Coordination Chemistry Reviews, 43 (1982) 233–250
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

PRINCIPLES OF CONCENTRATION DISTRIBUTIONS IN MULTICOMPONENT EQUILIBRIUM SYSTEMS

I. NAGYPÁL and M.T. BECK

Department of Inorganic and Analytical Chemistry, Department of Physical Chemistry, Kossuth Lajos University, Debrecen 10, 4010 (Hungary)

CONTENTS

A. INTRODUCTION

One of the most important aims of the equilibrium studies of complexes is to calculate the concentration of each species in a system based on the total concentrations and the stability constants. The concentration or the partial mole fraction of the different species can be conveniently plotted as a function of the equilibrium concentration (or logarithm of equilibrium concentration) of one of the components, keeping the total concentration of the other components at a constant value. In case of stepwise formation of mononuclear complexes, usually the partial mole fractions are plotted as a function of $-\log[L] = pL$. The rules of the concentration distribution in this case are well known. The concentration of M decreases, that of the complex with maximum number of ligands (ML_N) increases monotonously with

0010-8545/82/0000–0000/$04.50 © 1982 Elsevier Scientific Publishing Company

increasing free ligand concentration. The concentrations of the ML_i complexes ($O < i < N$) is represented by maximum curves, the maxima are found at the integer values of the formation curves.

In the last decade a number of studies indicated deviations from this simple pattern. There are two distinct possibilities for the appearance of several maxima on the distribution curves: (i) If the formation of complexes is accompanied by a change of the medium, no single set of stability constants can be applied in the calculation, and the shape of the distribution curve cannot be predicted. (ii) Unusual concentration distribution may occur in multicomponent complex systems as a consequence of peculiar competitive reactions.

Such concentration distributions were found in different three- and four-component systems. The very first example was published by Agarwall and Perrin [1], who found that the partial mole fraction of bis-glycinato-copper(II) species in the copper(II)–glycine–diglycine–hydrogen ion system exhibits three extrema as a function of pH (Fig. 1).

In another four-component system (Ca^{2+}–Zn^{2+}–glutathion–H^+) studied by Rouche and Williams [2] the partial mole fraction of the uncomplexed calcium ion shows two extrema as a function of pH (Fig. 2).

A number of examples of unusual distribution pattern are available for three-component systems, which will be analyzed in detail later.

Mathematical analysis of the metal ion–ligand–proton system and mixed ligand–metal ion systems were given earlier [3,4]. In the present paper the authors treat a novel approach of multicomponent systems which offers the necessary conditions of several extrema in the distribution curves explicitly and outlines the sufficient conditions implicitly. For the sake of simplicity

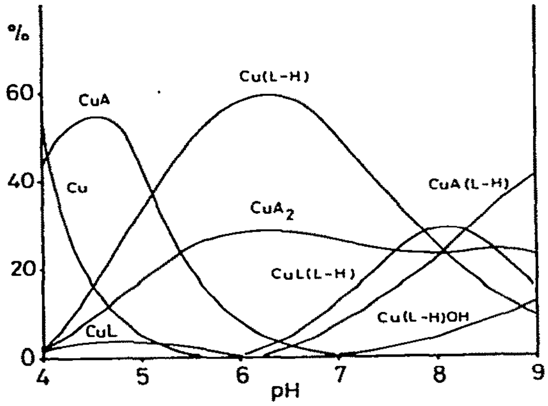


Fig. 1. Concentration distribution of the complexes formed in the copper(II)–glycine–diglycine system [1].

