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GRAPHICAL ANALYSIS OF THE FORMATION FUNCTION—II

THE PSEUDO CROSS-OVER POINT

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Summary—In a further attempt to enhance the possibility of interpreting the formation function, a number of special shapes of the formation function are discussed, which give rise to a pseudo cross-over point. It is shown that under certain conditions a pseudo cross-over point can be found in the following cases: (1) two series of homonuclear complexes, (2) a mixture of a series of homonuclear and polymeric complexes, (3) a series of mononuclear complexes and two polynuclear complexes with nearly the same composition, (4) a system which gives a real cross-over point, and one or more polynuclear complexes, (5) a system of two polynuclear complexes. The conditions are mainly discussed in terms of the composition of the complexes. Calculated curves illustrate the different possibilities.

In a previous paper[1] it was reported that a system composed of mononuclear and homonuclear or polymeric complexes gives rise to a family of formation functions showing a real cross-over point: all curves intersect at one single point. Taking into account the experimental uncertainty, however, the experimentally obtained formation curves will intersect each other within a small range. Nevertheless for a number of systems it can be proved that the theoretical formation curves will intersect each other not in a single point but within a small range. This can be called a pseudo or apparent[2] cross-over point.

In the case of acid–base systems some authors make the same distinction. Byé[3] and Souchay[4] assert that in acid–base equilibria a real isohydric point is found in a system where two species dominate. The cross-over point is called here the isohydric point, since it appears at a fixed pH value. According to these authors a pseudo isohydric point will be found when at least three species are present in solution. Other authors, such as Carpéni[5–7] and McBryde[8] make no distinction between those two forms of cross-over points.

In this paper a number of systems are discussed which give under certain conditions a pseudo cross-over point. In this discussion the cases for which the probability of fulfilling all conditions is extremely low are excluded. The discussion is essentially restricted to the composition of the complexes.

MATHEMATICAL TREATMENT

For a series of complexes B_qA_p the degree of formation Z is given by

$$Z = \frac{\sum_q \sum_p p\beta_{qp} b^{q-1} a^p}{1 + \sum_q \sum_p q\beta_{qp} b^{q-1} a^p} \qquad (1)$$

where b is the concentration of free metal ion, a the concentration of free ligand, β_{qp} the overall concentration stability constant of the complex B_qA_p, defined as

$$\beta_{qp} = \frac{[B_qA_p]}{b^q . a^p}. \tag{2}$$

In these equations B stands for the metal ion and A for the ligand. In a previous paper[1] it was proved that the sign of $(\partial Z/\partial B)_a$ was determined by the function ψ_A which in its general form is given by equation (3)

$$\psi_A = \sum_q \sum_p (q-1)(p - Zq)\beta_{qp} b^{q-2} a^p. \tag{3}$$

The conditions for a pseudo cross-over point can be given by: (a) $(\partial Z/\partial B)_{a'} = 0$ for a value of a' in the range $pa - \Delta pa \leqslant pa' \leqslant pa + \Delta pa$, Δpa having an arbitrary value of about 0·01; (b) $(\partial Z/\partial B)_{a'}$ has a sign different from $(\partial Z/\partial B)_{a''}$ for $pa' \leqslant pa - \Delta pa$ and $pa'' \geqslant pa + \Delta pa$; (c) the conditions under (a) and (b) must be fulfilled for a relatively large range of total metal ion and ligand concentration.

The following systems can be discussed.

1. Two series of homonuclear complexes $B_{Q'}A_p$ and $B_{Q''}A_p$ in a region where b is negligibly small in comparison with B. The functions ψ_1 and ψ_2 are defined as:

$$\psi_1 = \frac{\sum p\beta_{Q'p}a^p}{Q'\sum \beta_{Q'p}a^p}, \tag{4}$$

$$\psi_2 = \frac{\sum p\beta_{Q''p}a^p}{Q''\sum \beta_{Q''p}a^p}. \tag{5}$$

If the minimum value for p in the first homonuclear series is $p_{1\,min}$ and the maximum value is $p_{1\,max}$, then ψ_1 will go from $p_{1\,min}/Q'$ to $p_{1\,max}/Q'$. In the same way ψ_2 will vary from $p_{2\,min}/Q''$ to $p_{2\,max}/Q''$. These limits are called $\psi_{i\,min}$ and $\psi_{i\,max}$. Substitution of ψ_1 and ψ_2 in equation (1), taking into account that $b \ll B$ gives:

$$Z \sim \frac{\psi_1 Q' b^{Q'} \sum \beta_{Q'p}a^p + \psi_2 Q'' b^{Q''} \sum \beta_{Q''p}a^p}{Q' b^{Q'} \sum \beta_{Q'p}a^p + Q'' b^{Q''} \sum \beta_{Q''p}a^p}. \tag{6}$$

