrm{l}}$, and $\bar{e}''_{\mathrm{h}}$, constructed as in (24)–(26), are in principle more revealing of polynuclear and ternary species.

The process of residual analysis is quite general, but its successful application critically depends on the accuracy of the EVM-calculated Sillen sum, S, and the accuracy of the constants used to construct the subtractant. For the residual sums to be meaningful, clearly, the experimental uncertainty in the subtractant must be significantly smaller in magnitude than the residual quantity. This will be a topic of further investigation for us. At present we wish to focus on the definition of the method and its most direct applications.

Experimental Section

Potentiometric Data. Twelve titrations of the copper(II) ethylenediamine system were performed at 25 °C and 0.2 M ionic strength (adjusted with $\mathrm{KNO_3}$). Our general procedure is described in more detail elsewhere.[17] Copper(II) nitrate stock solutions were standardized by titrations with EDTA.[17] Ethylenediamine was prepared and standardized as described previously.[14] The potentiometric data were collected with a microcomputer-controlled automatic titration system.[14] The 2.5-mL Gilmont buret incorporated into the titrator can deliver the volume of titrant with a total-volume precision of less than 0.001 mL. A Beckman 39501 combination glass electrode was used. The pH meter readings were converted to those based on concentration, $\mathrm{p[H^+]}$, according to the relation[14,18]

$$\mathrm{pH_{meter}} = 0.083\ (3) + (1.0012\ (3))\mathrm{p[H^+]} + (0.5\ (3))[\mathrm{H^+}] - (0.20\ (7))[\mathrm{OH^-}] \quad (31)$$

which is valid for our experimental configuration in the range pH 1.8–12.0. Over 700 pH measurements were utilized for the analysis. The experimental details are summarized in Table I.

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(15) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination", Macmillan, New York, 1968.

(16) C. F. Baes, Jr., and R. E. Mesmer, "The Hydrolysis of Cations", Wiley-Interscience, New York, 1976, pp 267–274.

(17) J. A. Brown, D. L. Kearney, and A. Avdeef, submitted for publication in *Anal. Chem.*

(18) The number in parentheses following a numerical quantity refers to the estimated standard deviation in the least significant digit of that quantity.

Table II. Variation Results for the "Common Point" Sets[a]

pH	$(\partial H/\partial M)_{L,h}$	$(\partial H/\partial L)_{M,h}$	$\bar{n}_H$	$\bar{n}$	pM	pL	S, mM	$\bar{e}_m$	$\bar{e}_l$	$\bar{e}_h$
3.5	−0.03	1.98	2.00	0.02	2.58	12.32	8.53	0.00	1.00	1.97
4.0	−0.30	1.93	2.00	0.16	2.65	11.34	8.57	0.04	0.99	1.89
4.5	−1.19	1.79	2.00	0.66	3.00	10.42	8.32	0.19	1.02	1.64
5.0	−2.16	1.76	1.99	1.23	3.85	9.53	7.45	0.33	1.13	1.43
5.5	−3.01	1.71	1.98	1.76	5.13	8.66	6.18	0.42	1.36	1.26
6.0	−3.68	1.93	1.94	1.93	7.20	7.54	5.93	0.44	1.42	1.08
6.5	−3.74	1.88	1.84	1.99	8.70	6.78	6.25	0.41	1.34	0.95
7.0	−3.32	1.64	1.62	2.02	10.48	5.89	6.35	0.41	1.32	0.83
7.5	−2.74	1.35	1.34	2.03	11.99	5.14	6.33	0.41	1.32	0.68
8.0	−2.31	1.12	1.13	2.06	13.25	4.53	6.20	0.42	1.35	0.58
8.5	−2.05	1.01	1.02	2.02	14.33	3.99	5.98	0.43	1.39	0.55
9.0	−1.87	0.96	0.93	1.95	15.31	3.50	5.79	0.45	1.39	0.52

[a] Expression 34 was used to calculate $\bar{n}_H$. McBryde's expression 35 was used to calculate $\bar{n}$, by using a formalism that is model independent. $K'_w = 1.78 \times 10^{-14}$ was used.