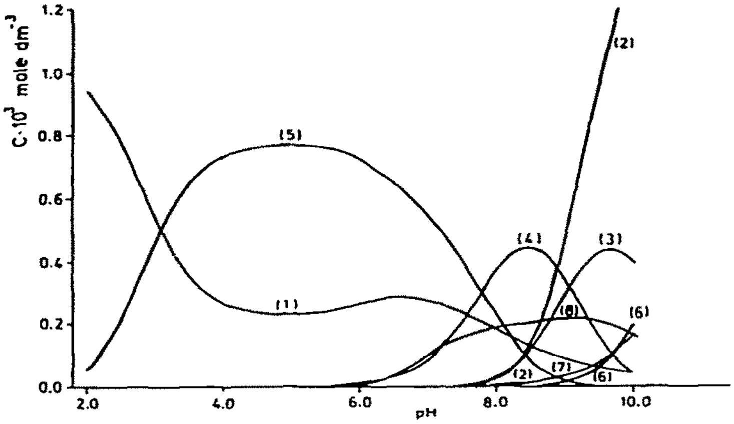


Fig. 2. Concentration distribution of the complexes formed in the Ca^{2+}–Zn^{2+}–glutathion system [2]. Curve No. 1 refers to the uncomplexed calcium ion.

three-component systems will be treated in detail, but the considerations can be easily extended to more complicated systems.

B. THREE-COMPONENT SYSTEMS AND THEIR CLASSIFICATION

There are four different types of three-component systems: (i) metal ion–ligand–proton; (ii) metal ion with two different ligands; (iii) two different metal ions–ligand; and (iv) two different ligands–proton.

In each of these systems three features (characteristics) should be considered:

(1) The number of two-component subsystems.
(2) The additivity of subsystems.
(3) Symmetry and asymmetry.

(i) The number of two-component subsystems

Evidently each of the three-component systems may consist of two or three two-component sub-systems, depending on the possibility of interactions between the three pairs of components. For example, in the metal ion–ligand–proton system if, besides complex formation, both the hydrolysis of metal ion (loss of proton) and protonation of the ligand occur in the pH range studied, three subsystems can be distinguished: metal ion–ligand; metal ion–proton; and ligand–proton. If either the metal ion hydrolysis or the protonation of ligand can be disregarded, only two subsystems should be considered.

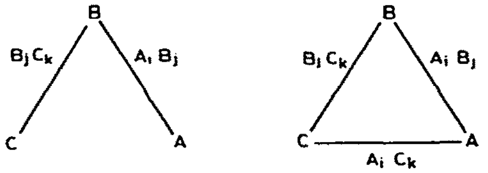
(ii) The additivity of subsystems

If there is no formation of species involving all the three components, the system is regarded as additive. In such a case the three-component system is fully characterized by the equilibrium constants referring to the two or three two-component subsystems. In the opposite case, the system is called non-additive.

These two features are independent on the composition of the individual species formed, and are illustrated in Fig. 3.

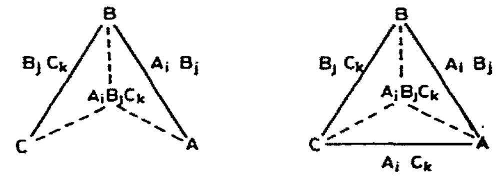
(iii) Symmetry and asymmetry

The triangle can be applied for the representation of the composition of the species formed in the system, too. Any $A_iB_jC_k$ species is denoted as a point on the triangle diagram, with the coordinates i/m, j/m and k/m, where $m = i + j + k$. Thus the components are at the vertices, the species involving two components are on the corresponding axes, while the species involving all the three components are inside the triangle. The points reflect the ratio of the stoichiometric numbers only, and not their absolute values. The symmetry/asymmetry refer to the distribution of the points on the triangle diagram. The possible maximum of the symmetry is that there are three two-fold symmetry axes of the diagram, i.e., it is represented by D_{3h}. This kind of symmetry is, however, chemically unrealistic. For our purposes it is sufficient to consider the C_{2v} symmetry. In the majority of the three-



Additive system with two subsystems

Additive system with three subsystems



Non-additive system with two subsystems

Non-additive system with three subsystems

Fig. 3. Schematic illustration of the four different types of three-component equilibrium systems.

component equilibrium systems there is only one common component. For example, in the metal ion–ligand–proton system the ligand is the common component, in the metal ion–two different ligands system the metal ion is the common component. If the common component is taken to the upper vertex of the triangle, those systems may be symmetric, which have a vertical two-fold symmetry axis. In the opposite case the system is regarded to be stoichiometrically asymmetric.

