Table I. Mole Fraction Equilibrium Constants for $Al_2Cl_7^-$ Ion Formation in $AlCl_3$–MCl^a Melts from Potentiometric Data

system	K_3^b	temp, °C	ref
$AlCl_3$-1-BupyCl	$<3.8 \times 10^{-13}$	30	this work
	$<5.7 \times 10^{-12}$	60	this work
	$<3.6 \times 10^{-10}$	120	this work
	$<1.2 \times 10^{-8}$	175	this work
$AlCl_3$-NaCl	1.06×10^{-7}	175	6
	8.00×10^{-8}	175	7
	7.77×10^{-8}	175	10
	1.33×10^{-7}	175	9
$AlCl_3$-LiCl	1.6×10^{-4}	400	11
$AlCl_3$-NaCl	1.0×10^{-5}	400	11
$AlCl_3$-KCl	1.6×10^{-6}	400	11
$AlCl_3$-CsCl	4.0×10^{-8}	400	11
$AlCl_3$-NaCl	5.78×10^{-7}	450	8
$AlCl_3$-RbCl	2.87×10^{-7}	450	8
$AlCl_3$-CsCl	7.58×10^{-7}	450	8

[a] M represents a cationic species. [b] Dissociation constant for $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$.

more stable with decreasing cationic polarizability.[11] The value of K_3 obtained with the relatively large, organic 1-butylpyridinium cation is consistent with this general trend.

The major effect of temperature variation, from 30 to 175 °C, is consistent with a change in the reaction equilibrium, according to the relation

$$\Delta G^\circ = -RT \ln K_3$$

On the basis of the equilibrium constants obtained from the potentiometric curves for this system (Table I), the free energy remains approximately constant throughout the 145 °C temperature span at $(7.1 \pm 0.3) \times 10^4$ J mol^{-1}. Unfortunately, precise thermodynamic data is precluded because of the corrosion process which occurs in the basic $AlCl_3$–1-butylpyridinium chloride systems. One practical consequence of the increased $Al_2Cl_7^-$ ion formation and the lower activity of free Al_2Cl_6 in these molten mixtures, relative to the $AlCl_3$–NaCl system, is that sublimation losses of Al_2Cl_6 are minimal even at 175 °C. They may be also useful solvent systems for stabilizing unusually low valence metallic ion species.

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Registry No. $AlCl_3$, 7446-70-0; 1-BupyCl, 1124-64-7; $Al_2Cl_7^-$, 27893-52-3.

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Free Metal and Free Ligand Concentrations Determined from Titrations Using Only a pH Electrode. Partial Derivatives in Equilibrium Studies

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In the studies of metal 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 makes no assumptions about the associated species present in solution and is thus model independent. We present an alternate general derivation of the expressions and attempt to clarify the technique. Although the approach described below is applicable to any number of components (metals, ligands), in a manner analogous to Hedström's treatment of two-component systems we treat the three-component system by introducing six Jacobian unit determinants for the six variables (M, L, H, m, l, h), that is, the three total and three free concentrations of the metal, ligand, and hydrogen respectively:

$$J\left(\frac{M, \ln m, \ln h}{\ln l, L, \ln h}\right) = 1 \qquad J\left(\frac{M, \ln m, H}{\ln l, L, H}\right) = 1$$

$$J\left(\frac{L, \ln l, \ln m}{\ln h, H, \ln m}\right) = 1 \qquad J\left(\frac{L, \ln l, M}{\ln h, H, M}\right) = 1$$

$$J\left(\frac{H, \ln h, \ln l}{\ln m, M, \ln l}\right) = 1 \qquad J\left(\frac{H, \ln h, L}{\ln m, M, L}\right) = 1$$

These Jacobians are very useful in deriving numerous variational expressions. Using computer-generated data, we test the techniques under a variety of conditions. A useful Fortran computer program is discussed. A simple technique for analytically evaluating implicit functions such as $(\partial \mathrm{pH}/\partial M)_L$ or $(\partial \mathrm{pH}/\partial L)_M$ is presented. This enables one to avoid the use of numerical methods in the least-squares refinement of formation constants, thus leading to substantial reduction in the computational effort.

Introduction

Osterberg[1] and, later, Sarkar and Kruck[2] and McBryde[3] introduced an extremely valuable technique for evaluating the free metal and free ligand concentrations in multicomponent equilibria by the use of pH titration data alone. That is, one could indirectly measure pM (−log [M], [M] = free metal concentration) and pL ([L] = free (unassociated) ligand concentration) values by using only a pH electrode. The