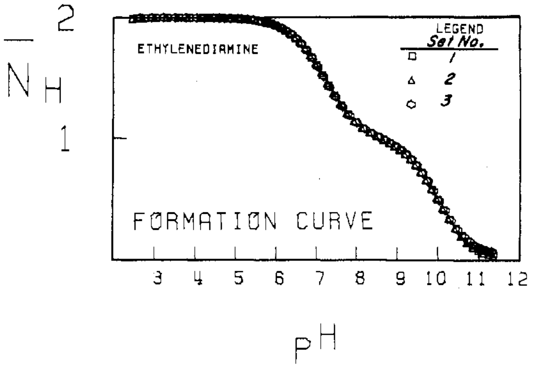

Figure 1. Plot of the average number of bound protons per ethylenediamine, $\bar{n}_H = (H - h + K'_w/h)/L$, as a function of pH. $M = 0$; $L = 5.20$ (square), 5.20 (triangle), 8.61 mM (hexagon).

Results

Ethylenediamine Protonation Constants. The three metal-free ligand sets (1–3 in Table I) were processed by DATA REDUCTION and the two pK_a's were refined by NONLINEAR LS REFINE subprograms of STBLTY. The 228 pH measurements were weighted according to the scheme[13]

$$(\text{weight})^{-1} = 0.02^2 + (0.001\text{d}pH/\text{d}V)^2 = \sigma_{pH}^2 \quad (32)$$

where dpH/dV represents the slope of the titration curve. The refinement terminated at a goodness-of-fit (GOF) of 0.45, with the protonation constants converging to log K_1^H = 9.992 (3) and log K_2^H = 7.183 (2).[18,19] The agreement with literature values is superb: 9.99 and 7.19,[20] respectively. The three formation curves,[13,14] which are plots of the average number of coordinated protons as a function of pH, shown in Figure 1, display overlap and symmetry that are consistent with good data.

Metal–Ligand Mononuclear Constants. Figures 2 and 3 show the Bjerrum (formation) plots[21] for the metal and the ligand variation series, respectively. The values of $\bar{n}$ were calculated from

$$\bar{n} = [L - (H - h + K'_w/h)/\bar{n}_H]/M \quad (33)$$

where

$$\bar{n}_H = \sum_{j=0}^{N_h} j h^j \beta_j^H / \sum_{j=0}^{N_h} h^j \beta_j^H \quad (34)$$

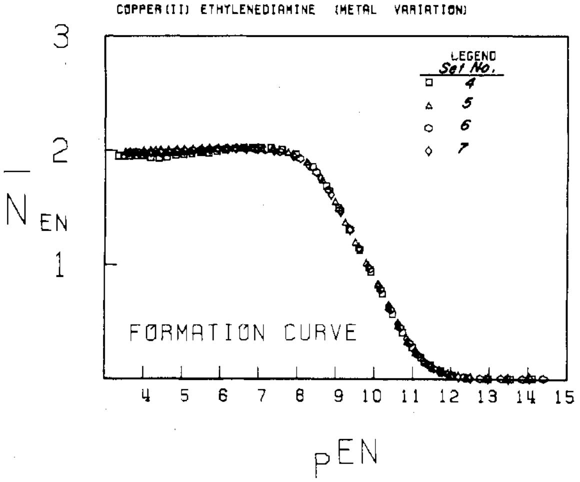

Figure 2. Bjerrum plot of $\bar{n}$ [according to (33)] as a function of −log [en] = p[en] for the metal-variation series. L = 8.66 mM; M = 0.89 (square), 1.78 (triangle), 2.67 (hexagon), and 3.55 mM (diamond).

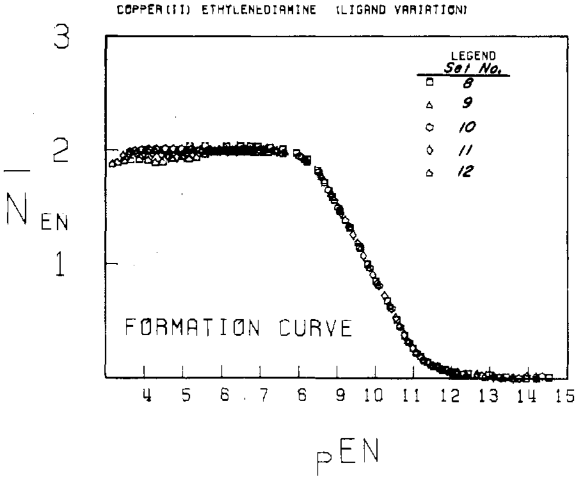

Figure 3. Bjerrum plot of $\bar{n}$ [according to (33)] as a function of −log [en] = p[en] for the ligand-variation series. M = 2.67 mM; L = 5.54 (square), 6.93 (triangle), 8.66 (hexagon), 12.12 (diamond), and 15.58 mM (pentagon).