Evidently, a metal ion–ligand–proton system can be symmetrical only in exceptional cases. Two series of binary species are formed in general: ML_i $(O < i \leqslant N)$ and H_jL $(O < j \leqslant Q)$. Symmetry may occur if HL and ML complexes (and/or their polymeric forms) are formed alone, i.e. $N = Q = 1$. Similarly, a metal ion–two different ligands system may be symmetrical if the maximum number of ligands in the two series are the same. The fulfillment of this condition alone does not necessarily mean that the system is symmetrical. It may happen that an intermediate complex is missing from the series of complexes which may also lead to asymmetry.

The asymmetry is the necessary (but not sufficient) condition of the occurrence of more than one extremum on the concentration distribution diagram.

C. MATHEMATICAL CONSIDERATIONS

Any three-component system is fully characterized by three equations expressing the mass-balance based on the law of mass-action:

$$\begin{aligned} T_A &= \sum_{j=1}^{n} a_j\beta_j[A]^{a_j}[B]^{b_j}[C]^{c_j} \\ T_B &= \sum_{j=1}^{n} b_j\beta_j[A]^{a_j}[B]^{b_j}[C]^{c_j} \\ T_C &= \sum_{j=1}^{n} c_j\beta_j[A]^{a_j}[B]^{b_j}[C]^{c_j} \\ [S_j] &= \beta_j[A]^{a_j}[B]^{b_j}[C]^{c_j} \end{aligned} \qquad (1)$$

where T_A, T_B, T_C are the total concentrations of the components; n is the number of species in the system, including the components; a_j, b_j, c_j are the stoichiometric numbers, giving the numbers of components A, B and C in the jth species; β_j is the formation constant of the jth species. The formation constants of the components are unity by definition; and S_j is the general symbol for any species in the system.

The concentration distribution in terms of eqns. (1) means that the T_B and T_C total concentrations are kept constant, and the equations relating to these are solved for [B] and [C] at different fixed values of [A]. Then the concentrations of species S_j are calculated and plotted against [A] or $-\log[A]$. In this way the concentration of any species, at the given values of T_B and T_C, depends on [A] only, although it is rarely possible to express the $[S_j] = f([A])$ functions explicitly. For the mathematical analysis of the concentration distribution, however, the derivatives of these functions are necessary, which may be expressed by using the rules of derivation of implicit function-systems for eqns. (1) [3,5]:

$$\frac{\mathrm{d}T_B}{\mathrm{d}\log[A]} = \Sigma a_j b_j[S_j] + \Sigma b_j^2[S_j]\frac{\mathrm{d}\log[B]}{\mathrm{d}\log[A]} + \Sigma b_j c_j[S_j]\frac{\mathrm{d}\log[C]}{\mathrm{d}\log[A]} = 0$$

$$\frac{\mathrm{d}T_C}{\mathrm{d}\log[A]} = \Sigma a_j c_j[S_j] + \Sigma b_j c_j[S_j]\frac{\mathrm{d}\log[B]}{\mathrm{d}\log[A]} + \Sigma c_j^2[S_j]\frac{\mathrm{d}\log[C]}{\mathrm{d}\log[A]} = 0 \qquad (2)$$

The d log[C]/d log[A] derivative is given from the above equations by the appropriate determinants:

$$\frac{\mathrm{d}\log[C]}{\mathrm{d}\log[A]} = \frac{\Sigma a_j c_j[S_j] * \Sigma b_j^2[S_j] - \Sigma a_j b_j[S_j] * \Sigma b_j c_j[S_j]}{\Sigma b_j^2[S_j] * \Sigma c_j^2[S_j] - (\Sigma b_j c_j[S_j])^2} \qquad (3)$$