Table I. Glossary of Terms

C_j	concentration of the jth associated species: $C_j = M_{e_{mj}}L_{e_{lj}}H_{e_{hj}} = \beta_j m^{e_{mj}} l^{e_{lj}} h^{e_{hj}}$
e_{kj}	stoichiometric coefficient, referring to the number of kth type of atoms in the jth associated species (For example, for the jth species $[Th(cat)_2(OH)]^-$ (cat = dianionic ligand), $e_{mj} = 1$, $e_{lj} = 2$, $e_{hj} = -1$. The value of e_{hj} is negative to signify a hydroxide. Positive values refer to hydrogen ions.)
H	total hydrogen concentration, defined by $A - B + NH'L$, where A = [HCl] and B = [KOH] or any other monoprotic mineral acid and base
h	free hydrogen ion concentration, $[H^+]$
$J\left(\frac{U, V, W}{u, v, w}\right)$	$\begin{vmatrix} (\partial U/\partial u)_{v,w} & (\partial U/\partial v)_{u,w} & (\partial U/\partial w)_{u,v} \\ (\partial V/\partial u)_{v,w} & (\partial V/\partial v)_{u,w} & (\partial V/\partial w)_{u,v} \\ (\partial W/\partial u)_{v,w} & (\partial W/\partial v)_{u,w} & (\partial W/\partial w)_{u,v} \end{vmatrix}$ Jacobian determinant of the variation of functions U, V, W with respect to the independent variables u, v, w
$\mathbf{J}\left(\frac{U, V, W}{u, v, w}\right)$	Jacobian matrix, having elements of the above determinant
K_w'	$[H^+][OH^-]$
L	total concentration of the ligand, in all of its forms
l	concentration of the unassociated (free) ligand
$\ln h$, $\ln l$, $\ln m$, $\ln x$	logarithm, base e, of the concentration of the unassociated (free) reactants
M	total concentration of the metal, in all of its forms
m	concentration of the free metal
N	number of associated species under consideration
NH	maximum number of dissociable hydrogens on the ligand
NH′	number of dissociable hydrogens on the ligand, in the form it was introduced to the solution (For example, if the ligand were the acetate ion and if it were introduced as the potassium salt, then NH = 1 but NH′ = 0.)
pH, pL, pM, pX	negative of the logarithm, base 10, of the free concentrations (X refers to M or L.)
pM_1	$= -\log M$ if pH_1 is sufficiently low so no metal–ligand complexation occurs
pL_1	$= -\log \left[L/\left(1 + \Sigma_{i=1}^{NH}\beta_i^H h^i\right)\right]$ if pH_1 is sufficiently low so no metal–ligand complexation occurs (Here, β_i^H refers to the cumulative proton–ligand equilibrium quotient, $[LH_i]/[L][H]^i$.)
pX^0	"true" pX values, those calculated from a correct equilibrium model
pX^V	pX values calculated by the model-independent variation technique
X	general designation for M or L
x	general designation for m or l
β_j	cumulative formation constant for the jth associated species $\beta_j = C_j/m^{e_{mj}} l^{e_{lj}} h^{e_{lj}}$, referring to the equilibrium $e_{mj}M + e_{lj}L + e_{hj}H \rightleftarrows M_{e_{mj}}L_{e_{lj}}H_{e_{hj}}$ (≡species C_j)
δ	$pX^0 - pX^V$, the difference between the "true" pX values and those calculated by the variation technique

technique is an extension of earlier work of Hedström[4] and Sillén.[5] It is based on partial differential relations arising from the mass balance equations (vide infra) and requires several titrations, per reactant, performed in a special way. Surprisingly, the method is not widely known, judging by the near absence of its reported use. Sarkar and co-workers[6-9] have experimentally applied it to rather complicated equilibria, involving the determination of as many as three different nonhydrogen reactants. The technique has been very important in our studies of the equilibria involving Th^{4+}, U^{4+}, and Pu^{4+} complexes with catechol and hydroxamate ligands, where evidence for mixed-ligand and polynuclear species is abundant.[10]

We feel that the past presentation of the technique (which can be called the "variation" method—especially as it applied to determining several different reactant concentrations) needs additional clarification, which is the primary purpose of this paper. Also, we wish to introduce some general differential relations of which the above-mentioned technique is a special case. The general relations will be presented in the form of unit Jacobians of third and higher order in exactly the same form as that presented by Hedström for two-component systems. A very simple method for analytically evaluating partial derivatives of implicit functions, such as $(\partial pH/\partial M)_L$ or $(\partial pH/\partial L)_M$, will be presented. Such derivatives are used by least-squares refinement of equilibrium constants and in the past have been evaluated numerically rather than analytically—a process requiring considerably more computational effort. Finally, we wish to introduce some relevant aspects of a new computer program, STBLTY,[11] which was used for all the calculations and most of the drawings presented here.

For solutions containing one type of metal and one type of ligand as reactants, along with hydrogen and hydroxide ions, the species present in solution may be represented by equilibria of the sort

$$e_m M + e_l L + e_h H \rightleftharpoons M_{e_m}L_{e_l}H_{e_h} \ (\equiv \text{species } C_j) \quad (1)$$

The stability constant of the jth associated species is given by

$$\beta_j = C_j / m^{e_{mj}} l^{e_{lj}} h^{e_{hj}} \quad (2)$$

where e_{kj} is the stoichiometric coefficient of the kth reagent, C_j is the concentration of the jth associated species, and m, l, and h are the free (unassociated) concentrations of metal, ligand, and hydrogen. (See Table I for a more complete definition of terms used in this presentation.) Usually only h (in addition to the total concentrations) is known from a simple pH titration. In refinement programs such as SCOGS[12a] and MINIQUAD[12b] unknown values of pM and pL are calculated only after a model is assumed along with the corresponding β values. Thus such values of pM and pL can be model-biased. Osterberg's[1] proposal is the *model-independent* "variation" relation

$$\Delta pL(M_0,L_0) = pL_2 - pL_1 = \left[\int_{pH_2}^{pH_1}\left(\frac{\partial H}{\partial L}\right)_{M_0,h} dpH\right]_{L_0} \quad (3)$$

where M, L, and H are the total metal, ligand, and hydrogen concentrations. The relation states that for given values of M and L (M_0, L_0) the change in pL (from some *known* value pL_1, which can be determined in a number of ways[1-3] as for example in Table I) corresponding to a change in pH is related to the extent the variation of L affects H. One thus needs at least two titrations where L is the only varied nonhydrogen