In the absence of the formation of ternary complexes, $\bar{n}$ refers to the average number of coordinated molecules of ethylenediamine per metal ion as a function of pL (=−log [en]).[21] The region for pL >8 shows no detectable dependence on the total metal and ligand concentrations for all of the nine curves in the two figures. From this we can conclude that $Cu(en)_2^{2+}$ forms in a simple stepwise fashion (under the conditions

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[19] The nonlinear weighted least squares minimizes the function $\sum(pH^{obsd} - pH^{calcd})^2/\sigma_{pH}^2$, summed over all pH measurements. The stepwise constants are defined as $K_j^H = [H_jL]/[H_{j-1}L][H]$ and $K_n = [ML_n]/[ML_{n-1}][L]$.

[20] D. H. Everett and B. R. W. Pinsent, *Proc. R. Soc. London, Ser. A*, **215**, 416 (1952).

[21] F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants", McGraw-Hill, New York, 1961, Chapter 3.

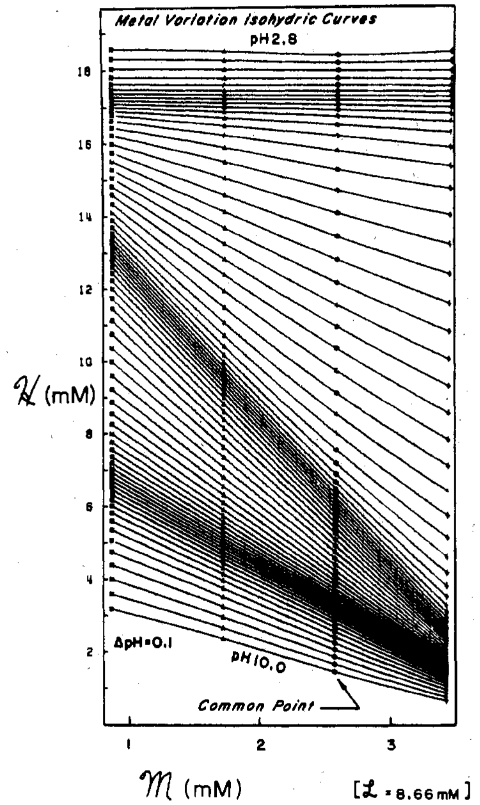

Figure 4. $(H, M)_{L,\mathrm{pH}}$ plots with pH 2.8–10.0 for copper(II) ethylenediamine for the metal-variation series. The discrete points are connected with cubic splines. The regions of closely spaced curves correspond to equivalence regions, where the slopes of the titration curves maximize.

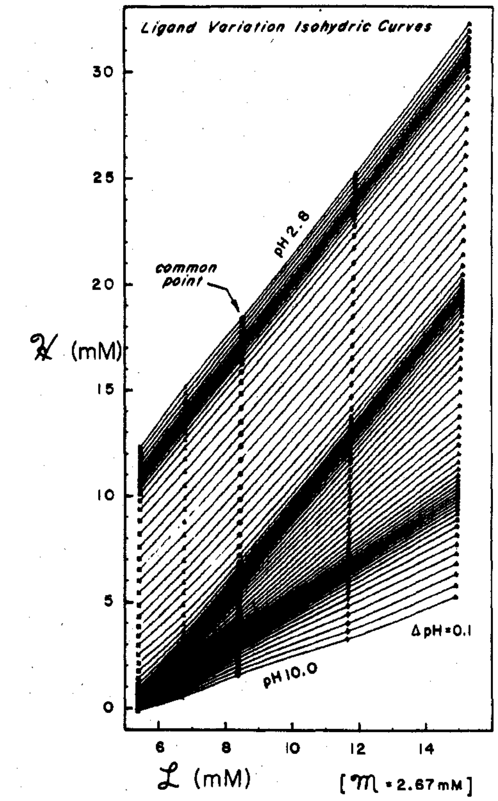

Figure 5. $(H, L)_{M,\mathrm{pH}}$ plots with pH 2.8–10.0 for copper(II) ethylenediamine, for the ligand-variation series.

specified in Table I), free of detectable complications.

According to McBryde[3] one can also calculate $\bar{n}$ for the "common point" set by the VM algorithm as

$$\bar{n} = -[(\partial H/\partial M)_{L,h}/(\partial H/\partial L)_{M,h}]_{M,L} \qquad (35)$$

McBryde's $\bar{n}$ applies to mononuclear and polynuclear complexes, contrary to original considerations.[3,5] The $\bar{n}$ values listed in Table II are derived from (35).

