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GRAPHICAL ANALYSIS OF THE FORMATION FUNCTION—I

THE REAL CROSS-OVER POINT

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Summary—From a mathematical treatment, it has been proved that a family of formation curves shows a real cross-over point in the following cases: (*a*) a mixture of mononuclear complexes BA, $BA_2 \ldots BA_N$ and polynuclear complexes of general formula $(B_qA_p)_n$, provided that $p/q < N$; (*b*) a mixture of homonuclear complexes B_QA_p, where Q is constant, and mononuclear complexes shows at least one cross-over point if the maximum value for p is smaller than NQ and at least two cross-over points if NQ lies between the minimum value and the maximum value for p. Curves calculated for three different examples are in perfect agreement with the theory.

The formation function Z is a versatile tool in identifying the complex species present in solution and determining their stability constants,[1,2] especially in studying mononuclear complexes and polynuclear complexes of the 'core + links' type $B(A_tB)_n$, where B is the metal ion and A the ligand. However, in the case where neither coinciding curves nor a family of equidistant formation curves are found, it is not easy to interpret the experimental results by means of a graphical analysis. In this series of papers a number of special shapes of the family of $Z\ (\log a)_B$ curves (where a is the concentration of uncombined A and the total metal ion concentration B is constant) will be discussed in order to enhance the possibility of interpreting the formation function. This is important when nothing is known about the composition of the complexes in solution, since difficulties may arise when the experimental results are treated by a computer programme based on a least-squares procedure. In that case it is convenient to have at least some idea about the possible composition of the complexes present.

A special form of the formation function is encountered when the $Z\ (\log a)_B$ curves show a cross-over point: all formation curves intersect at one point. We can distinguish between a real cross-over point and a pseudo cross-over point, *i.e.*, when all formation curves intersect one another in so small a range that this can hardly be distinguished from a single point. In this paper only the real cross-over point will be discussed. The main question that will be answered is what is the composition of the complexes that gives rise to a cross-over point? There is some controversy in the literature about this question. The cross-over point in acid-base systems, called the isohydric point by Carpéni,[3,4] would according to this author[5] be found at a acid–base ratio equal to $(Z/n)_m$, Z being the charge of the ion, n the number of atoms of the central element in the most probable species and m an integer. A similar relation is given by MacBryde.[6] On the other hand Byé[7] and Souchay[8] are convinced that the cross-over point is due to equilibria between species of two different degrees of condensation. Rossotti and Rossotti[1] reported that an equilibrium of mononuclear complexes BA_n and a set of $B_Q A_p$ complexes, with constant Q and varying p, can give a cross-over point.

MATHEMATICAL TREATMENT

There are two conditions for a cross-over point. (*a*) $(\partial Z/\partial B)_a = 0$ for a fixed value of Z and a finite value for a. B is the total concentration of metal ion, and a the free ligand concentration. (*b*) The sign of $(\partial Z/\partial B)_a$ must change at the cross-over point.

Z can be expressed as:

$$Z = \frac{\sum_q \sum_p p\beta_{qp} b^{q-1} a^p}{1 + \sum_q \sum_p q\beta_{qp} b^{q-1} a^p}, \tag{1}$$

where b is the concentration of free metal ion and β_{qp} is the stability constant of $B_q A_p$, defined as

$$\beta_{qp} = \frac{[B_q A_p]}{b^q \,.\, a^p}.$$

The mass-balance equation with respect to B is given by

$$B = b + \sum_q \sum_p q\beta_{qp} b^q a^p. \tag{2}$$

From equation (2) the following equation can be obtained:

$$\left(\frac{\partial b}{\partial B}\right)_a = 1 \Bigg/ \left(1 + \sum_q \sum_p q^2 \beta_{qp} b^{q-1} a^p\right). \tag{3}$$

Differentiation of equation (1) and insertion of equation (3) into the expression obtained gives

$$\left(\frac{\partial Z}{\partial B}\right)_a = \frac{\left|\sum_q \sum_p (q-1)(p-Zq)\beta_{qp} b^{q-2} a^p\right|}{\left(1 + \sum_q \sum_p q^2 \beta_{qp} b^{q-1} a^p\right)\left(1 + \sum_q \sum_p q\beta_{qp} b^{q-1} a^p\right)}. \tag{4}$$