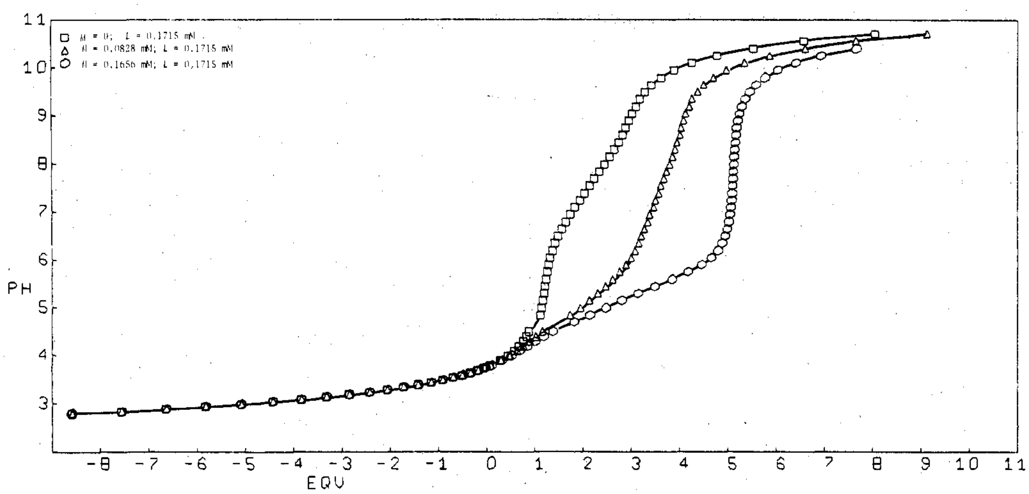

Figure 1. Titration curves for copper(II) diglycyl-L-histidine, calculated from the constants determined by Lau, Kruck, and Sarkar.[8] The total ligand concentration is the same in each of the three curves, while the total metal concentration is varied. EQV refers to moles of base added per mole of ligand.

total concentration. A plot of H vs. L at constant pH[17] shows curves that are ordinarily *nearly* straight lines. Since the slopes $(\partial H/\partial L)$ are dependent on L, so must be ΔpL in eq 3, a subtle but very important point which McBryde[3] notes (his eq 11 and 17) but which Sarkar and Kruck[2] apparently do not. However, in the description of their calculation procedure, Sarkar and Kruck propose the evaluation of the partial derivatives at the "midpoint" of a series of curves. Presumably, "midpoint" refers to the concentration of the curve nearest the mean concentration of the varied reagent.

Using a procedure that bears some resemblance to the one proposed earlier by Sillén (eq 49, ref 5), Sarkar and Kruck[2] extended Osterberg's relation to the calculation of *any* ΔpX for any general multicomponent equilibria, using relations like eq 3 for each reactant. Thus each reactant would require a separate series of variation titrations.

In eq 3, any L_0 within the ligand variation range may be chosen for the integration to produce pL values as a function of pH. In the series M is kept constant (M_0). However, when the variation is extended to metal components as well, the choice of M_0 and L_0 is no longer arbitrary *only when* one complete data set of pM, pL, and pH values is to be constructed. That is, in the first series, L is varied ($M = M_0$) to produce pL values with integration performed at L_0 (eq 3). In the subsequent series, M is varied to determine pM values. In this series L must be fixed at the L_0 of the first series *and* the integration must be performed at the same M_0 value fixed in the preceding ligand series. The intersection of the two series is at (M_0, L_0), the "common point". Since the plots of H vs. M or L appear *nearly* linear, the above qualification apparently was not appreciated. An uncritical reader may still infer from the presentations of the variation technique that ΔpM and ΔpL are only functions of pH! We hope to show to what extent this is not true.

Analysis of the Variation Technique

How much can the results be affected if one were to disregard the "common point" requirement mentioned above? An examination of past applications[6-9] of the technique to multireactant determinations suggests that perhaps the minor qualification was not always appreciated.[8,9] In the determination of the formation constants of copper(II) diglycyl-L-histidine[8] the "midpoint" values (M_0, L_0) in the metal and ligand variation series are different. (We must point out that in their other applications of the technique[6,7] it appears that the "midpoints" are also the "common points".) We proceeded to test the reported results. Figure 1 shows the calculated titration curves[10] using the reported constants and conditions,[13]

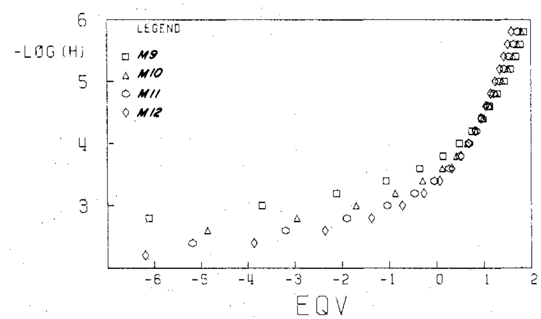

Figure 2. Calculated titration curves for copper acetylacetonate,[15] as a function of the variation of the total metal concentration. EQV refers to moles of base added per mole of copper.