The products of the different sums in eqn. (3) may be rearranged to give the sums of the concentration products of two species S_i and S_j:

$$\frac{\mathrm{d}\log[C]}{\mathrm{d}\log[A]} = \frac{\sum_{j=1}^{n}\sum_{i=j+1}^{n}(a_j b_i - a_i b_j)(c_j b_i - b_j c_i)[S_i][S_j]}{\sum_{j=1}^{n}\sum_{i=j+1}^{n}(b_j c_i - b_i c_j)^2[S_i][S_j]} \qquad (4)$$

It follows from eqn. (4) that the denominator is always positive; thus, only the nominator is to be analyzed for the possibility and the number of extrema on the concentration distribution of component C.

For the further analysis of eqn. (4) it is expedient to arrange the stoichiometric coefficients in a three column and n row matrix form, which is called the composition matrix of the system. The stoichiometric coefficients of any species forms a row-vector and the three row-vectors of the components A, B, and C form a unit matrix. It is seen from eqn. (4) that only the concentration products of those species are found in the denominator for which the b_i/b_j and c_i/c_j ratios are different. In other words, if the a_i, b_i, c_i and a_j, b_j, c_j vectors are extended by the vector of component A $(1, 0, 0)$ then the $3*3$ square matrix is non-singular.

In a very similar way it can be proved that only the concentration products of those species found in the nominator for which the stoichiometric numbers extended by either $(1, 0, 0)$ or $(0, 0, 1)$ (component C) form a non-singular matrix. It means that an equilibrium process can always be written between the species A, C, S_i and S_j:

$$x(1,0,0)+(0,0,1)+y(a_i,b_i,c_i)+z(a_j,b_j,c_j)=0 \tag{5}$$

The appropriate equilibrium constant is

$$K_{i,j}=[\mathrm{A}]^x[\mathrm{C}][\mathrm{S}_i]^y[\mathrm{S}_j]^z \tag{6}$$

The unknowns x, y, and z may be expressed easily from the following system of linear equations

$$x+a_iy+a_jz=0$$

$$0+b_iy+b_jz=0$$

$$0+c_iy+c_jz=-1$$

$$x=(a_jb_i-a_ib_j)/(b_ic_j-c_ib_j)$$

$$y=b_j/(b_ic_j-b_jc_i)$$

$$z=-b_i/(b_ic_j-b_jc_i)$$

Let us suppose for a while that d log[C]/d log[A] is influenced only by the concentration product of $[\mathrm{S}_i][\mathrm{S}_j]$. Then, from eqn. (6), d log[C]/d log[A] would be $-x=(a_jb_i-b_ja_i)/(b_jc_i-b_ic_j)$.

These considerations clearly illustrate the chemical meaning of eqn. (4). The d log[C]/d log[A] derivative is influenced by all of the possible equilibrium processes between A, C, S_i and S_j species. The stoichiometric numbers in S_i and S_j determine whether the increase of log[A] increases or decreases the log[C] through the appropriate equilibrium process. As far as the more than one extremum is concerned, the question is the sign of the x values of the processes and their order on the log[A] scale. If there is no change in the sign of the x values, then no extremum may be found. If there is a change of the signs, there may be extremum. Finally, if the equilibrium processes influencing the d log[C]/d log[A] derivative follow each other in such an order that more than one change of the sign may occur, then more than one extremum may be found on the log[C] = f(log[A]) distribution curve.

The above considerations were deliberately restricted to the log[C] = f(log[A]) function only. In fact this does not mean any restriction, because any species of a three-component system, apart from A, can be selected as component C, only the composition matrix should be transformed in such a way that the vectors of component A (B or C) and the species in question should form the unit matrix. Some examples in the following section will clearly illustrate this transformation and the above considerations.

