Direct Calculation of Successive Stability Constants from an Experimental Formation Curve

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After a brief review of the most important pre-computer methods for calculating successive stability constants of mononuclear chelates, J. Bjerrum's "half $\bar{n}$" method is discussed. The refinement by successive approximations is found unnecessary, since direct expressions for the true values are easily obtained.

The determination of successive stability constants of mononuclear complexes has aroused steadily growing interest in the last 25 years. Many of these studies have been undertaken in accordance with the method published in 1941 by J. Bjerrum, "Metal Ammine Formation in Aqueous Solution".[1] J. Bjerrum's studies have given rise to many related methods. Sillén's[2] fundamental work on polynuclear complexes is not treated in the present paper, which deals with mononuclear complexes.

When it is possible to determine the concentration of free metal ion, *e.g.* by potentiometric measurements, extrapolation methods as described by Leden[3] and Fronæus[4] are convenient. Considering a system with the mononuclear complexes MX, MX_2, MX_3......, MX_N, the over-all stability constants are:

$$\beta_i = \frac{[MX_i]}{[M]\cdot[X]^i} \tag{1}$$

The total concentration of metal ions is

$$C_M = [M] + \sum_{i=1}^{N} [MX_i] \tag{2}$$

and of the ligand,

$$C_X = [X] + \sum i\,[MX_i] \tag{3}$$

From eqns. (1) and (2):

$$\frac{C_M - [M]}{[M]\cdot[X]} = F_1([X]) = \beta_1 + \beta_2[X] + \cdots\beta_N[X]^{N-1} \tag{4}$$

Knowledge of the function F_1 ([X]) enables one to determine all the successive stability constants.

According to Leden,[3] F_1 ([X]) is plotted *vs*. [X], and extrapolating to [X] = 0, the stability constant β_1 is determined. The subtraction of β_1 from F_1 ([X]) and division by [X] enables one to determine β_2 by a new extrapolation, *etc*. Successive approximations may be used in the determination of the free ligand concentration.

The most frequently used methods of calculating stability constants from experimentally obtained data are based on the "formation function" $\bar{n}$. This function is defined as the average number of ligands X bound to each central group M (*e.g.* metal). The step stability constants are

$$K_i = \frac{[MX_i]}{[X]\cdot[MX_{i-1}]} = \frac{\beta_i}{\beta_{i-1}} \tag{5}$$

and the formation function $\bar{n}$ is

$$\bar{n} = \frac{C_X - [X]}{C_M} = \frac{\sum i[MX_i]}{[M] + \sum [MX_i]} \qquad \text{or} \tag{6}$$

$$\bar{n} = \frac{K_1[X] + 2K_1K_2[X]^2 + \dots + NK_1K_2\dots K_N[X]^N}{1 + K_1[X] + K_1K_2[X]^2 + \dots K_1K_2\dots K_N[X]^N} \tag{6a}$$

By plotting $\bar{n}$ *vs* $-\log[X]$, the "formation curve" is obtained.

$$\text{As X ([X])} = \int_0^{[X]} \frac{\bar{n}}{[X]} \; \mathrm{d}([X]) = 1 + \beta_1[X] + \beta_2[X]^2 + \dots \beta_N[X]^N \tag{7}$$

an extrapolation method very similar to the one proposed by Leden (see eqn. (1)) may be applied to determine the successive stability constants.[4] The method may be extended for use with mixed complexes.

Graphical methods are frequently used. For example, if $N = 2$ the following expression is represented by a straight line:

$$\frac{\bar{n}}{(\bar{n}-1)[X]} = \frac{(2-\bar{n})[X]}{(\bar{n}-1)} \times K_1K_2 - K_1 \tag{8}$$

with the slope $K_1 \times K_2$ and the intercept $-K_1$. These constants may thus be found by the "method of least squares".