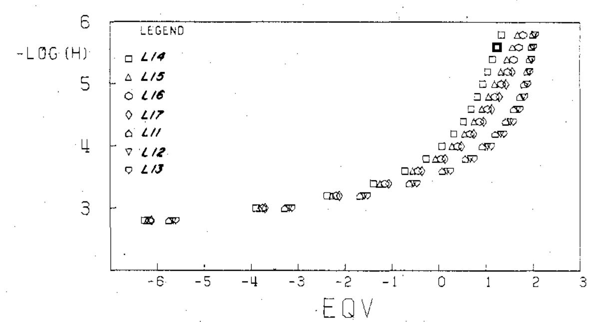

Figure 3. Calculated titration curves for copper acetylacetonate,[15] as a function of the variation of the total ligand concentration. EQV refers to moles of base added per moles of copper.

which should be compared to the observed curves in the upper part of Figure 2 in ref 8. Two minor differences are noted. There is a clearly discernible equivalence point around pH 6.2 in the observed titration curve, which is not substantiated by the constants. Also, the calculated curves nearly coalesce at pH 11, whereas the observed curves do not.[14] We could not conclude with certainty that the "common point" requirement was the source of these discrepancies.

In order to test the "common point" requirement more reliably, we next proceeded entirely with computer-generated data.[18] For our purpose, we chose to use a relatively simple system, that of copper(II) acetylacetonate, whose formation constants are reliably known.[15] Table II lists the conditions of variation. Figures 2 and 3 show typical titration curves for metal and ligand variation series, respectively.

The conditions we proceeded to test involved variation of metal and ligand over a small interval about a common point,

Table II. Synthetic Data for Copper Acetylacetonate Complexes[a]

series A				series B				series C[d]			
calcn no.	M, mM	L, mM	variation	calcn no.	M, mM	L, mM	variation	calcn no.	M, mM	L, mM	variation
M-1	0.75	3.00	metal variation with small interval	M-6[c]	0.25	20.0	metal variation with large ligand excess	M-9	0.25	2.00	metal variation
M-2	0.90	3.00		M-7	0.50	20.0		M-10	0.50	2.00	
M-3[b]	1.00	3.00		M-8	0.75	20.0		M-11	0.75	2.00	
M-4	1.10	3.00						M-12	1.00	2.00	
M-5	1.25	3.00		L-11	0.25	10.0	ligand variation with large ligand excess				
				L-12	0.25	15.0		L-14	0.25	0.50	ligand variation
L-1	1.00	2.75	ligand variation with small interval	L-13[c]	0.25	20.0		L-15	0.25	1.00	
L-2	1.00	2.90						L-16	0.25	1.50	
L-3[b]	1.00	3.00						L-17	0.25	2.00	
L-4	1.00	3.10									
L-5	1.00	3.25									
L-6	1.00	2.00	ligand variation with large interval								
L-7[b]	1.00	3.00									
L-8	1.00	4.00									
L-9	1.00	6.00									
L-10	1.00	8.00									

[a] The synthetic titration curves were calculated for solution volumes of 30 mL, using base titrant concentration of 1 M, 25 °C, 0.1 M ionic strength, using the reported constants[15] $[LH]/[L][H] = 10^{8.82}$, $[ML]/[M][L] = 10^{8.16}$, and $[ML_2]/[ML][L] = 10^{6.60}$. All calculations were performed with the computer program STBLTY.[11] [b] Common point for series A: $(M_0, L_0) = (1 \times 10^{-3}$ M, 3×10^{-3} M). [c] Common point for series B (2.5×10^{-4} M, 2×10^{-2} M). [d] In series A and B, H vs. M or L was fitted with a parabola, while in series C, a linear fit was used.

Table III. Slopes

calcn no.	$(\partial H/\partial M)_{L,h}$ pH 3	pH 4	pH 5
M-1	−0.382	−0.782	−1.404
M-2	−0.368	−0.802	−1.300
M-3	−0.358	−0.816	−1.231
M-4	−0.349	−0.829	−1.161
M-5	−0.334	−0.850	−1.057
M-6	−0.923	−1.173	−1.848
M-7	−0.919	−1.362	−1.979
M-8	−0.916	−1.552	−2.111

calcn no.	$(\partial H/\partial L)_{M,h}$ pH 3	pH 4	pH 5
L-1	0.917	0.890	0.825
L-2	0.921	0.878	0.819
L-3	0.923	0.871	0.815
L-4	0.925	0.863	0.811
L-5	0.929	0.852	0.805
L-6	0.910	0.884	0.813
L-7	0.920	0.899	0.846
L-8	0.929	0.914	0.879
L-9	0.948	0.944	0.946
L-10	0.968	0.974	1.012
L-11	0.994	1.005	0.977
L-12	0.996	0.979	0.992
L-13	0.998	0.952	1.007

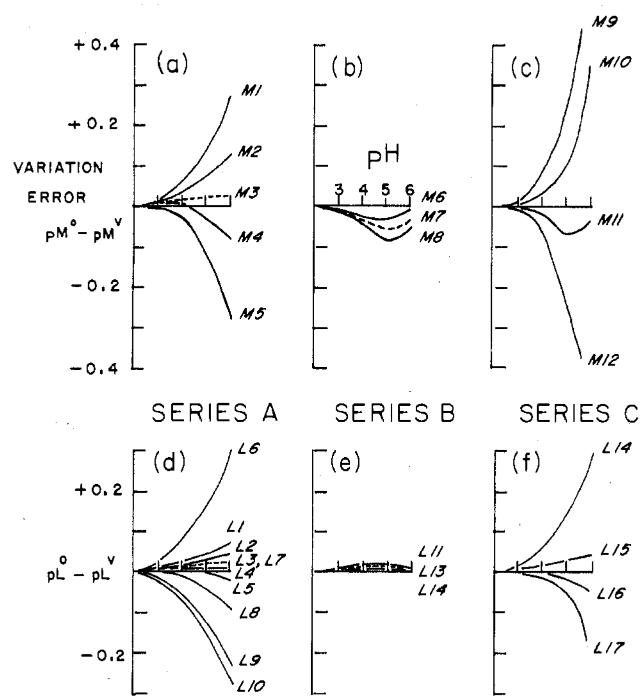

Figure 4. Variation errors (see text) for the copper acetylacetonate system. The calculation conditions are identified in Table I. The dashed curves refer to the "common point" errors.