D. ANALYSIS OF SEVERAL THREE-COMPONENT SYSTEMS

(i) Copper(II)–diethylenetriamine–proton system

Three extrema of the H_2L* form of the ligand were found in this system by Kaden and Zuberbühler [6]. For sake of simplicity, only the formation of the ML complex, besides the H_3L, H_2L, and HL forms of the ligand, is considered in the following analysis, although some other species are also formed in the system.

The composition matrix in its original form and by choosing the H_2L species as component C is seen in Table 1. Using eqn. (4) for the transformed matrix:

$$-\frac{\mathrm{d}\log[H_2L]}{\mathrm{d}\log[H]}=\frac{\mathrm{d}\log[H_2L]}{\mathrm{d\,pH}}$$

$$=\frac{[H_3L][M]+[H_3L][ML]-2[L][M]-[HL][M]-2[L][ML]-[HL][ML]-2[M][ML]}{[M][L]+[M][HL]+[M][H_2L]+[M][H_3L]+[ML][L]+[ML][HL]+[ML][H_2L]+[ML][H_3L]+[M][ML]}$$

Using eqn. (5) for the seven concentration products of the nominator, it turns out that there are only four equilibrium processes influencing d $\log[H_2L]/\mathrm{d}$ pH. The concentration products, the appropriate equilibrium processes, the x values representing the effect of the given equilibrium process, and the pH range of the equilibria are summarized below

Concentration product	Equilibrium	x	pH range
$[M][H_3L]$; $[ML][H_3L]$	$H_3L=H_2L+H$	+1	$pH<(pK_2+pK_3)/2$
$[M][HL]$; $[ML][HL]$	$H_2L=HL+H$	−1	$(pK_2+pK_3)/2<pH<(pK_1+pK_2)/2$
$[M][L]$; $[ML][L]$	$H_2L=L+H$	−2	$pH>(pK_1+pK_2)/2$
$[M][ML]$	$M+H_2L=ML+2H$	−2	depends on $\log \beta_{ML}$ and T_L, T_M

The x values give the slope of the $\log[H_2L]=f(pH)$ function in that pH range where the appropriate equilibrium process is dominating in the system. It is evident that at low pH, where $H_3L>>H_2L$, a unit pH change causes a unit change of $\log[H_2L]$. This relation is valid until about $[H_3L]\approx[H_2L]$, i.e.

---

* The charges are omitted throughout the paper for simplicity.

TABLE I

Composition matrix of a system containing H, M, L, H_3L, H_2L, HL, and ML species in original form and by choosing H_2L as component C

	A	B	C	A	B	C
	H	M	L	H	M	H_2L
S_j	a_j	b_j	c_j	a_j	b_j	c_j
H	1	0	0	1	0	0
M	0	1	0	0	1	0
L	0	0	1	−2	0	1
HL	1	0	1	−1	0	1
H_2L	2	0	1	0	0	1
H_3L	3	0	1	1	0	1
ML	0	1	1	−2	1	1

$pH \approx pK_3$. If the log β_{ML} is large enough the formation of the ML complex may take place in this low pH range and thus cause a quadratic decrease of $[H_2L]$ with the decrease of [H] (increase of pH). Thus, the $M + H_2L \rightleftharpoons ML + 2H$ process may overcompensate the effect of the $H_3L \rightleftharpoons H_2L + H$ dissociation. This overcompensation is evidently the consequence of the asymmetry in the composition of ML and H_2L, which is seen in Fig. 4. The overcompensation is responsible for the three extrema of the $[H_2L] = f(pH)$ function, illustrated in Fig. 5. It is worth noticing that [HL] cannot show three extrema in this system because the $M + HL \rightleftharpoons ML + H$ process can overcompensate neither the $H_3L \rightleftharpoons HL + 2H$ nor the $H_2L \rightleftharpoons HL + H$ process.