According to J. Bjerrum,[1] the formation function may be rewritten from eqn. 6 as follows:

$$\sum_{n=0}^{N} (\bar{n}-n) \; [X]^n \cdot \beta_n = 0 \tag{9}$$

Each point on the formation curve provides in principle an equation to determine the constants, and it is thus possible to determine all the stability constants from N different points on the curve. Such calculations are very tedious when N is large, and the points on the formation curve selected for these calculations may be inconsistent. Bjerrum has therefore proposed approximation methods

in the calculations. Two methods are applicable. The first method makes use of the concentration of ligand at $\bar{n} = N/2$ and the slope of the formation curve at $\bar{n} = N/2$ to determine the constants. The second method utilizes the fact that in solutions with $\bar{n} = n - \frac{1}{2}$, the concentrations of the complexes MX_{n-1} and MX_n are equal when the stability constants are so widely different that only these two complexes are present in appreciable concentrations. This makes a determination of the constants possible, since

$$K_n^\circ = [X]^{-1}\bar{n}_{=n-1/2} \tag{10}$$

may be taken as the approximate constant.

The first method is preferred when K_n and K_{n+1} are nearby equal, the second one is applicable only when $K_n >> K_{n+1}$, as no interaction with other complexes occurs in that case. With the ratio $K_n/K_{n+1} > 10^4$ the constants found from the last method may be used without correction; for lower ratios the true constants are found by multiplying the approximate ones by correction factors. When the preliminary constants are known, the correction term is found from eqn. 9:

$$K_i = \frac{1}{[X]_{\bar{n} = n-1/2}} \quad \frac{1 + \sum_{t=1}^{n-1} (1 + 2t)/[X]^t \cdot K_1....K_t}{1 + \sum_{t=1}^{N-n} (1 + 2t) \cdot [X]^t \cdot K_{n+1}....K_{n+t}} \tag{11}$$

For example for $N = 2$:

$$K_1 = \frac{1}{[X]_{\bar{n} = 1/2}} \cdot \frac{1}{1 + 3K_2[X]_{\bar{n} = 1/2}} \tag{12}$$

and

$$K_2 = \frac{1}{[X]_{\bar{n} = 3/2}} \cdot \left(1 + \frac{3}{K_1[X]_{\bar{n} = 3/2}}\right) \tag{13}$$

Rough knowledge of K_1 and K_2 enables one to refine the values by means of successive approximations. If the constants are not too close together these equations yield correction factors of unity after very few cycles.

Table 1. Stability constants found from "half $\bar{n}$ values" and refined by successive approximations until the ratio of the values obtained between two cycles did not exceed 0.001.

