

On Equilibria in Systems with Polynuclear Complex Formation

IV. The Transition from Polynuclear to Mononuclear Products

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The behavior of Z (average number of A bound per B) as a function of $\log a$ and $\log B$ is discussed for a system, where both mononuclear complexes A_tB and polynuclear "core + links" complexes $B(A_tB)_n$ exist. At high values of B , the family of curves $Z(\log a)_B$ are parallel with a constant spacing. With decreasing values of B they approach to a limiting curve $Z(\log a)$, the "mononuclear wall". The transition range from a predominantly polynuclear to a predominantly mononuclear mechanism may be only about two units in $\log B$.

"Normalized projection maps" and numerical methods are given for finding the first or first two mononuclear constants. The corresponding treatment of the function η is indicated.

In our studies of hydrolysis equilibria¹, the data have often indicated the formation of "core + links" complexes, *i. e.* complexes that can be written in the general form $B(A_tB)_n$, where t is a constant and n may have one or several values. For $B = \text{cation}$, and $A = \text{OH}^-$, examples of this type of complex are $\text{UO}_2((\text{OH})_2\text{UO}_2)_n^{2+}$ and $\text{In}((\text{OH})_2\text{In})_n^{(3+n)+}$. The occurrence of such complexes was one reason for treating them rather thoroughly in the papers "AB I"² and "AB II"³; in the following we shall use, as a rule, the notation of these papers. (See "Symbols" below).

When "core + links" complexes of the type $B(A_tB)_n$ predominate, the curves $Z(\log a)_B$ are parallel, and Z (the average number of A bound per B) is a function of (AB I, eqn. 26)

$$x = t \log a + \log B \quad (1)$$

A plot of Z against $\log a^t B$ may thus be used as an experimental test of this type of mechanism; if the correct value of t has been chosen, the points should fall on a single curve, irrespective of the value of B .

In several systems, the data for high values of B are explained by a "core + links" mechanism, within the experimental accuracy, whereas for low values

of B deviations are observed which might be explained by the formation of species richer in A than $B(A_iB)_n$, such as $AB(A_iB)_n$ and $B(A_{i+1}B)_n$.

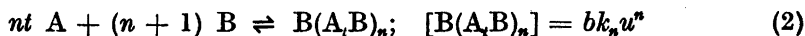
If B is made sufficiently low, one may always expect that the concentrations of *mononuclear complexes* A_iB will become appreciable in comparison with those of polynuclear complexes, and finally predominate completely. The aim of the present paper is to discuss the behavior of the experimental quantities Z and $\eta = \log(B/b^{-1})$ in a transition range where both mononuclear and polynuclear "core + links" complexes exist in comparable amounts, and to indicate methods for the evaluation of data from such a transition range.

Symbols

a, b	concentrations of free A and B
B	total concentration of B
\bar{B}	normalized B (12)
$g(v)$	function for polynuclear complexes (7)
i	number of ligands in mononuclear complex A_iB (3)
k	constant, ratio k_{n+1}/k_n with hypothesis IIIa (18)
k_n	constant, k_1/k in hypothesis IIIa (18)
k_n	equilibrium constant (2)
l	$\beta_i\beta_1^{-1}$ (27)
n	number of links in polynuclear complex $B(A_iB)_n$ (2)
t	number of A in link A_iB
u	auxiliary function, $a^t b$ (2a)
$v = ka^t b$	(6)
X, Y	normalized values for x and y , particularly (13), (14)
x, y	variables determined experimentally, particularly (1), (15)
Z	average number of A bound per B
α	normalized a (10)
β_i	equilibrium constant for mononuclear complexes (3)
$\eta = \log B - \log b$	