The denominator of equation (4) is always positive, so the sign of the numerator will determine the sign of $(\partial Z/\partial B)_a$, and therefore the function ψ_A is defined as:

$$\psi_A = \sum_q \sum_p (q-1)(p-Zq)\beta_{qp} b^{q-2} a^p. \tag{5}$$

If only mononuclear complexes are present, ψ_A will be zero for all values of Z: all formation curves will coincide. ψ_A will also be zero for polynuclear complexes $B_q A_p$ for a fixed value of Z, if the ratio p/q is constant and equal to that fixed value. However, when only polynuclear complexes exist in solution, this value of Z will be obtained for an infinite value of a. If there are also a number of mononuclear complexes BA, BA_2 . . . BA_N and N is greater than p/q, Z will be equal to p/q for a finite value of a. Moreover ψ_A and consequently $(\partial Z/\partial B)_a$ will be positive for Z smaller than p/q, and negative for Z greater than p/q. This means that all conditions for a cross-over point are fulfilled. Thus a system composed of mononuclear complexes BA, BA_2, . . . BA_N and a series of polynuclear complexes with formula $(B_q A_p)_n$ will always give a cross-over point, provided that N is greater than p/q. Mononuclear complexes with one polynuclear complex can be considered as a special case of the system described above and will give a cross-over point if $N > p/q$.

When a series of mononuclear complexes BA_n coexists with a series of homonuclear complexes $B_Q A_p$, there is also a possibility of a cross-over point, as discussed by Rossotti and Rossotti.[1] The function ψ_A then becomes

$$\psi_A = (Q - 1)b^{Q-2} \sum_p (p - QZ)\beta_{Qp} a^p. \tag{6}$$

Let the functions ψ_Q and ψ_M be defined as:

$$\psi_Q = \frac{\sum_p p\beta_{Qp} a^p}{Q \sum_p \beta_{Qp} a^p}, \tag{7}$$

$$\psi_M = \frac{\sum_n n\beta_{1n} a^n}{1 + \sum_n \beta_{1n} a_n}. \tag{8}$$

It can easily be proved that according as ψ_M is smaller than, equal to or greater than ψ_Q, Z will also be smaller than, equal to or greater than ψ_Q.

The functions ψ_M and ψ_Q are continuous and increasing with increasing a, except when only one polynuclear complex is present. ψ_M tends from zero for very small values of a to N for very large values of a. ψ_Q goes from p_{min}/Q to p_{max}/Q, p_{min} and p_{max} being respectively the minimum and the maximum value for p. The following cases can be differentiated.

(*a*) $p_{max}/Q < N$. The functions ψ_M and ψ_Q will always have at least one intersection point for a finite value of a. At that point ψ_Q will be equal to ψ_M and thus equal to Z, and ψ_A will be zero. If a is smaller, ψ_Q will be greater than ψ_M and consequently Z will be smaller than ψ_Q, and ψ_A positive. At higher a, ψ_Q will be smaller than ψ_M, Z will be greater than ψ_Q, and ψ_A negative. So the conditions for a cross-over point are fulfilled. The value for Z where the cross-over point will be found, lies between p_{min}/Q and p_{max}/Q and is dependent on the values of the stability constants.

(*b*) $p_{min}/Q > N$. There exists no intersection point between ψ_M and ψ_Q and consequently no cross-over point will be found.

(*c*) $p_{min}/Q < N < p_{max}/Q$. It is possible that ψ_M and ψ_Q do not intersect one another. In this case no stable mononuclear complexes are present. Otherwise at least two intersection points will be found. The same reasoning holds as for case (*a*) with the result that $(\partial Z/\partial B)_a$ will be positive before the first intersection point, zero at it, negative between the two intersection points, zero at the second intersection point and positive after the second intersection point, *etc*. The two cross-over points will be found between p_{min}/Q and N and their positions will be dependent on the values of the stability constants. The formation curves tend to p_{max}/Q.