In the limited pH 2.5–6.0 region (pL >8) the nine metal-containing sets were used to determine (half-$\bar{n}$ method)[21] and refine (STBLTY) the two metal–ligand stepwise constants.[19] Refinement converged at GOF = 1.05 for 184 pH measurements with log K_1 = 10.55 (1) and log K_2 = 9.12 (1).[18] The comparable literature values[22] ($NaClO_4$ medium) are 10.59 and 9.20, respectively. The refinement included as fixed contributions the known copper hydrolysis constants[16] for the species $Cu(OH)^+$, $Cu(OH)_2$, $Cu(OH)_3^-$, $Cu(OH)_4^{2-}$, and $Cu_2(OH)_2^{2+}$.

Derivation of the Free Metal and Free Ligand Concentrations. Isohydric interpolations of the two series of titration curves[6] (pH, $H)_M$ and (pH, $H)_L$ allowed us to construct the plots $(H, M)_\mathrm{pH}$ and $(H, L)_\mathrm{pH}$, shown in Figures 4 and 5. Evaluations of these plots at the "common point"[6] produced the $(\partial H/\partial L)_{M,h}$ and $(\partial H/\partial M)_{L,h}$ terms needed to deduce pM and pL as well as the Sillen sum of (18) and (19). A substantial improvement of the previous algorithm[6] for the above interpolation was achieved by introducing the use of cubic splines[23] for the fitting of the discrete pH measurements to a smooth curve.

Table III. Residual Composition Analysis

A. Subtracting enH^+ and enH_2^{2+}

pH	S', mM	$\bar{e}'_\mathrm{m}$	$\bar{e}'_\mathrm{l}$	$\bar{e}'_\mathrm{h}$
4.5	1.55	1.0	1.1	0.1
5.0	2.15	1.1	1.5	0.0
5.5	2.21	1.2	2.0	−0.0
6.0	2.49	1.0	2.0	−0.1
6.5	2.73	1.0	1.8	−0.2
7.0	2.70	1.0	1.8	−0.3
7.5	2.60	1.0	1.8	−0.3
8.0	2.49	1.0	1.9	−0.3
8.5	2.38	1.1	2.0	−0.2
9.0	2.39	1.1	2.0	−0.2

B. Subtracting enH^+, enH_2^{2+}, $Cu(en)^{2+}$, $Cu(en)_2^{2+}$, $CuOH^+$, $Cu(OH)_2$, $Cu(OH)_3^-$, $Cu(OH)_4^{2-}$, and $Cu_2(OH)_2^{2+}$

pH	S'', mM	$\bar{e}''_\mathrm{m}$	$\bar{e}''_\mathrm{l}$	$\bar{e}''_\mathrm{h}$
8.0	0.23	1.4	0.6	−2.8
8.2	0.24	1.7	1.2	−2.4
8.4	0.24	1.8	1.6	−2.2
8.6	0.25	1.8	1.8	−2.0
8.8	0.25	1.9	1.8	−1.8
9.0	0.24	1.8	1.5	−1.8

Table II shows a sample of the VM-calculated pM and pL values.

Composition Analysis. Table II contains the values of the Sillen sum, S, and the average stoichiometric coefficients at various values of pH. Since the total ligand concentration is considerably larger than the metal concentration, the $\bar{e}_k$ values contain large contributions from the species enH^+ and enH_2^{2+}. The residual analysis allows us to "unmask" the problem. The ligand protonation constants obtained in this study were used to calculate concentrations of enH^+ and enH_2^{2+}. The deletion of these species produced the modified S' and $\bar{e}'_\mathrm{m}$, $\bar{e}'_\mathrm{l}$, $\bar{e}'_\mathrm{h}$, shown in Table IIIA.

The slightly negative $\bar{e}'_\mathrm{h}$ coefficients (Table IIIA) and the dip in the S' function near pH 8 (Figure 6) prompted our

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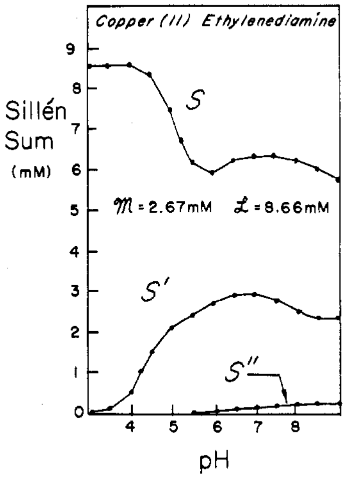