General equations

Let us assume that A and B form two series of complexes: polynuclear species $B(A_iB)_n$ and mononuclear species A_iB , and that the equilibrium constants of their formation are k_n and β_i , thus



$$u = a^t b \quad (2a)$$

and



The total concentration of B , and the concentration of A bound to B , will be expressed by

$$B = [B] + \Sigma [A_iB] + \Sigma (n+1) [B(A_iB)_n] = b(1 + \Sigma \beta_i a^i + \Sigma (n+1) k_n u^n) = b10^\eta \quad (4)$$

$$BZ = \Sigma i [A_iB] + \Sigma nt [B(A_iB)_n] = b(\Sigma i \beta_i a^i + t \Sigma n k_n u^n) \quad (5)$$

Introducing from AB II³ the symbols

$$v = ku = ka^t b \quad (6)$$

$$g(v) = \Sigma k_n u^n; \quad v \frac{dg}{dv} = vg' = \Sigma nk_n u^n \quad (7)$$

we obtain from (4) and (5)

$$B = b (1 + \Sigma \beta_i a^i + g + vg') \quad (8)$$

$$BZ = b (\Sigma i \beta_i a^i + tvg') \quad (9)$$

In AB II³, expressions for $g(v)$ have been derived for a few simple hypotheses: I (no soluble complex, precipitate formed), II (a single complex formed, with $n = N$), and III (complexes with all values of n are formed, three different simple assumptions about the k_n). In the following we shall treat the simple cases, where only one or two mononuclear complexes are formed, and shall calculate diagrams for the additional simple assumption that the polynuclear complexity constants follow "hypothesis IIIa"³, with an integer t . On these assumptions it seems possible to explain approximately the experimental data for the hydrolysis of scandium(III)^{4,5} and uranium(IV)⁶. Even in more complicated cases the behavior should be analogous, and a similar mathematical treatment could be applied.

ONLY ONE MONONUCLEAR COMPLEX

If only one mononuclear complex, AB, is formed, all $\beta_i = 0$ except β_1 . To eliminate the constant β_1 we introduce the auxiliary "normalized" variable

$$\alpha = \beta_1 a \quad (10)$$

Then (8) and (9) take the form

$$B = b (1 + \alpha + g + vg'); \quad BZ = b (\alpha + tvg') \quad (8a, 9a)$$

Hence

$$Z = \frac{\alpha + tvg'}{1 + \alpha + g + vg'} \quad (11)$$

Multiplying B by $k \beta_1^{-t}$ we obtain a new function, B , which like Z is a function of v and α only and does not contain the constants k and β_1 (8a, 10, 6):

$$B = B k \beta_1^{-t} = v \alpha^{-t} (1 + \alpha + g + vg') \quad (12)$$

If the constant t and the function $g(v)$ (including constants like k_0 below) are known, one may use (11) and (12) and suitable values of the auxiliary variable v to calculate corresponding values of α and B for a series of fixed values of Z . These figures may be used for plotting projection maps $Y(X)_Z$, for the variables

$$X = \log (B \alpha^t) = \log B + t \log \alpha + \log k = x + \log k \quad (13)$$

$$Y = \log B = \log B + \log k - t \log \beta_1 = y + \log k - t \log \beta_1 \quad (14)$$

As seen from (13) and (14) X and Y are normalized variables^{7,8} corresponding to the experimental variables

$$x = \log B + t \log \alpha; \quad y = \log B \quad (15)$$

Fig. 1 and Fig. 2. Variation of Z with other variables for a system $A-B$ with a single mononuclear complex AB , and polynuclear "core + links" complexes $B(A_nB)_n$, hypothesis IIIa, $k_0 = 5$.

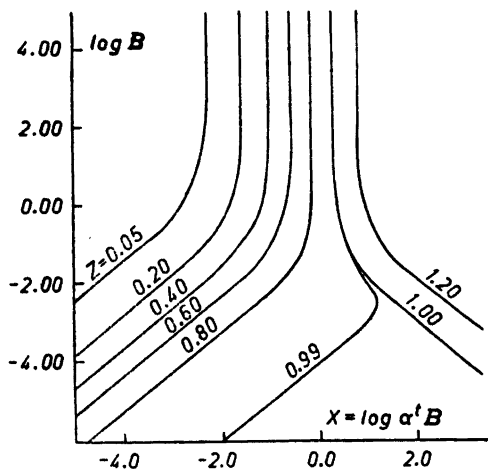


Fig. 1a. Projection map of $Y(X)_Z$, with $Y = \log B$ and $X = \log(\alpha^t B)$.