It should be noted that it is not necessary, in studying complex systems showing a cross-over point, to keep the total metal ion concentration constant.

THEORETICAL CURVES

Theoretical curves were calculated by using the computer programme ALTH written in Fortran IV. This programme calculates and plots the $Z(\log a)_B$ curves obtained from the equations

$$B - b - \sum_q \sum_p q\beta_{qp} b^q a^p = 0, \tag{9}$$

$$Z = \frac{\sum_q \sum_p p\beta_{qp} b^q a^p}{B}. \tag{10}$$

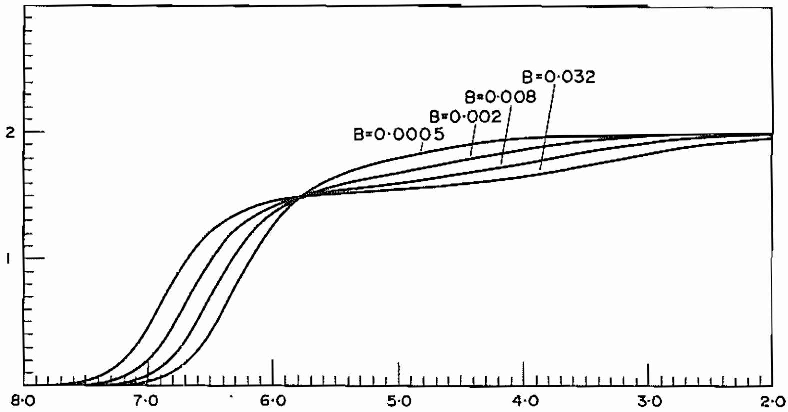

Fig. 1. Theoretical curves for four complexes; BA_2, B_2A_3, B_4A_6, B_6A_9.
Log $\beta_{1,2} = 12{\cdot}0$; log $\beta_{2,3} = 22{\cdot}0$; log $\beta_{4,6} = 34{\cdot}0$; log $\beta_{6,9} = 46{\cdot}0$.

The most efficient method for solving this problem is to start with various given values for B and a, for an appropriate set of values of β_{qp}, solving equation (9) for b by means of a "*regula falsi*" method, and calculating Z from the given values for B and a and the calculated value of b. Instead of a, p$a = -\log a$ was varied, since this gives a more regular spread of the points of the formation curve. At the beginning of the programme a search was made for an upper limit for pa by starting with a high value (*e.g.*, 20) and reducing it successively by 1 until the calculated Z value was greater than 0·01. This pa value, increased by 1, was chosen as the start value for pa, which was then systematically changed over a range of 6 or 7 units.

A large number of $Z(\log a)_B$ curves were calculated for various sets of possible complexes. Three examples are given here. In Fig. 1 the formation curves for a mixture of a mononuclear complex and polynuclear complexes B_2A_3, B_4A_6 and B_6A_9 are shown. The cross-over point falls exactly at a Z value of 1·5. Varying the constants does not

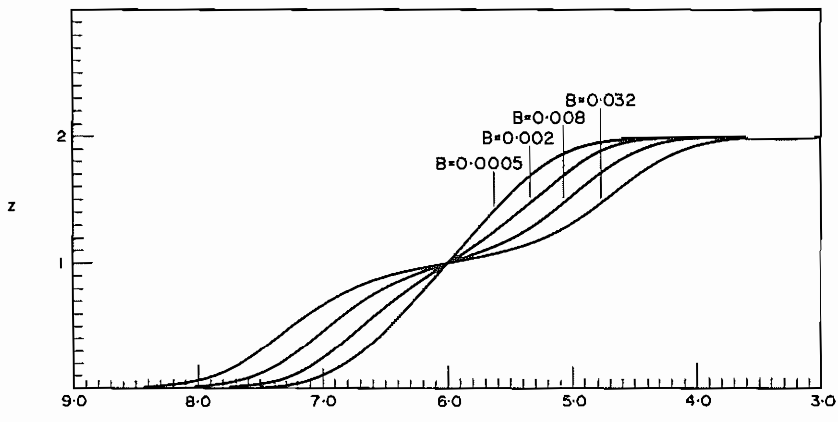

Fig. 2. Theoretical curves for three complexes; BA_2, B_2A_2, B_2A_3.
log $\beta_{1,2} = 12{\cdot}0$; log $\beta_{2,2} = 16{\cdot}0$; log $\beta_{2,3} = 18{\cdot}0$.