This can be transformed into:

$$Q' b^{(Q'-2)}(\psi_1 - Z)\sum \beta_{Q'p}a^p \sim -Q'' b^{(Q''-2)}(\psi_2 - Z)\sum \beta_{Q''p}a^p. \tag{7}$$

Substitution of ψ_1 and ψ_2 in ψ_A gives

$$\begin{aligned}\psi_A = {} & Q'(Q'-1)b^{(Q'-2)}(\psi_1 - Z)\sum \beta_{Q'p}a^p, \\ & + Q''(Q''-1)b^{(Q''-2)}(\psi_2 - Z)\sum \beta_{Q''p}a^p.\end{aligned} \tag{8}$$

Substitution of (7) in (8) gives

$$\psi_A = (Q' - Q'')Q' b^{(Q'-2)}(\psi_1 - Z)\sum \beta_{Q'p}a^p, \tag{9}$$

or

$$\psi_A \doteq (Q'' - Q')Q'' b^{(Q''-2)}(\psi_2 - Z)\sum \beta_{Q''p}a^p. \tag{10}$$

It can be derived from equation (6) that if $\psi_1 = \psi_2$ then $\psi_1 = \psi_2 = Z$; if $\psi_1 < \psi_2$ then $\psi_1 < Z < \psi_2$ and if $\psi_1 > \psi_2$ then $\psi_1 > Z > \psi_2$.

The following two cases can be discussed:

(*a*) $\psi_{1\,min} < \psi_{2\,min}$ and $\psi_{1\,max} > \psi_{2\,max}$.

ψ_1 and ψ_2 will have an odd number of intersection points. Suppose there is one intersection point. At that point $\psi_1 = \psi_2 = Z$ and $\psi_A = 0$. Below that point $\psi_1 < Z < \psi_2$ and from (9), $\psi_A > 0$ if $Q' < Q''$ and $\psi_A < 0$ if $Q' > Q''$. Beyond that point, $\psi_1 > Z > \psi_2$ and ψ_A will take the sign of $Q' - Q''$.

(*b*) $\psi_{1\,min} < \psi_{2\,min}$ and $\psi_{1\,max} < \psi_{2\,max}$.

ψ_1 and ψ_2 will have an even number of intersection points or none at all. Suppose there are two intersection points. The sign of ψ_A is given below as a function of ψ_1 and ψ_2.

	$\psi_A(Q' > Q'')$	$\psi_A(Q' < Q'')$
$\psi_1 < \psi_2$	< 0	> 0
$\psi_1 = \psi_2$	$= 0$	$= 0$
$\psi_1 > \psi_2$	> 0	< 0
$\psi_1 = \psi_2$	$= 0$	$= 0$
$\psi_1 < \psi_2$	< 0	> 0.

In Figs. 1 and 2 these two possibilities are illustrated. The curves are calculated with the computer program ALTH described before.[1] In Fig. 1 the formation curves for a mixture of complexes with composition B_2A, B_2A_4 and B_4A_5, B_4A_7 are shown. ψ_1 varies from 0·5 to 2 and ψ_2 from 1·25 to 1·75. One cross-over point is found. In Fig. 2 a mixture of a series B_2A, B_2A_2 and a series B_4A_3, B_4A_8 is considered. Here ψ_1 varies from 0·5 to 1 and ψ_2 from 0·75 to 2. Two cross-over points are found.

2. A series of homonuclear complexes $B_{Q'}A_p$ and a polymeric series $(B_{q''}A_{p''})_n$ when b is negligibly small in comparison with B gives a pseudo cross-over point.