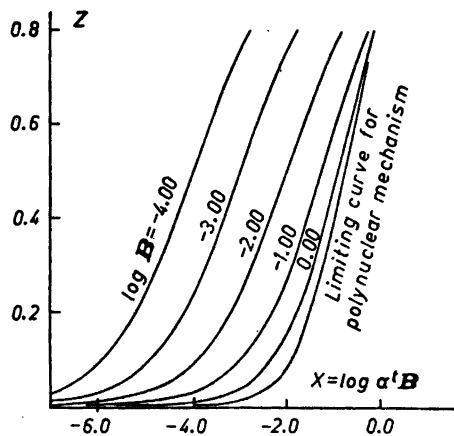


Fig. 1b. Family of curves $Z(X)_B$. For $\log B > 1$, the curves practically coincide with the limiting curve.

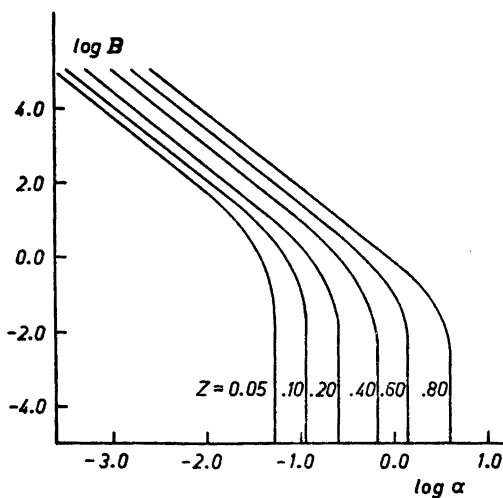


Fig. 2a. Projection map $\log B(\log \alpha)_Z$.

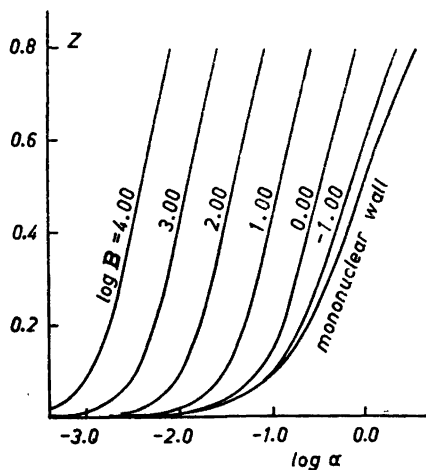


Fig. 2b. Family of curves $Z(\log \alpha)_B$. For $\log B < -1.5$, the curves practically coincide with the limiting curve, the "mononuclear wall".

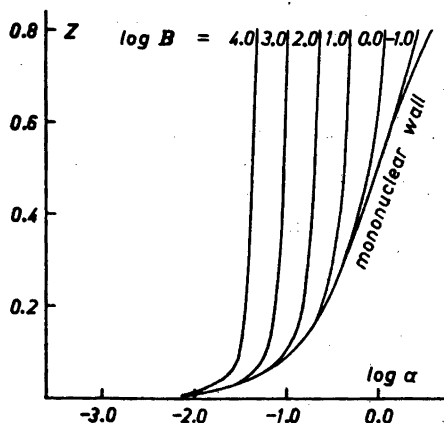


Fig. 3. Family of curves $Z(\log \alpha)_B$ calculated for single mononuclear complex + polynuclear "IIIa" complexes with $t = 3$, $k_0 = 0.06$.