with only a slight excess of ligand over the amount of metal present (series A). The plots of H vs. M or L at constant pH were fitted quadratically to obtain the slopes (Table III). The other series (series B) contained a very large ligand excess. The slopes were fitted both linearly and quadratically in this category. Finally we tested the effects of linearly fitting the slopes under conditions of only slight ligand excess (series C).

Figure 4 shows the kind of "variation errors" δ in pX we observed for the above three cases. The errors were defined to be the difference between pX^0 calculated in the usual model-dependent manner[12] (using mass balance constraints) assuming the model to be absolutely correct and the pX^v calculated from the variation technique: $\delta = pX^0 - pX^v$. In each of the δ plots in Figure 4 we calculated slopes at the "common point" and applied the resultant ΔpX values to all other non-common-point data sets, using the appropriately different starting values pX_1. Figures 5 and 6 show plots of H vs. M and H vs. L, respectively. Table III shows a selection of $(\partial H/\partial X)$ values under a variety of conditions.

The error trends can be summarized in the following observations. There are two kinds of errors present. One kind is related to δ's associated with the common-point curves, which should ideally have no errors. These amount to only 0.05 pX unit at pH 6, under the chosen conditions. We relate these δ's to the accumulation of systematic, principally round-off, errors in the variation method, where we used a simple Simpson's integration procedure with an interval of 0.2 pH and where we used a quadratic fitting function for (H, X) slopes. The errors observed amount to a loss of approximately 0.002 pX unit/integration interval. This should emphasize the need for extremely accurate data over a sufficiently broad region of total concentrations in order to apply the technique successfully to real systems.

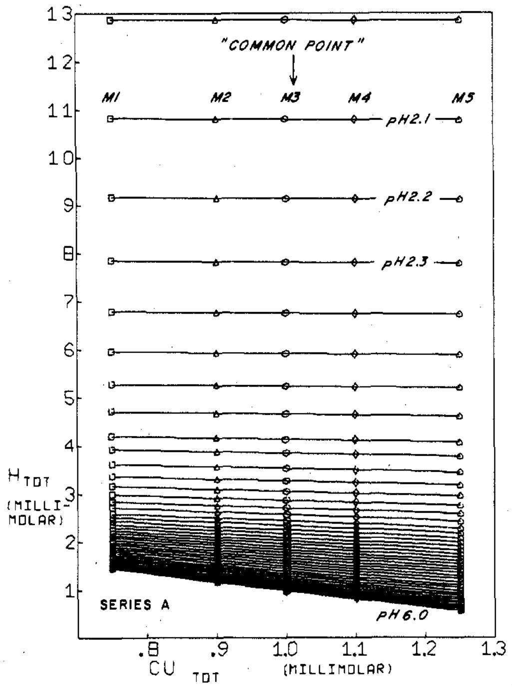

Figure 5. H vs. M isohydric plots for copper acetylacetonate. Table I identifies conditions. Table II contains selected values of $(\partial H/\partial M)_{L,h}$.

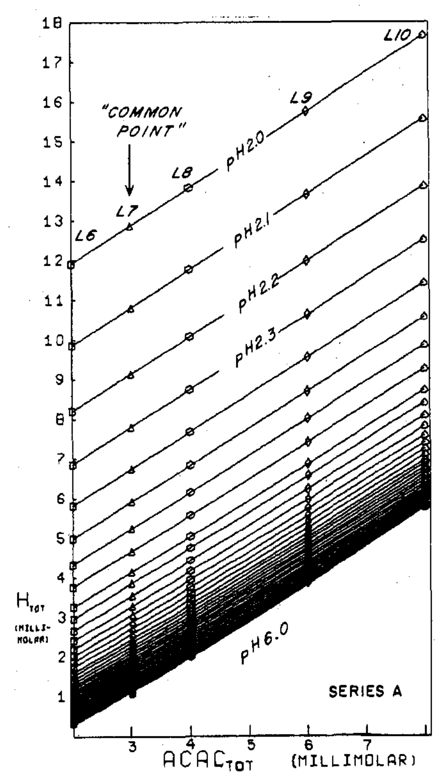

Figure 6. H vs. L isohydric plots for copper acetylacetonate. Table I identifies conditions. Table II contains selected values of $(\partial H/\partial L)_{M,h}$.

The other types of errors, the dispersion about the common point curve, is more interesting. In general, these errors are larger than the integration errors—up to 0.6 pX unit. (One may note that an error of this magnitude in pH in a buffer region such as pH 12 can cause the refinement of constants sensitive to that region to diverge.) In general, the pL errors are slightly smaller than pM errors (compare δ curves, Figure 4c vs. 4f). The higher the ligand excess, the smaller the errors (Figure 4b,e). Finally, the largest errors occur when one linearly fits H vs. X, as in series C. Whether or not one linearly fits the curves under conditions of a large ligand excess (series B) makes practically no difference on the errors. These observations are related to the extent curves in (H, X) plots, such as in Figures 5 and 6, deviate from linearity. The deviation becomes larger when the pH is higher and when the L/M ratio is small.