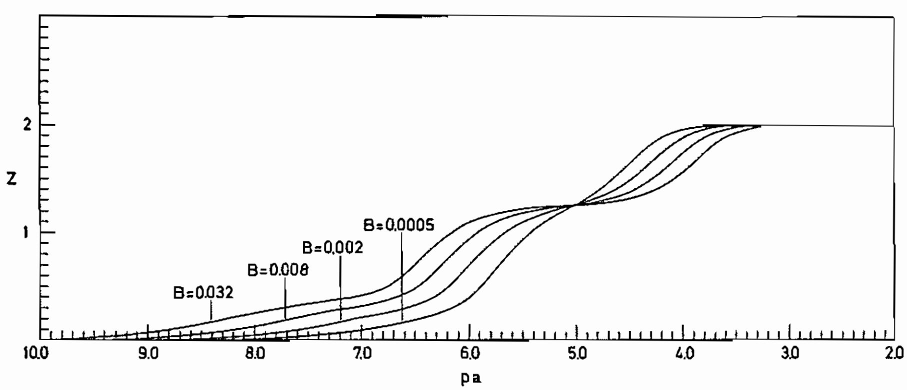

Fig. 1. Theoretical curves for two series of homonuclear complexes: B_4A_5, B_4A_7 and B_2A, B_2A_4.
$\log \beta_{45} = 40{\cdot}0$, $\log \beta_{47} = 45{\cdot}0$
$\log \beta_{21} = 9{\cdot}5$, $\log \beta_{24} = 25{\cdot}0$.

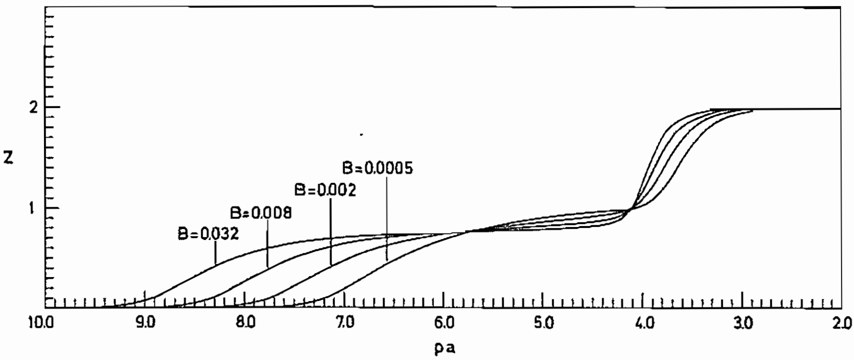

Fig. 2. Theoretical curves for two series of homonuclear complexes: B_2A, B_2A_2 and B_4A_3, B_4A_8.
$\log \beta_{21} = 9{\cdot}0$, $\log \beta_{22} = 16{\cdot}0$
$\log \beta_{43} = 30{\cdot}0$, $\log \beta_{48} = 50{\cdot}0$.

Let ψ_1 and ψ_2 be defined as:

$$\psi_1 = \frac{\sum p\beta_{Q'p}a^p}{Q'\sum \beta_{Q'p}a^p}, \tag{11}$$

$$\psi_2 = \frac{p''}{q''}. \tag{12}$$

ψ_A can be expressed as:

$$\psi_A = (Q' - 1)b^{(Q'-2)}\sum_p (p - Q'Z)\beta_{Q'p}a^p + \sum_n (nq'' - 1)(np'' - nZq'')\beta_n b^{(nq''-2)}a^{np''}, \tag{13}$$

where β_n is the stability constant of the complex $B_{nq''}A_{np''}$. Substitution of ψ_1 and ψ_2 in ψ_A gives:

$$\psi_A = Q'(Q - 1)(\psi_1 - Z)b^{(Q'-2)}\sum_p \beta_{Q'p}a^p + q''(\psi_2 - Z)\sum_n n(nq'' - 1)\beta_n b^{(nq''-2)}a^{np''}. \tag{14}$$

Substitution of ψ_1 and ψ_2 in Z gives, after some transformations:

$$(\psi_1 - Z)Q'b^{Q'}\sum \beta_{Q'p}a^p = -(\psi_2 - Z)q''\sum_n nb^{nq''}\beta_n a^{np''}. \tag{15}$$

Substitution of the left-hand term of equation (15) into equation (14) gives:

$$\psi_A = (\psi_2 - Z)q''\{q''\sum n^2\beta_n b^{(nq''-2)}a^{np''} - Q'\sum n\beta_n a^{np''}b^{(nq''-2)}\}. \tag{16}$$

The sign of ψ_A is determined by both the expression $(\psi_2 - Z)$ and the expression between curly brackets. However it is very improbable that the sign of the latter will change in the neighbourhood of the cross-over point, thus the sign of ψ_A is determined by $(\psi_2 - Z)$. For $\psi_2 = Z$, ψ_A will vanish. It can be seen from equation (16) that the sign of ψ_A will change at that point: a pseudo cross-over point will be found.