The following formulas are useful for the calculations, (11, 12, 13)

$$\alpha = \frac{Z}{1-Z} (1 + g + v g') - \frac{t v g'}{1-Z} \quad (16)$$

$$X = \log v + \log [1 + g - v g' (t-1)] - \log (1-Z) \quad (17)$$

Diagrams for single mononuclear complex + hypothesis IIIa

In Fig. 1a, a projection map is given of $\log B(X)_Z$ calculated using (13, 14, 16, 17) assuming "hypothesis IIIa"³,

$$k_n = k_0 k^n \quad (18)$$

with $t = 2$ and $k_0 = 5$. These values give a good agreement with the data for scandium(III)^{4,5}.

Hypothesis IIIa with integer t would give (AB II³, eqn. 31)

$$g(v) = k_0 v (1-v)^{-1}; \quad v g'(v) = k_0 v (1-v)^{-2} \quad (18a)$$

The irregular shape of the curves for $Z = 0.99, 1.00$, and 1.20 in Fig. 1a should be disregarded. It is due to the fact that with the reactions assumed, the mononuclear complex can give at most $Z = 1$, whereas with polynuclear complexes, higher values of Z can be achieved. The case of a non-integer t has been treated by Rossotti and Rossotti⁹.

The same values of t and k_0 have been used to construct the diagrams $Z(X)_B$ (Fig. 1b), $\log B(\log \alpha)_Z$ (Fig. 2a), and $Z(\log \alpha)_B$ (Fig. 2b). When considering these diagrams one should remember that the normalized variables $X = \log(\alpha^t B)$, $\log B$, and $\log \alpha$ differ from the experimental variables $x = \log(\alpha^t B)$, $\log B$, and $\log \alpha$, only by constant terms (13, 14, 10).

For high total concentrations B , the polynuclear complexes predominate and Z is a function of x only (vertical lines in upper part of Fig. 1a, limiting curve $Z(X)$ to the right of Fig. 1b, constant spacing in Fig. 2b). For very low

values of B , on the other hand, the polynuclear complexes become negligible in comparison with the mononuclear complexes. Then Z is effectively a function of a only (vertical lines in lower part of Fig. 2a, lines of slope 1 in lower part of Fig. 1a). The limiting curve $Z(\log a)$ is referred to as the "mononuclear wall", (Fig. 2b), since with decreasing B the curves $Z(\log a)_B$ approach to it indefinitely but never pass it. For intermediate values of B there is a transition range, of a breadth of 2—3 units in $\log B$. This range of transition from a practically mononuclear reaction (within ordinary experimental errors) to a practically pure "core + links" reaction may seem surprisingly narrow, which may partly be due to the fact that in Fig. 2b the polynuclear and mononuclear curves have a rather similar shape.

Fig. 3 shows $Z(\log a)_B$ calculated for $t = 3$ and hypothesis IIIa with $k_0 = 0.06$; these values describe approximately the hydrolysis of uranium(IV)⁸. Here the polynuclear curves are steeper, and the transition range in $\log B$ is much broader.

Similar behavior would be expected for the function $Z(\log a)_B$ on transition between a mononuclear reaction and polynuclear reactions of other types, and also for the function $\eta(\log a)_B$, where $\eta = \log \frac{B}{b}$ (see (4)).

Evaluation of data by normalized projection map

In very favorable systems, the experiments cover a range of B such that at low values of B the mononuclear, at high values of B the polynuclear processes predominate. Then approximate equilibrium constants for both processes can be calculated separately, and refined values may be obtained by considering, at each end, the other process as a small disturbance. Such a procedure was possible for the hydrolysis of iron(III) (Hedström¹⁰) and indium(III) (Biedermann¹¹). These cases were additionally favorable in that both the free concentrations a and b could be measured.

In other systems, the polynuclear process certainly predominates at high values for B , so that one may use the methods in AB II³ to find a mechanism that gives a good agreement, and an approximate value for $\log k$. At low values for B , deviations from the "core + links" curve are observed; however, the mononuclear process is too small a disturbance to be treated independently.

In such cases, the accuracy of the data may not allow one to determine more than one equilibrium constant for the mononuclear reactions; it has seemed reasonable to start by assuming that the first mononuclear complex AB is formed and testing this assumption by "surface-fitting", using projection maps.