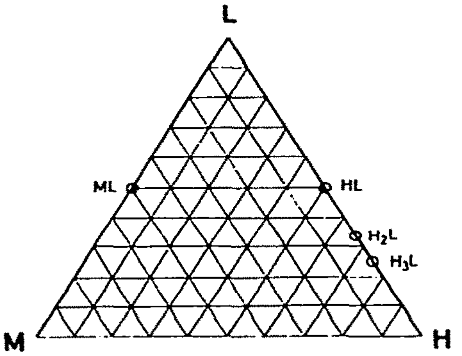


Fig. 4. Representation of the composition of the species formed in the copper(II)–diethylenetriamine–proton system below pH 7 [6].

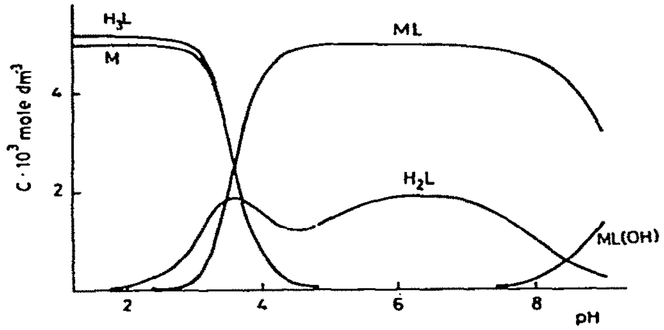


Fig. 5. Concentration distribution of the species formed in the copper(II)–diethylenetriamine–proton system below pH 9 [6]. $T_L = 0.0052$, $T_{Cu} = 0.005$ mol dm^{-3}. The curve for the H_2L represents ten times its real concentration.

In our earlier paper [3] three extrema of [HL] were illustrated on the $[HL] = f(pH)$ function in the H, L, M, H_2L, HL, and ML_2 model system. In the light of the above, the $M + 2\,HL \rightleftharpoons ML_2 + 2\,H$ process is responsible for the minimum of HL, i.e. it is also the consequence of the asymmetry in the composition of HL and ML_2.

There is asymmetry of the composition between the H_3L and ML also, but there is no change in the signs of the concentration product determining the numerator of $d \log[H_3L]/d\,pH$, thus this asymmetry may not cause concentration minimum on the $[H_3L] = f(pH)$ function.

It can be concluded that the necessary condition of the three extrema on the $[H_2L] = f(pH)$ function is the asymmetry of the system. The more than one extremum, however, is exhibited only if ML is formed in that pH range where mainly the $H_3L \rightleftharpoons H_2L + H$ dissociation would take place in the absence of a metal ion. This semi-quantitative statement can be proved explicitly by the derivation and analysis of the second derivative $d^2 \log[H_2L]/d\,pH^2$, which will be given later [7].

(ii) Methylmercury–acetate–proton system

This system was investigated by Rabenstein et al. [8]. The authors stated that $M(OH) = MH_{-1}$ and $M_2(OH) = M_2H_{-1}$ hydroxo complexes are formed in aqueous solution of methylmercury, and ML complex is also formed in the presence of acetate ion. The authors found three extrema on the binuclear hydroxo complex as a function of pH, as is seen in Fig. 6.