An example of such a cross-over point is given in Fig. 3. A series of homonuclear complexes B_2A, B_2A_4 and a polymeric series $(B_3A_3)_n$ gives a pseudo cross-over point at $Z \sim 1$.

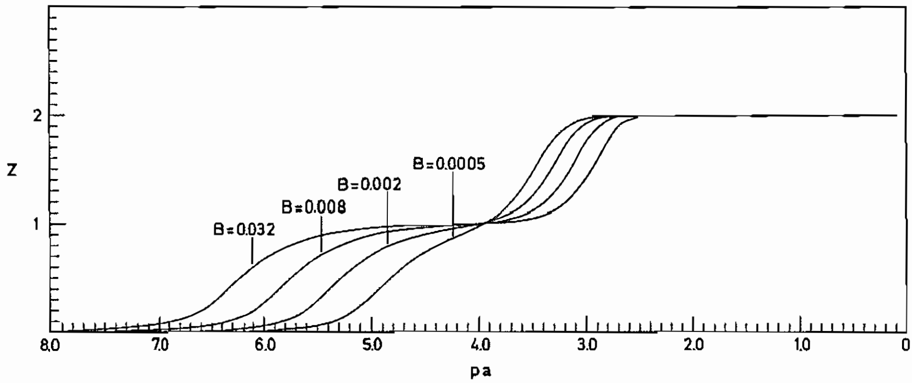

Fig. 3. Theoretical curves for a series of homonuclear complexes and a polymeric series: B_2A, B_2A_4 and B_3A_3, B_6A_6.
$\log \beta_{21} = 7{\cdot}5$, $\log \beta_{24} = 20{\cdot}0$
$\log \beta_{33} = 21{\cdot}0$. $\log \beta_{66} = 46{\cdot}0$.

3. Mononuclear complexes with two polynuclear complexes with nearly the same composition give a pseudo cross-over point. Let ψ_1 and ψ_2 be defined as

$$\psi_1 = \frac{p'}{q'}, \tag{17a}$$

$$\psi_2 = \frac{p''}{q''}. \tag{17b}$$

If $\psi_2 > \psi_1$ and $Z = \psi_1$ then

$$\psi_A = q''(q'' - 1)(\psi_2 - \psi_1)\beta_{q''p''}b^{(q''-2)}a^{p''} > 0, \tag{18}$$

For $Z = \psi_2 = p''/q''$

$$\psi_A = q'(q' - 1)(\psi_1 - \psi_2)\beta_{q'p'}b^{(q'-2)}a^{p'} < 0. \tag{19}$$

If mononuclear complexes BA ... BA_N with $N > \psi_{2\max}$ are present, all formation functions intersect each other between ψ_1 and ψ_2. If ψ_1 and ψ_2 do not differ too much, this system gives a real cross-over point. In Fig. 4 an example of a mixture of BA, BA_2 and $B_{10}A_{10}$, $B_{10}A_{11}$ is shown. As can be seen, all formation curves intersect between $Z = 1$ and $Z = 1{\cdot}1$.

4. A system consisting of a series of complexes which gives a real cross-over point, and one or more complexes the contribution of which to the formation function may be neglected in the region of that point, can give a pseudo cross-over point. This case is obvious and needs no further proof.