| No. of cycles necessary	$[X]_{\bar{n}=\frac{1}{2}}$ $\times 10^6$	$[X]_{\bar{n}=\frac{3}{2}}$ $\times 10^6$	$\dfrac{[X]_{\bar{n}=\frac{3}{2}}}{[X]_{\bar{n}=\frac{1}{2}}}$	Starting values		"refined"		"true"	
				K_1° $\times 10^{-6}$	K_2° $\times 10^{-6}$	K_1	K_2	K_1 $\times 10^{-6}$	K_2 $\times 10^{-6}$
4	0.125	1.000	8.000	8.000	1.000	5.000×10^6	1.600×10^6	5.000	1.600
5	0.143	1.000	7.000	7.000	1.000	4.000×10^6	1.750×10^6	4.000	1.724
5	0.167	1.000	6.000	6.000	1.000	3.001×10^6	2.000×10^6	2.980	2.010
7	0.200	1.000	5.000	5.000	1.000	2.001×10^6	2.500×10^6	2.000	2.500
11	0.250	1.000	4.000	4.000	1.000	1.001×10^6	3.997×10^6	1.000	4.000
17	0.286	1.000	3.500	3.500	1.000	5.013×10^5	6.984×10^6	0.4960	7.040
998	0.333	1.000	3.000	3.000	1.000	1.499×10^3	2.003×10^9	0	∞
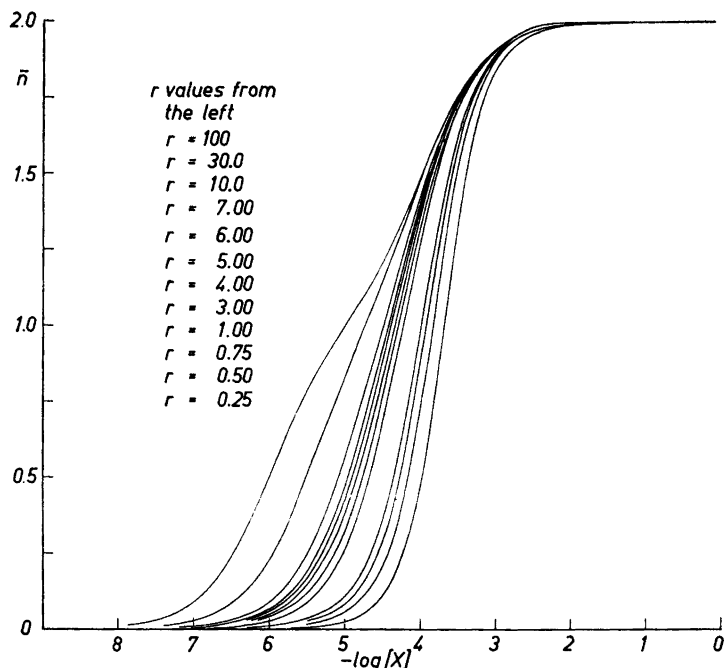
Fig. 1. Formation curves for systems with $N = 2$. The curves represent systems with $K_1 = 1.00 \times 10^4 \times r$ and $K_2 = 1.00 \times 10^4$.

A computer programme was set up to make such refinements. The cycles were repeated until the ratio of the values in two succeeding cycles was lower than 0.001 for all the constants. This corresponds to deviations much lower than those due to experimental errors. The calculations were tested in case of $N = 2$. The $[X]_{\bar{n} = 1/2}$; $[X]_{\bar{n} = 3/2}$ ratio was first eight; with successive decreases in the ratio, the results were as is given in Table 1. When the ratio is small many cycles are necessary and erroneous results may be obtained even in the case when the ratio of the constants obtained from one cycle to another is very small.

A direct expression for the convergence value of the successive approximations is easily found directly from (6a), and from the refinement formulas 12 and 13:

$$K_1 = \frac{[X]_{\bar{n} = 3/2} - 3[X]_{\bar{n} = 1/2}}{[X]_{\bar{n} = 1/2} \cdot [X]_{\bar{n} = 3/2}} = \frac{1}{[X]_{\bar{n} = 1/2}} - \frac{3}{[X]_{\bar{n} = 3/2}} \qquad (14)$$

and

$$K_2 = \frac{1}{[X]_{\bar{n} = 3/2} - 3[X]_{\bar{n} = 1/2}} \qquad (15)$$

In Fig. 1, n is plotted $vs.$ $-\log [X]$ for systems with $N = 2$. In all examples given, K_2 is 1.00×10^4, and the curves represent plots where the ratio K_1/K_2

Table 2. Step stability constants found from the $\bar{n}$ plots in Fig. 1.

log $K° = -$log [X]		log K found		theoretical		
$n = 0.5$	$n = 1.5$	log K_1	log K_2	log K_1	log K_2	r
4.00	3.40	3.39	4.01	3.40	4.00	0.25
4.18	3.53	3.70	4.01	3.70	4.00	0.50
4.29	3.59	3.89	3.99	3.88	4.00	0.75
4.37	3.64	4.01	4.00	4.00	4.00	1.00
4.69	3.79	4.48	4.00	4.48	4.00	3.00
4.77	3.83	4.59	4.01	4.60	4.00	4.00
4.85	3.85	4.70	4.00	4.70	4.00	5.00
4.91	3.86	4.78	3.99	4.78	4.00	6.00
4.97	3.88	4.85	4.00	4.85	4.00	7.00
5.10	3.91	5.01	4.00	5.00	4.00	10.00
5.52	3.97	5.48	4.01	5.48	4.00	30.00
6.01	3.98	6.00	3.99	6.00	4.00	100