For interpretation of the concentration minimum, the transformed matrix

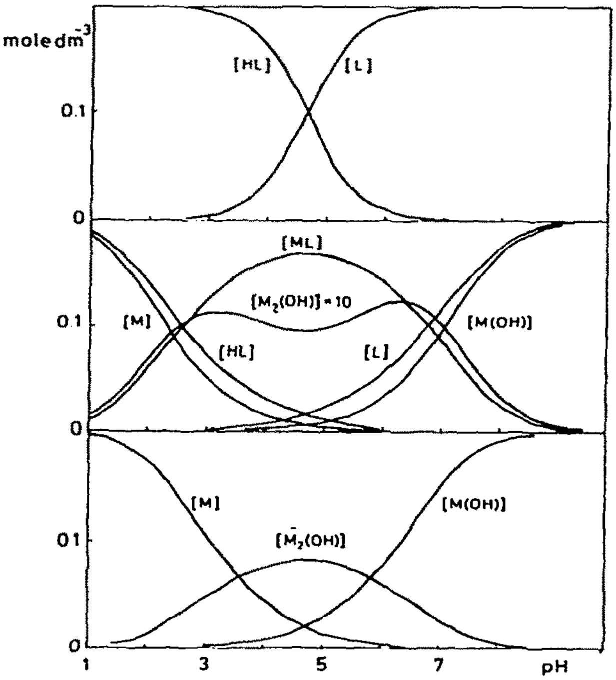


Fig. 6. Concentration distribution of the complexes formed in the methylmercury–acetate–proton system [8]. Top: HL–L distribution in absence of methylmercury. Bottom: M–M_2H_{-1}–MH_{-1} distribution in absence of acetate. The distribution of the three-component system is seen in the middle of the figure.

and the d $\log[M_2H_{-1}]/\mathrm{d\,pH}$ function is given:

	H	L	M_2H_{-1}
H	1	0	0
L	0	1	0
M	$\frac{1}{2}$	0	$\frac{1}{2}$
ML	$\frac{1}{2}$	1	$\frac{1}{2}$
HL	1	1	0
MH_{-1}	$-\frac{1}{2}$	0	$\frac{1}{2}$
M_2H_{-1}	0	0	1

$$\frac{\mathrm{d}\log[M_2H_{-1}]}{\mathrm{d\,pH}} = \frac{([L]+[HL]+[ML])([M]-[MH_{-1}])+[ML]([L]-[HL])}{([L]+[HL]+[ML])([M]+[MH_{-1}]+4[M_2H_{-1}])+[ML]([HL]+[L])}$$

Using eqn. (5) for the eight concentration products in the numerator, four independent processes can be found. The concentration products, the appropriate equilibrium processes, and the x values are summarized below.

No.	Concentration product(s)	Equilibrium	x
1.	[L][M], [HL][M], [ML][M]	$2\,M \rightleftharpoons M_2H_{-1} + H$	1
2.	[L][MH_{-1}], [HL][MH_{-1}], [ML][MH_{-1}]	$2\,MH_{-1} + H \rightleftharpoons M_2H_{-1}$	−1
3.	[ML][HL]	$2\,ML + H \rightleftharpoons M_2H_{-1} + 2\,HL$	−1
4.	[ML][L]	$2\,ML \rightleftharpoons M_2H_{-1} + 2L + H$	1

At low pH evidently the [M][HL] concentration product dominates over all of the others, thus [M_2H_{-1}] increases with increasing pH, due to equilibrium No. 1. At the pH range, however, where the ML complex is formed but the ligand is in the form HL, equilibrium No. 3 becomes important and this causes the decrease of [M_2H_{-1}] with increasing pH. At a higher pH range, where the $HL \rightleftharpoons H + L$ dissociation is already practically completed, the increase of pH increases [M_2H_{-1}] through equilibrium No. 4. Finally, [M_2H_{-1}] decreases again because of equilibrium process No. 2. This order of equilibria causes three extrema on the [M_2H_{-1}] $= f$(pH) function.

For the construction of the triangle diagram of this and similar systems, the axes should be extended to include OH, which is regarded as $-$H in aqueous solution. This is illustrated in Fig. 7 for the methylmercury–acetate–proton system. It is seen in the diagram that the system is asymmetrical. This is the consequence of the formation of M_2H_{-1}, which shows the unusual distribution.