In order to illustrate this case theoretical curves were calculated. The initial set of complexes was BA_2 and B_4A_6. As mentioned before, a real cross-over point at $Z = 1{\cdot}5$ is found. To this system a complex B_2A_2 was added, with increasing stability constant: a pseudo cross-over point at $Z = 1{\cdot}5$ is found. For still higher values of β_{22} the contribution of B_4A_6 is small and the pseudo cross-over point is found at $Z = 1$. For intermediate values of β_{22} both complexes contribute to the formation function and the intersection

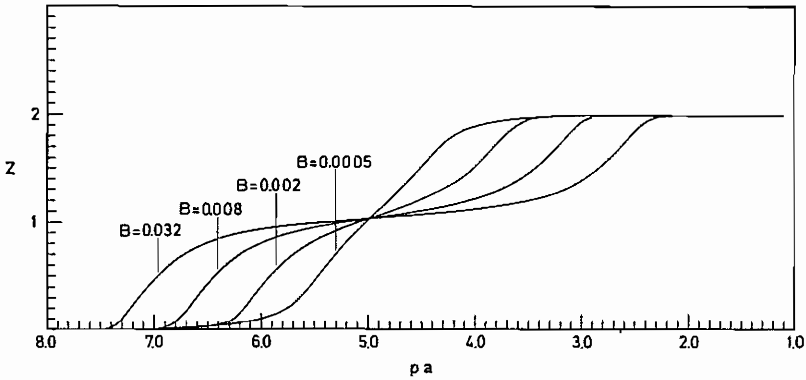

Fig. 4. Theoretical curves for a mixture of mononuclear complexes and two polynuclear complexes with nearly the same composition: BA, BA_2 and $B_{10}A_{10}$, $B_{10}A_{11}$.
$\log \beta_{11} = 5{\cdot}0$, $\log \beta_{12} = 10{\cdot}0$
$\log \beta_{10,10} = 85{\cdot}0$, $\log \beta_{10,11} = 90{\cdot}0$.

points will fall between 1 and 1·5. This is shown in Fig. 5. It certainly cannot be considered as a pseudo cross-over point, but it illustrates that a family of formation curves which at first sight cross each other at random is theoretically well possible. Therefore it should be emphasized that only if there is sufficient evidence, may formation curves with an abnormal shape be rejected on account of too great experimental errors.

5. A system consisting of two polynuclear complexes $B_{q'}A_{p'}$ and $B_{q'}A_{p''}$ can give a cross-over point.

Substitution of equation (1) into ψ_A gives

$$\psi_A = \frac{\begin{aligned}[p'(q'-1)\beta_{q'p'}b^{(q'-2)}a^{(p'-2)} + p''(q''-1)\beta_{q''p''}b^{(q''-2)}a^{p''} \\ + (p'q''-p''q')(q'-q'')\beta_{q'p'}\beta_{q''p''}b^{(q'+q''-3)}a^{(p'+p'')}]\end{aligned}}{(1 + q'\beta_{q'p'}b^{(q'-1)}a^{p'} + q''\beta_{q''p''}b^{(q''-1)}a^{p''})}. \quad (20)$$

A necessary condition that the formation curves intersect each other is that the third term of the numerator is negative. Thus if $p'/q' < p''/q''$ then $q' > q''$: the complex with the

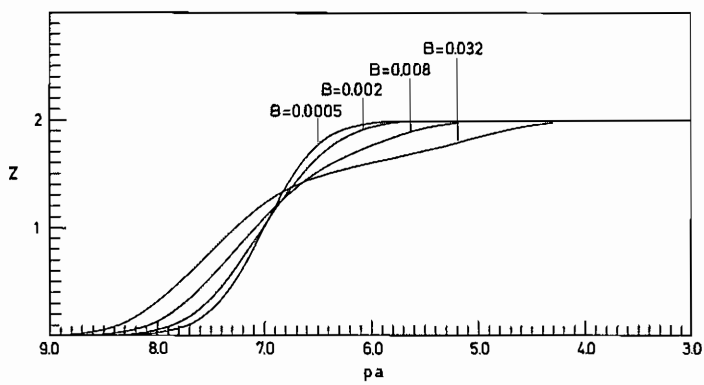

Fig. 5. Theoretical curves for three complexes BA_2, B_2A_2, B_4A_6.
$\log \beta_{12} = 14{\cdot}0$; $\log \beta_{22} = 17{\cdot}0$; $\log \beta_{46} = 50{\cdot}0$