In summary, the need to evaluate a complex set of pX values at a common point becomes apparent from the above observations. At this point we proceed to a more general presentation of the variation technique.

General Variational Relations

For each point, the equilibrium concentrations of the species present in solution, including polynuclear and mixed ligand–hydroxy species, are defined by the three mass balance equations

$$M(m,l,h) = m + \sum_{j=1}^{N} e_{mj}C_j \tag{4}$$

$$L(m,l,h) = l + \sum e_{lj}C_j \tag{5}$$

$$H(m,l,h) = h + \sum e_{hj}C_j - K_w'/h \tag{6}$$

(j is an index over all the N associated species). The partial derivative relations deduced from these equations

$$(\partial M/\partial \ln l)_{m,h} = (\partial L/\partial \ln m)_{l,h} = \sum e_{mj}e_{lj}C_j \tag{7}$$

$$(\partial M/\partial \ln h)_{m,l} = (\partial H/\partial \ln m)_{h,l} = \sum e_{mj}e_{hj}C_j \tag{8}$$

$$(\partial L/\partial \ln h)_{m,l} = (\partial H/\partial \ln l)_{m,h} = \sum e_{lj}e_{hj}C_j \tag{9}$$

are easily demonstrated with the aid of eq 2. Note that $(\partial M/\partial l)_{m,h} \neq (\partial L/\partial m)_{l,h}$, etc. By choosing as variables the logarithms of the free reactants, the Jacobian matrix (see Table I), $\mathbf{J}[(M, L, H)/(\ln m, \ln l, \ln h)]$, becomes symmetric. One consequence of this is that there exists an *exact* differential[16] of the form $M \, d \ln m + L \, d \ln l + H \, d \ln h$. Sillén's[5] eq 49 deals with this in greater detail. Again, any number of metal or ligand components can be treated by corresponding additional mass balance equations. In a manner proposed by Hedström[4] for a two-component system, we can convert eq 7–9 into the form of unit Jacobian determinants[16] as

$$J\left(\frac{M, \ln m, \ln h}{\ln l, L, \ln h}\right) = 1 \tag{10}$$

$$J\left(\frac{L, \ln l, \ln m}{\ln h, H, \ln m}\right) = 1 \tag{11}$$

$$J\left(\frac{H, \ln h, \ln l}{\ln m, M, \ln l}\right) = 1 \tag{12}$$

The explicit expression for eq 10 is matrix 10′. One notes

$$\begin{vmatrix} \left(\dfrac{\partial M}{\partial \ln l}\right)_{L,h} & \left(\dfrac{\partial M}{\partial L}\right)_{l,h} & \left(\dfrac{\partial M}{\partial \ln h}\right)_{l,L} \\ \left(\dfrac{\partial \ln m}{\partial \ln l}\right)_{L,h} & \left(\dfrac{\partial \ln m}{\partial L}\right)_{l,h} & \left(\dfrac{\partial \ln m}{\partial \ln h}\right)_{l,L} \\ \left(\dfrac{\partial \ln h}{\partial \ln l}\right)_{L,h} & \left(\dfrac{\partial \ln h}{\partial L}\right)_{l,h} & \left(\dfrac{\partial \ln h}{\partial \ln h}\right)_{l,L} \end{vmatrix} \tag{10'}$$

that h in (10), m in (11), and l in (12) are held constant. It should be apparent that Hedström's unit Jacobian is valid for any number of components, provided that no more than two components are effectively independent. Adding constant variables does not alter the determinant from unity. Thus

$$1 = J\left(\frac{X, \ln x}{\ln y, Y}\right) = J\left(\frac{X, \ln x, A}{\ln y, Y, A}\right) = J\left(\frac{X, \ln x, A, B}{\ln y, Y, A, B}\right) = \ldots \quad (13)$$

where the added variables A and B are held constant. This is essentially the basis of Osterberg's application of Hedström's equation to a three-component system, to obtain from the Jacobian the relation

$$\left(\frac{\partial \ln l}{\partial \ln h}\right)_{M,L} = -\left(\frac{\partial H}{\partial L}\right)_{M,h} \quad (14)$$

which reduces to eq 3. Thus using (13) we can increase the number of unit Jacobians to six, which is the number of variables (M, L, H, ln m, ln l, ln h), both dependent and independent, which we consider in (4)–(6):

$$J\left(\frac{M, \ln m, H}{\ln l, L, H}\right) = 1 \quad (15)$$

$$J\left(\frac{L, \ln l, M}{\ln h, H, M}\right) = 1 \quad (16)$$

$$J\left(\frac{H, \ln h, L}{\ln m, M, L}\right) = 1 \quad (17)$$

The proof for (10)–(12) has its basis in the relations (7)–(9). The proof for (15)–(17) can be procured from Sillēn's[5] eq 49.