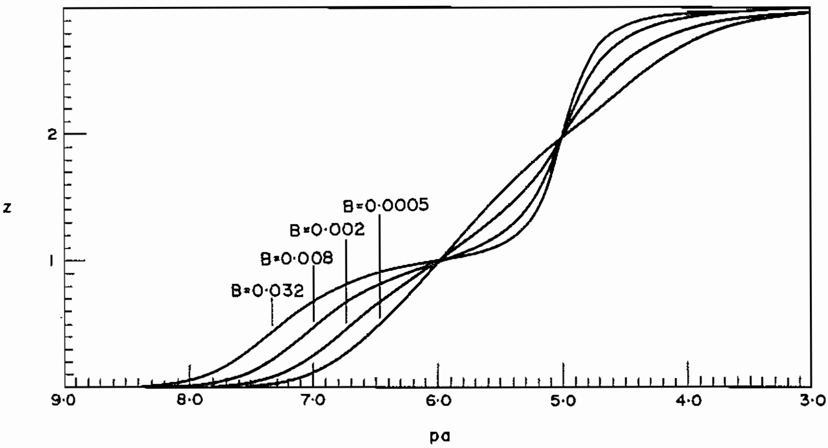

Fig. 3. Theoretical curves for three complexes; BA_2, B_2A_2, B_2A_6. Log $\beta_{1,2} = 12{\cdot}0$; log $\beta_{2,2} = 16{\cdot}0$; log $\beta_{2,6} = 36{\cdot}0$.

change the place of the cross-over point. In Fig. 2 an example of a cross-over point encountered with a mixture of mononuclear complexes and homonuclear complexes with $N > p_{max}/Q$ is given. A cross-over point is found as predicted by the theory. An example with two cross-over points is shown in Fig. 3 for a mixture of one mononuclear complex BA_2 and two polynuclear complexes B_2A_2 and B_2A_6.

The calculations and plots were performed by means of an IBM 360/30.

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Zusammenfassung—Aus einer mathematischen Verhandlung wird bewiesen daß, in den folgenden Fällen, eine Schar Bildungskurven einen echten "cross-over" Punkt vorzeigt:

(*a*) Eine Mischung von mononuklearen Komplexen BA, BA_2 ... BA_N und polynuklearen Komplexen $(B_qA_p)_n$ unter der Bedingung daß $p/q < N$.

(*b*) Eine Mischung von mononuklearen Komplexen und homonuklearen Komplexen B_QA_p mit konstantem Q. Wenn der Höchstbetrag für p kleiner ist als $N.Q$ gibt es wenigstens einen "cross-over" Punkt. Liegen die $N.Q$ Werte zwischen dem Mindeswert und dem Maximumwert von p dann sind wenigstens zwei "cross-over" Punkte vorhanden.

Theoretische Kurven werden für drei verschiedene Beispiele berechnet. Die Übereinstimmung mit der Theorie ist vollkommen.

Résumé—On a démontré mathématiquement qu'un réseau de courbes de formation possède un point isohydrique réel dans les cas suivants:

(*a*) Un mélange de complexes mononucléaires BA, BA_2 ... BA_N et de complexes polynucléaires $(B_qA_p)_n$, à condition que $p/q < N$.

(*b*) Un mélange de complexes homonucléaires $B_Q A_p$, Q étant constant, et de complexes mononucléaires possède au moins un point isohydrique quand la valeur maximale de p est plus petite que $N.Q$ et au moins deux points isohydriques quand la valeur de $N.Q$ se situe entre la valeur minimale et la valeur maximale de p.

Les courbes théoriques, calculées pour trois exemples, correspondent parfaitement avec la théorie.