To find the formation constant β_1 for this complex, and a refined value of $\log k$, one may plot the experimental data in the form $y(x)_Z$, (15), and move this projection map parallel with the axes on a calculated normalized plot $Y(X)_Z$, (13, 14), until the best agreement is found. From the coordinates $x_0 = x - X$ and $y_0 = y - Y = \log B - \log B$ of the points coinciding with the point $X = 0$, $Y = 0$, one may then find the best values for $\log k$ and $\log \beta_1$, using (13) and (14). An example is given in Fig. 4a, where the experimental values of Kilpatrick and Pokras⁴ (dots) are shown in the position of best fit with calculated

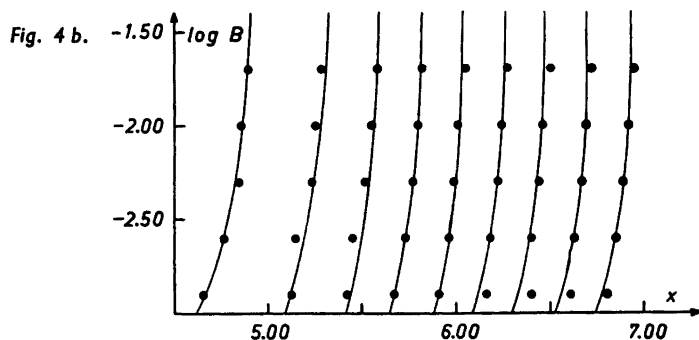
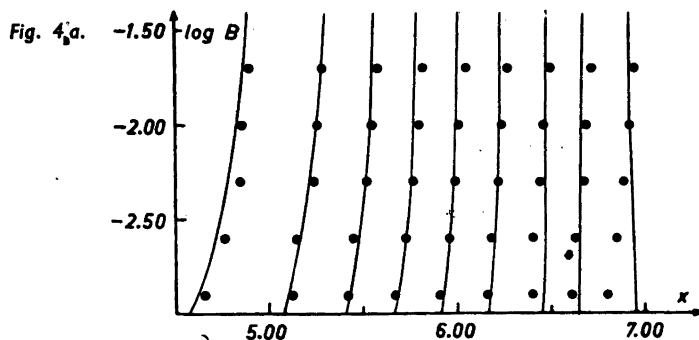


Fig. 4. "Surface-fitting" of Kilpatrick's and Pokras' data for scandium(III) hydrolysis⁴ (dots), plotted as $\log B(\log h^{-2} B)_Z$. Curves: projection map $\log B(X)_Z$ in best fit; a) only one mononuclear complex, $k_0 = 5$: $\log \beta_1 = -5.02$ and $\log k = -6.85$. The curves are the same as in Fig. 1a but on a larger scale. b) two mononuclear complexes $l = 1$: $\log \beta_1 = -5.1$, $\log \beta_2 = -10.2$ and $\log k = -6.87$.

curves for a single mononuclear complex + hypothesis IIIa with $k_0 = 5$. In this case, $x_0 = 6.85$ and $y_0 = -3.15$, which give $\log k = -6.85$ and $\log \beta_1 = -5.0$.

Numerical approach

One may use a numerical approach to find β_1 if the equilibrium constants k_n of the polynuclear reactions are known, or, which is the same, if k and $g(v)$ are known. If there is only one mononuclear complex, one may conveniently start with (8a), (9a) and (6) and eliminate b and a to find

$$a'B(1-Z) = k^{-1}v(1 + g - (t-1)vg') \quad (19)$$

Thus $a'B(1-Z)$ is a function of v only. Using the known k and $g(v)$ one may calculate and plot the expression to the right of (19) as a function of v . For each experimental point one may then calculate $a'B(1-Z)$ from the experim-

ental data, read off the value of v from the plot of (19), and use it to calculate (9a, 6)

$$\beta_1 = a^{-1} (a^t B Z k v^{-1} - t v g') \quad (20)$$

This can be done for a series of experimental points, and the average value of β_1 is taken. This method was used in the study of the Cu^{2+} hydrolysis¹².