Hedström showed that such unit Jacobians are extremely useful in deriving new partial derivative expressions, especially of (implicit) functions such as $m(M, L, H)$ or the like, which cannot in general be stated explicitly. To illustrate this, we shall derive the corresponding equation for ΔpM (M_0,L_0) analogous to (3). By utilizing the chain rule for Jacobians,[16] we can restate (17) in terms of any three independent variables x, y, z as

$$J\left(\frac{H, \ln h, L}{x, y, z}\right) = J\left(\frac{\ln m, M, L}{x, y, z}\right) \quad (18)$$

By choosing the variables M, L, ln h, we have

$$\begin{vmatrix} \left(\frac{\partial H}{\partial M}\right)_{L,h} & \left(\frac{\partial H}{\partial L}\right)_{M,h} & \left(\frac{\partial H}{\partial \ln h}\right)_{M,L} \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{vmatrix} = \begin{vmatrix} \left(\frac{\partial \ln m}{\partial M}\right)_{L,h} & \left(\frac{\partial \ln m}{\partial L}\right)_{M,h} & \left(\frac{\partial \ln m}{\partial \ln h}\right)_{M,L} \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{vmatrix} \quad (I)$$

which reduces to

$$\left(\frac{\partial \ln m}{\partial \ln h}\right)_{M,L} = -\left(\frac{\partial H}{\partial M}\right)_{L,h} \quad (19)$$

or

$$\Delta \mathrm{pM}\ (M_0, L_0) = \mathrm{pM}_2 - \mathrm{pM}_1 = \left[\int_{\mathrm{pH}_2}^{\mathrm{pH}_1} \left(\frac{\partial H}{\partial M}\right)_{L,h} \mathrm{dpH}\right]_{M_0} \quad (20)$$

This is McBryde's[3] eq 17. Other useful relations can be obtained similarly. For the six variables M, L, H, m, l, and h there are 20 choices for three independent variables x, y, and z. Some of these choices, when combined with the unit Jacobians (eq 10–12 and 15–17), lead to redundant results. The particular choice is dictated by what one can experimentally measure. Once a useful triplet can be decided on, any one of the unit Jacobians (10)–(12), (15)–(17) can be rearranged in the form of (18). Thus equations similar to (3) and (20) can be obtained.

Applications of the Jacobian Matrix to Equilibrium Calculations

One least-squares procedure[11] for the refinement of formation constants β_j calls for minimization of the differences between observed pHs and those calculated from an assumed set of constants. In the normal equations, partial derivatives (∂pH/∂ log β_j) are required. These can be calculated numerically but such a procedure requires a considerable computational effort. If one recognizes that pH is also a function of the total concentrations, one can state

$$\left(\frac{\partial \mathrm{pH}}{\partial \log \beta_j}\right)_{\beta_{k\neq j}} = \left(\frac{\partial \mathrm{pH}}{\partial M}\right)_{L,H}\left(\frac{\partial M}{\partial \log \beta_j}\right)_{\beta_{k\neq j},L,H} + \left(\frac{\partial \mathrm{pH}}{\partial L}\right)_{M,H}\left(\frac{\partial L}{\partial \log \beta_j}\right)_{\beta_{k\neq j},M,H} + \left(\frac{\partial \mathrm{pH}}{\partial H}\right)_{M,L}\left(\frac{\partial H}{\partial \log \beta_j}\right)_{\beta_{k\neq j},M,L} \quad (21)$$

The partial derivatives of the explicit functions on the right side of eq 21 are easily evaluated. For example, $(\partial L/\partial \log \beta_j)_{\beta_{k\neq j}} = 2.303 e_{lj} C_j$. The evaluation of the implicit function derivatives (∂pH/∂X) is less direct.

One needs to set up the Jacobian matrix $\mathbf{J}[(M, L, H)/(\ln m, \ln l, \ln h)]$ (see Table I) which linearly relates dX to d ln x (eq 22). This matrix is symmetric and its elements are easily

$$\begin{pmatrix} \mathrm{d}M \\ \mathrm{d}L \\ \mathrm{d}H \end{pmatrix} = \mathbf{J}\begin{pmatrix} \mathrm{d} \ln m \\ \mathrm{d} \ln l \\ \mathrm{d} \ln h \end{pmatrix} \quad (22)$$

evaluated, as shown in (24). In fact, this matrix is used to calculate pM and pL values by the nonvariational methods.[11,12] In the process, its inverse is computed.

It is a remarkable fact that the elements of the inverse matrix are precisely the partial derivatives of the implicit functions that we need to compute (∂pH/∂ log β_j) and are given by (23)–(25).

$$\begin{pmatrix} \left(\frac{\partial M}{\partial \ln m}\right)_{l,h} & \left(\frac{\partial M}{\partial \ln l}\right)_{m,h} & \left(\frac{\partial M}{\partial \ln h}\right)_{m,l} \\ \left(\frac{\partial L}{\partial \ln m}\right)_{l,h} & \left(\frac{\partial L}{\partial \ln l}\right)_{m,h} & \left(\frac{\partial L}{\partial \ln h}\right)_{m,l} \\ \left(\frac{\partial H}{\partial \ln m}\right)_{l,h} & \left(\frac{\partial H}{\partial \ln l}\right)_{m,h} & \left(\frac{\partial H}{\partial \ln h}\right)_{m,l} \end{pmatrix}^{-1} \quad (23)$$

$$= \begin{pmatrix} m + \sum_{j=1}^{N} e_{mj}^2 C_j & \Sigma e_{mj} e_{lj} C_j & \Sigma e_{mj} e_{hj} C_j \\ \Sigma e_{mj} e_{lj} C_j & l + \Sigma e_{lj}^2 C_j & \Sigma e_{lj} e_{hj} C_j \\ \Sigma e_{mj} e_{hj} C_j & \Sigma e_{lj} e_{hj} C_j & h + \frac{K_w'}{h} + \Sigma e_{hj}^2 C_j \end{pmatrix}^{-1} \quad (24)$$

$$= \begin{pmatrix} \left(\frac{\partial \ln m}{\partial M}\right)_{L,H} & \left(\frac{\partial \ln m}{\partial L}\right)_{M,H} & \left(\frac{\partial \ln m}{\partial H}\right)_{M,L} \\ \left(\frac{\partial \ln l}{\partial M}\right)_{L,H} & \left(\frac{\partial \ln l}{\partial L}\right)_{M,H} & \left(\frac{\partial \ln l}{\partial H}\right)_{M,L} \\ \left(\frac{\partial \ln h}{\partial M}\right)_{L,H} & \left(\frac{\partial \ln h}{\partial L}\right)_{M,H} & \left(\frac{\partial \ln h}{\partial H}\right)_{M,L} \end{pmatrix} \quad (25)$$