($= r$) is between 0.25 and 100. The theoretical K_1 is therefore $1.00 \times 10^4 \times r$. Table 2 shows the values calculated, first by means of the "half $\bar{n}$ method", by refinements with (12) and (13), and then directly with (14) and (15). The direct method is applicable independent of the ratio $K_1°/K_2°$.

Conditions for the divergence of the convergence formulas. A correction chart is given in Fig. 2. If $[X]_{\bar{n} = 3/2} \leq 3[X]_{\bar{n} = 1/2}$ (which is never the case), then $K_2 \leq 0$, which corresponds to divergence when formulas 14 and 15 are used. The chart, or formulas 14 and 15, show that the preliminary constants are always separated to a ratio higher than 3, that is to a difference in the

Fig. 2. Nomogram for correction of the preliminary stability constants found with the "half $\bar{n}$ method" for systems with $N = 2$. Log K_2 is found on scale B when a straight line is drawn between log K_2 on scale A and log $K_1°$ at scale C. Log K_1 is then found on scale C at the intersection between the straight line from log $K_2°$ on scale B and through the intersecting point of L and the line used in the determination of log K_2. For constants of inconvenient magnitude, equal values may be subtracted on all scales. Example, log $K_1° = 4.10$ and log $K_2° = 3.33$. The intersection between scale B and the line from $(3.33 - 2)$ on A and $(4.10 - 2)$ on C gives log $K_2 = 3.66$ (or $1.66 + 2$) on scale B. The other line on the figure from $(3.33 - 2)$ on B gives log $K_1 = 3.79$ (or $1.79 + 2$) on scale C.
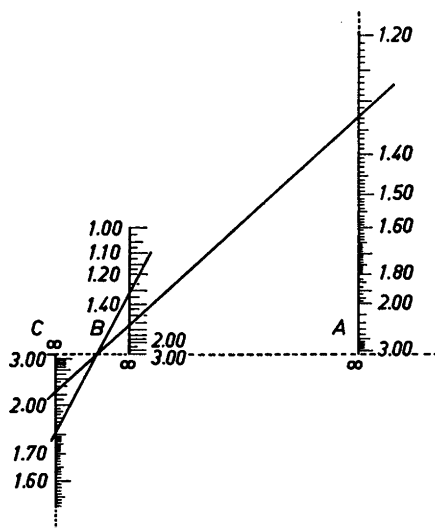
logarithmic values of the preliminary constants larger than log $3 = 0.4771$. This is in contrast to the value 0.4343 reported by Le Grand et al.[5] supposably found from successive approximations. The corrections always make the ratio of the true constants lower than the ratio of the preliminary ones. With an initial ratio of $3.5 + \sqrt{3.25} = 5.3$, the step stability constants become identical.

Systems with $N > 2$. The "extended $\bar{n}$ method" is also applicable to systems with greater complexity than $N = 2$.

In the general case, N points on the formation curve may be used with $\bar{n} = {}^1/_2, {}^3/_2, {}^5/_2.. N - {}^1/_2$. The corresponding $\bar{n}$ and $[X]$ values are inserted into (9) which gives N equations for the N unknown β_N (or K_n).