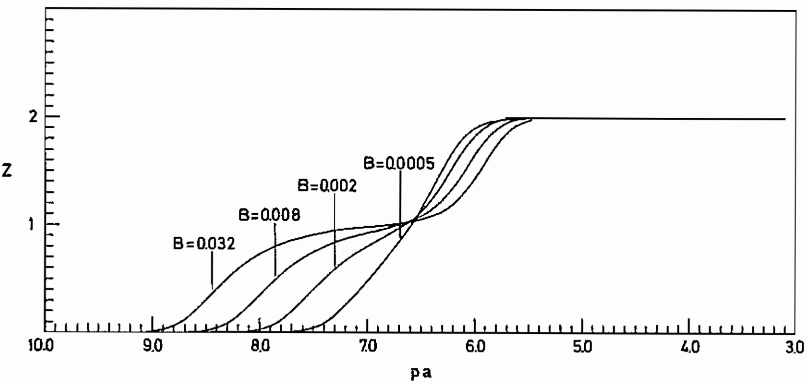

Fig. 6. Theoretical curves for two polynuclear complexes: B_4A_4, B_2A_4. $\log \beta_{24} = 30{\cdot}0$; $\log \beta_{44} = 38{\cdot}0$.

lowest p/q ratio must contain the most metal ions. It can easily be shown that two complexes belonging to a "core + links" series $B(A_tB)_n$ do not fulfil this condition and the formation curves will not intersect each other. Two complexes with the same amount of ligand molecules will always fulfil this condition. However, the observance of a pseudo cross-over point in this case will be critically dependent on the values of the stability constants and therefore it is not very probable that it will be found in a system consisting of two polynuclear complexes in a region where b is not negligible in comparison with B. Otherwise it is a special case of 1. In Fig. 6 an example of such a pseudo cross-over point is shown for the two complexes B_4A_4 and B_2A_4.

CONCLUSION

In this paper five systems of complexes are discussed, giving under certain conditions a family of formation curves with a pseudo cross-over point that can hardly be distinguished from a real cross-over point. The conditions are, with the exception of case 5, to a first approximation independent of the values of the stability constants.

When treating experimental data showing a cross-over point, methods should be used to distinguish a pseudo from a real cross-over point. This can be achieved by enlarging the concentration ranges and changing the ratio of total ligand to total metal ion concentration. This is mostly limited in scope, however. At higher concentrations precipitation may occur and at lower concentrations the accuracy of the measurements may be questioned. Also the change of the ratio of total ion to total ligand concentration is in some cases limited as has been shown by Cabani.[9] Another method is, when possible, to calculate the mean value for p and q, using methods described by Sillén.[10]

At any rate, to avoid premature conclusions about the composition of the complexes, care should be taken when treating experimental data showing formation curves with a cross-over point and all possible compositions should be thoroughly discussed.

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Zusammenfassung—In einem neuen Anlauf, die Interpretations-möglichkeiten der Bildungsfunktion zu verbessern, werden eine Anzahl besonderer Formen der Bildungsfunktion diskutiert, die zu einem Pseudo-Kreuzungspunkt führen. Es wurde gezeigt, daß unter bestimmten Bedigungen in folgenden Fällen ein Pseudo-Kreuzungspunkt gefunden werden kann: (1) zwei Reihen homonuklearer Komplexe; (2) ein Gemisch einer Reihe homonuklearer und polymerer Komplexe; (3) eine Reihe einkerniger und zwei mehrkernige Komplexe mit nahezu der gleichen Zusammensetzung; (4) ein System, das einen reellen Kreuzungspunkt und einen oder mehrere polynukleare Komplexe gibt; (5) ein System von zwei mehrkernigen Komplexen. Die Bedingungen werden hauptsächlich in Bezug auf die Zusammensetzung der Komplexe diskutiert. Berechnete Kurven verdeutlichen die verschiedenen Möglichkeiten.

Résumé—Dans un nouvel essai pour accroître la possibilité d'interprétation de la fonction de formation, on discute d'un certain nombre de formes spéciales de la fonction de formation, qui donnent naissance à un point de pseudo-chevauchement. On a montré que dans certaines conditions un point de pseudo-chevauchement peut être trouvé dans les cas suivants: (1) deux séries de complexes homonucléaires, (2) un mélange d'une série de complexes homonucléaires et polymères, (3) une série de complexes mononucléaires et deux complexes polynucléaires ave sensiblement la même composition, (4) un système qui donne un point de chevauchement réel, et un ou davantage de complexes polynucléaires, (5) un système de deux complexes polynucléaires. Les conditions sont principalement discutées en fonction de la composition des complexes. Des courbes calculées illustrent les différentes possibilités.