Treatment of data (a, b, B)

If both a and b are measured and t is known, one may calculate $u = a^t b$ for each point. Now from (4)

$$\eta = \log \frac{B}{b} = \log (1 + \sum \beta_i a^i + \sum (n+1) k_n u^n) \quad (21)$$

In this case, one may also treat mechanisms with more than one mononuclear complex in a comparatively simple manner. Assuming, however, that we need consider only one mononuclear complex, AB, (21) takes the form

$$\eta = \log (1 + a + g + v g') \quad (22)$$

If $g(v)$ is known, one may easily calculate a normalized projection map $\log v(\log a)_\eta$ for a set of values of η and $\log v$. This could be fitted to an experimental diagram $\log u(\log a)_\eta$. The position of best agreement gives (6, 10)

$$\log k = \log v - \log u; \quad \log \beta_1 = \log a - \log a \quad (23)$$

Alternatively one may calculate $X(\log a)_\eta$ and compare with the experimental $x(\log a)_\eta$. From (13), and (8)

$$X = \log v + \eta = x + \log k; \quad a = 10^\eta - (1 + g + v g') = \beta_1 a \quad (24)$$

So, by keeping η constant and varying v we may obtain sets of corresponding values for X and a .

To construct $\log u(\log a)_\eta$ one may draw the primary graphs $\eta(\log a)_B$ and $\log u(\log a)_B$, read the $\log a$ values for round values of η in the first diagram, mark out these points on corresponding curves in the second diagram, and finally join the points with the same η values in the latter diagram. The plot $x(\log a)_\eta$ is constructed in an analogous way.

TWO MONONUCLEAR COMPLEXES

Graphical method

If, in addition to AB, the second mononuclear complex A_2B must also be considered, there will be an additional term $b\beta_2 a^2$ in (8) and $2b\beta_2 a^2$ in (9). Defining the normalized functions a and B as before, (10, 12), we find from (8) and (9)

$$B = v a^{-t} (1 + a + l a^2 + g + v g') \quad (25)$$

$$BZ = v a^{-t} (\alpha + 2l a^2 + t v g') \quad (26)$$

$$l = \beta_2 \beta^{-2} \quad (27)$$

We may construct one normalized projection map $\log B(X)_Z$ for each value of l to be tested, and search for the best fit with the experimental data $\log B(x)_Z$, or alternatively construct $\log B(\log a)_Z$ and compare it with $\log B(\log a)_Z$.

Elimination of B from (25) and (26) leads to a second-degree equation in a , from which we get an explicit expression for $a(v, Z)$. Inserting this into (25) we find explicit expressions for $B(v, Z)$ and $X = \log Ba^l(v, Z)$. If the values of these functions are calculated for a series of values of v and Z , one may obtain the plots $\log B(X)_Z$ and $\log B(\log a)_Z$.

Alternatively we may construct intermediate plots of curves $X = \log Ba^l(v)_Z$, $\log B(v)_a$ and $Z(v)_a$, by means of (25) and (26), and read off corresponding values of B , Z , and X or a .

Fig. 4 gives the projection map $\log B(X)_Z$ for $k_0 = 5$ and $l = 0$ (Fig. 4a) or $l = 1$ (Fig. 4b) and the data for scandium(III). The agreement is improved by introducing the second complex.

It is true that we will have to construct as many projection maps as we want to test values for l . On the other hand, once this work is done, the "surface fitting" has several advantages over other methods (such as successive approximation) which might be devised. The normalized projection maps may be compared with a plot of experimental data, like $\log B(\log a)_Z$, where one may still retain a feeling for the influence of experimental errors, so that one may see whether a certain agreement is satisfactory or not. It is an important advantage with this method that the same experimental plot $\log B(\log a)_Z$ may also be used for testing other mechanisms that might be considered. One may then see where the significant differences between the various mechanisms arise, and whether the data suffice to make a certain decision between them.

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