Figure 6. Plot of the Sillen sum (S) and the residual sums with enH^+ and enH_2^{2+} deleted (S') and with enH^+, enH_2^{2+}, $Cu(en)^{2+}$, $Cu(en)_2^{2+}$, and $Cu_p(OH)_q$ (see text) deleted (S''), for the "common point" set.

performing yet another level of residual analysis. The constants for the formation of $Cu(en)^{2+}$ and $Cu(en)_2^{2+}$ determined in this study, along with the literature values[16] for the copper(II) hydrolysis constants, were used to further delete contributions to the Sillen sum. The S'' in Table IIIB indicates that up to ~10% of the metal ions participate in the formation of complexes other than $Cu(en)^{2+}$ and $Cu(en)_2^{2+}$. Figure 6 shows the three different Sillen sums S, S', and S''. The nearest integral values of the $\bar{e}''_m$, $\bar{e}''_l$, and $\bar{e}''_h$ (Table IIIB) suggest the presence of the dimeric species $[(en)Cu(OH)_2Cu(en)]^{2+}$. We fail to see strong evidence for either $Cu(en)_2OH^+$ or $Cu(en)_3^{2+}$ in the pH <9 region for the total concentrations used in this study. The identification of the dimer must at this point remain tentative since its concentration relative to the other species is low enough to make possible errors in data a serious problem.[24] The suggestion of its presence, such as it may be, convinces us that the proposed technique is a valuable addition to other methods in equilibrium analysis.

Conclusion

The recently described variation methods[4-6] in potentiometric titrations allow one to determine pM and pL values by using only a pH-sensitive electrode, while making no assumptions about the nature of the species present in solution. The present EVM algorithm extends these methods further, while requiring no additional data. That is, having the model-independent pM and pL values, one proceeds to determine the model. Specifically, the average stoichiometric coefficients are determined. The technique should prove to be a valuable addition in the study of complicated equilibrium reactions in aqueous solutions. However, the most important task remains—the acquisition of data of sufficient accuracy so that this technique can be successfully applied.

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Registry No. Copper, 7440-50-8; ethylenediamine, 107-15-3.

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[24] The $\bar{n}$ region for pL <6 (pH >7) is particularly sensitive to errors in the total concentration of ethylenediamine. One might suspect that the dip in the $\bar{n}$ curves (Figures 2, 3) in that region (pL 4, 5) is possibly due to analytical errors. For example, suppose the nine metal-ligand formation curves were to have $\bar{n} = 2.00$ (rather than the observed values ~1.90-1.95); in that region solution of eq 33 for L suggests that our ligand stock solution would have to be only 1% less concentrated. The results of our analyses of the stock solution (by independent titrations in the absence of metal ions) indicate an uncertainty of ~0.5%. For this reason, the results of the residual analysis for species other than $Cu(en)^{2+}$ and $Cu(en)_2^{2+}$ must remain tentative.

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Phosphorus-Ligand Cone Angles. Consequences of Alternate Definitions and Use of MINDO/3 Calculations

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Four specific definitions for cone angles, based on Tolman's general concept, are presented and discussed in terms of idealized phosphine geometries. Cone angles, computed from MINDO/3 optimized geometries and heats of formation data, are reported for the unique conformations and for conformer weighted averages of 15 phosphines: PH_2R (R = H, Me, Et, *i*-Pr, *t*-Bu, Ph, *o*-tol), PHRR′ (R = R′ = Me, Et, *i*-Pr, R = Ph, R′ = Me, Et), and PRR'_2 (R = R′ = Me, Et; R = Ph, R′ = Me). The consequences of using MINDO/3 as a data source for cone angle determinations are discussed.

Introduction

The importance of phosphorus-ligand steric effects in organometallic chemistry and homogeneous catalysis has been reviewed by Tolman.[1] It has been reported, for example, that phosphorus-ligand size affects reaction rates,[2] product distributions,[3,4] and the course of asymmetric syntheses.[5]

In order to quantify phosphorus-ligand sizes, Tolman introduced the concept of cone angle, θ.[1,6] It is generally defined as the apex angle of a right cylindrical cone centered 2.28 Å from the center of a phosphorus atom which just touches the van der Waals radii of the outermost atoms. For unsymmetrical ligands, Tolman introduced the concept of half cone angles, $\theta/2$.[1] These are defined as the angles between the metal-phosphorus vector and the vector that just touches the van der Waals radii of the outermost atoms. To aid in the

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