From the determinant

$$D_0 = \begin{vmatrix} +[X]_{\bar{n}=1/2} & +3[X]^2_{\bar{n}=1/2} & +5[X]^3_{\bar{n}=1/2} & \cdots \\ -[X]_{\bar{n}=3/2} & +[X]^2_{\bar{n}=3/2} & +2[X]^3_{\bar{n}=3/2} & \cdots \\ -3[X]_{\bar{n}=5/2} & -[X]^2_{\bar{n}=5/2} & +[X]^3_{\bar{n}=5/2} & \cdots \\ - - - - & - - - - & - - - - & - - \end{vmatrix} \quad (16)$$

new determinants are made by substituting the numbers: $1 \ 3 \ 5 \ 7 \ ...(2N - 1)$ in column No. i. These determinants are symbolized by D_i. The step stability constants are then given by

$$K_i = D_i/D_{i-1} \quad (17)$$

When $N = 2$, eqn. 17 gives K_1 and K_2 according to eqns. 14 and 15. The formula above enables one to determine the constants directly, but due to experimental errors, the values thus obtained will not be of the highest accuracy. It is preferable to recalculate the constants by means of eqn. 9 using $[X]$ values which correspond to K_1^{-1}, and the $\bar{n}$ from the experimentally obtained formation curve. The values may be recalculated if necessary with the $[X]$ taken to be the new K_i^{-1}, and corresponding $\bar{n}$, and so on.

The method is thus based on calculation of determinants. For example: When $N = 4$, five 4×4 determinants have to be calculated which is easily programmed for a digital computer, and the calculations, even for $N = 15$, are done in few seconds on the Danish GIER computer used by the author. The programme is given in Table 3. After the input of the programme, the number of constants N, followed by the decreasing $[X]_{\bar{n}=1/2}$ values, is written on the typewriter, and the constants are written out by the machine. The $\bar{n}$ values corresponding to concentrations equal to the reciprocal of the constants have then to be written down, and so on.

DISCUSSION

The present method for determining stability constants has the advantage of being very easy to perform, and of requiring no successive refinements. The recalculation of the constants makes optimal conditions possible since $\bar{n}$ values are used which make

$$\frac{\delta^2 K_i}{\delta \bar{n}_i \ \delta[X]_{\bar{n}_i}} = 0 \quad (18)$$

Table 3. Computer programme in Gier Algol for correction of preliminary step stability constants and recalculation at optimal experimental conditions. (The Danish expressions "tromleplads", "til tromle" and "fra tromle" are drum procedures; "tast" is the input procedure; "tryk", "trykvr", "tryktekst", "trykml" and the corresponding "skriv" expressions are output procedures.)

begin integer N; N: = tast; *begin array* M[1:N, 1:N], L[1:N], K[1:N], R[1:N], D[0:N];
integer q, n; *real procedure* Det(A); *array* A; *begin integer* p, i, j, k, imax;
real Diag, DP,S; p: = tromleplads; til tromle(A); S: = 1; *for* k: = 1 *step* 1 *until* N *do*
begin Diag: = abs(A[k,k]); imax: = k; *for* i: = k + 1 *step* 1 *until* N *do*
begin if abs (A[i,k]) > Diag *then begin* Diag: = abs (A[i,k]); imax: = i; *end; end;*
if imax ≠ k *then begin for* i: = k *step* 1 *until* N *do begin* DP: = A[k,i];
A[k,i]: = A[imax, i]; A[imax,i]: = DP; *end* S: = −S; *end;* Diag: = A[k,k]; S: = S×Diag;
if Diag = 0 *then go to* OUT; *for* i: = k + 1 *step* 1 *until* N *do* A[k,i]: = A[k,i]/Diag;
for i: = k + 1 *step* 1 *until* N *do begin* DP: = A[i,k]; *if* DP ≠ 0 *then for* j: = k + 1
step 1 *until* N *do* A[i,j]: = A[i,j] − DP×A[k,j]; *end; end;* OUT: tromleplads: = p;
fra tromle(A); tromleplads: = p; Det: = S; *end* of Det; trykvr; *for* n: = 1 *step* 1
until N *do begin* L[n]: = 2 × n−1; skrvvr; skrvtekst(✗ < −logX = ✗); K[n]: = 10 ↑
(·tast); *end; for* n: = 1 *step* 1 *until* N *do for* q: = 1 *step* 1 *until* N *do* M[n,q]: = (2×
(n−q) + 1) × (K[q]↑n); om: D[0]: = Det(M); *for* n: = 1 *step* 1 *until* N *do begin*
for q: = 1 *step* 1 *until* N *do begin* R[q]: = M[n,q]; M[n,q]: = L[q]; *end*
D[n]: = Det(M); *for* q: = 1 *step* 1 *until* N *do* M[n,q]: = R[q]; *end; for* n: = 1
step 1 *until* N *do* R[n]:=D[n]/D[n−1]; trykvr; tryktekst (✗<CONST. WITH ✗);
tryktekst(✗< WITHOUT CORRECTIONS✗); trykvr; *for* n: = 1 *step* 1 *until* N *do*
begin tryktekst(✗<k✗); tryk (✗dd✗, n); tryktekst(✗< = ✗);
tryk(✗d.ddd₁₀ + dd✗, 1/K[n], trykml(4), R[n], trykvr); skrvvr; skrv (✗dd.ddd✗,
0.434294 × ln(R[n])); *end;* tryktekst(✗<NEW CORRECTIONS✗); trykvr; skrvvr;
for q: = 1 *step* 1 *until* N *do* L[q]: = tast; *if* L[1] <0 *then go to* stop;
for n: = 1 *step* 1 *until* N *do for* q: = 1 *step* 1 *until* N *do* M[n,q]: =
(n·L[q]) × (1/R[q]) ↑ n; *go to* om; stop; *end; end;*