That is, for $\mathbf{K} = \mathbf{J}^{-1}$

$$\begin{pmatrix} \mathrm{d}\ln m \\ \mathrm{d}\ln l \\ \mathrm{d}\ln h \end{pmatrix} = \mathbf{K} \begin{pmatrix} \mathrm{d}M \\ \mathrm{d}L \\ \mathrm{d}H \end{pmatrix} \qquad \text{(II)}$$

A more general statement of eq 21 thus becomes

$$\left(\frac{\partial \mathrm{pX}_i}{\partial \log \beta_j} \right)_{\beta_{k \neq j}} = -\sum_{t=1}^{3} K_{it} e_{tj} C_j \qquad (26)$$

This simple relationship proves to be extremely useful and is a substantial shortcut in the least-squares refinement of equilibrium data.

Conclusion

The variation techniques presented by Osterberg,[1] Sarkar and Kruck,[2] and McBryde[3] are powerful extensions of the pH titration experiment, particularly for equilibria involving polymeric species. We have presented a completely general mathematical basis for these techniques to multicomponent systems. Very useful relationships involving partial derivatives were used in the process. One of the relations derived allows for the first time the use of analytical derivatives in the refinement of equilibrium constants. However, the most important task remains the acquisition of data of sufficient accuracy so that these techniques can be successfully applied.[18]

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Crystal and Molecular Structures of Tetrakis(catecholato)hafnate(IV) and -cerate(IV). Further Evidence for a Ligand Field Effect in the Structure of Tetrakis(catecholato)uranate(IV)

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Crystals of the isostructural title compounds, $Na_4[M(O_2C_6H_4)_4]\cdot 21H_2O$ (M = Hf, Ce), have been obtained from basic aqueous solutions and examined by X-ray diffraction, by using counter data. Previously a small structural distortion of the analogous uranium complex was observed which leads to a difference in metal–oxygen bond lengths of the A and B sites of the coordination polyhedron (trigonal-faced dodecahedron, D_{2d} molecular symmetry) formed by the catechol ligands. The present results on the undistorted cerium complex, in conjunction with previous results on the thorium compound (which is also undistorted), eliminate explanations based on differences in metal ionic radius since that of U(IV) is between those of Th(IV) and Ce(IV). The results reported here thus support earlier suggestions that the distortion observed for the uranium complex is attributable to a small ligand field effect of the two 5f electrons of U(IV). Ionic radius considerations alone do not lead to structural distortion until M = Hf, which has the smallest ionic radius of the four metals examined. Examination of the remarkably stable cerium complex, which is deep red (λ_{max} 517 nm; ϵ 2350), has shown this complex to be diamagnetic, militating against a cerium(III)–(semiquinone)tris(catecholato) formulation and in favor of a cerium(IV)–tetrakis(catecholato) description. The Ce(IV) complex is found by cyclic voltammetry to undergo a quasi-reversible one-electron reduction (in strongly basic solution with excess catechol) with $E_f = -692$ mV vs. SCE. The observed formal potential of the $Ce^{IV/III}(cat)_4$ couple, taken with the corresponding Ce(IV)/Ce(III) standard potential, implies that the tetrakis formation constants (i.e., K for $M^{n+} + 4cat^{2-} = [M(cat)_4]^{n-8}$) for Ce(IV) and Ce(III) differ by a factor of 10^{36}. Both the colorless Hf and the red Ce complexes have $\bar{4}$ site symmetry in the space group $I\bar{4}$, $Z = 2$ (with $a = 14.486$ (1) Å, $c = 9.984$ (1) Å for Hf; $a = 14.649$ (2) Å, $c = 9.976$ (1) Å for Ce). For Hf the 4549 independent data with $F_o^2 > 3\sigma(F_o^2)$ converged to unweighted and weighted R factors of 3.3 and 4.5%, respectively, upon full-matrix least-squares refinement with anisotropic thermal parameters for all nonhydrogen atoms. The corresponding R factors for the Ce complex are 4.3 and 5.3%, respectively, on the basis of 3106 independent data. Ring O–M–O angles of 71.5 (1)° for Hf and 68.3 (1)° for Ce are found, with M–O bond lengths of 2.194 (3) and 2.220 (3) Å for Hf, compared with 2.357 (4) and 2.362 (4) Å for Ce.

Introduction

Although the presence of ligand field effects has been suggested for actinide complexes, definitive recognition of such effects has been hampered by the complex interplay of 5f, 6d, and 7s orbitals for the actinides and the lack of a suitable isostructural series to preclude changes in crystal packing forces.

Previous investigations for actinide-specific chelators analogous to microbial iron transport chelates led us to examine the structures of the tetrakis(catecholato) complexes