The author has not yet succeeded in proving the assumption that eqn. 18 gives $[X]_{\bar{n}_i}^- = 1/K^i$ for systems with $N>2$ but has verified it numerically for a system with $N = 7$. The step stability constants were taken as known and the formation function was calculated. To the $\bar{n}$ found, $\Delta \bar{n} = 0.01$ was added and K_3 was recalculated with the other constants fixed. Then $\Delta K_3/\Delta \bar{n}$
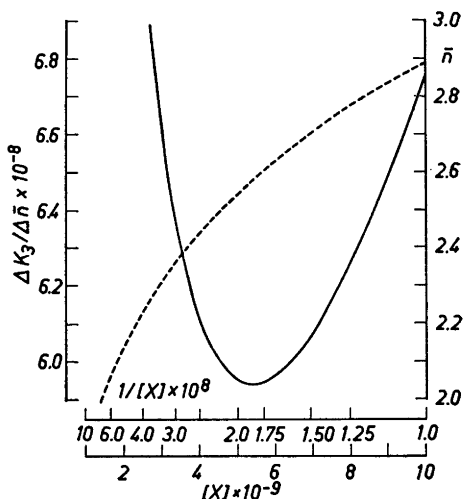

Fig. 3. Plots of $\Delta K_3/\Delta \bar{n}$ (full line) *vs.* [X] for a system with $N = 7$, and step stability constants (from K_1 to K_7): 2×10^{10}, 2.5×10^9, 1.8×10^8, 3.6×10^7, 1.0×10^6, 1.2×10^5 and 1.5×10^4. The dotted line is the formation function. The K_3 is then regarded as a variable and $\Delta K_3/\Delta \bar{n}$ is calculated and is represented by the solid line. ($\Delta \bar{n}$ is 0.01 in these calculations). The function has a minimum at $1/[X] = 1.8 \times 10^8$.

was calculated and plotted vs. [X]. The value of [X] which minimized this function, corresponded with eqn. 18. As found from Fig. 3, $[X]_{\bar{n}_3} = 1/K_3$.

The described method has been tested experimentally by determination of the acid dissociation constants of some polyaminepolycarboxylic acids. The results will be presented in a separate communication.

This method has the disadvantage that only a limited number of the experimental data is used in the calculations, even though the sets of data which give the best results are selected. But the advantage is that with N not too high, the calculation work may be done in a reasonable time without making use of a computer. If a high speed computer is available, methods using all the experimental data may be performed to obtain the best possible values and the standard deviations for the constants.

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