(iii) *Uranyl–BDTA–proton system*

The system has been studied by Gans et al. [9]. A number of different species are formed in the system; however, for the sake of simplicity, only

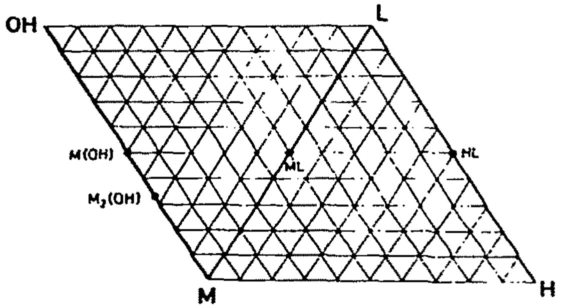


Fig. 7. Representation of the composition of the species formed in the methylmercury–acetate–proton system.

those which are important in explaining the minimum of $[H_2L]$ are plotted in Fig. 8.

A similar analysis, previously illustrated, led to the result is given below.

Equilibrium		pH range
$H_3L \rightleftharpoons H_2L + H$	1	<4
$H_2L + M \rightleftharpoons MLH + H$	−1	3.5–5.0
$2\,MLH + 2\,H_2O \rightleftharpoons M_2L(OH)_2 + H_2L + 2\,H$	2	5.3–7
$H_2L \rightleftharpoons HL + H$	−1	>8

It is clear that the hydrolysis of MLH is responsible for the minimum of $[H_2L]$, because this process results in a quadratic increase of H_2L in that pH range, where the $[H_2L]$ would be decreasing in the absence of a metal ion. Moreover, if an overcompensation originating from the $H_2L + M \rightleftharpoons ML + 2H$ equilibrium, illustrated in the copper(II)–diethylenetriamine–proton system, and an overcompensation shown in the present example would occur in the same system, then there would be five extrema on the $[H_2L] = f(\mathrm{pH})$ function, with two minima.

(iv) Al^{3+}–Cl^-–dimethylformamide system

The equilibrium relations in the $AlCl_3$–dimethyl-formamide system in nitromethane has been studied by Schipper [4] using ^{27}Al NMR method to determine the concentration of each of the species. He showed that the difference in the maximum coordination number in Al^{3+}–Cl^- and in the

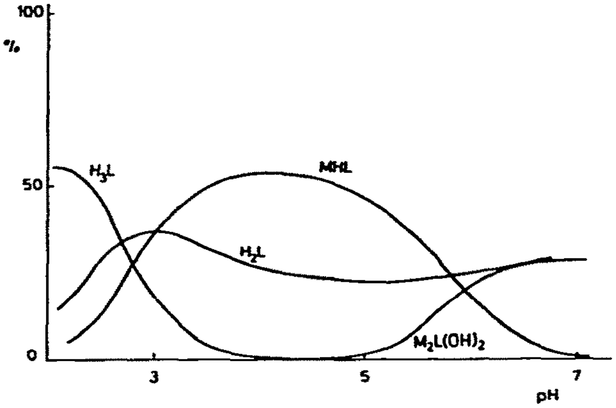


Fig. 8. Concentration distribution of some of the species formed in the uranyl–butylenediaminetetraacetate–proton system [9].

Al^{3+}–DMFA system was responsible for the concentration minimum. In terms of the classification of the three-component systems this difference causes the asymmetry illustrated in Fig. 9.

The distribution of complexes is illustrated in Fig. 10 as a function of the total concentration ratio of the two ligands. The very sharp maximum of $[AlCl_4^-]$ and $[Al(DMFA)_6^{3+}]$ may be surprising at first, but comparison of this distribution with Fig. 11, where the distribution is plotted in the usual way, clearly shows that the sharp maximum is the consequence of the very large change of log[DMFA] at around $T_{DMFA}/T_{Cl^-} \approx 0.5$.

A total analysis of the system showed that there are 23 concentration products influencing the concentration of $Al(DMFA)_6^{3+}$. For the sake of simplicity, only those three which are mainly responsible for the minimum are shown.

Equilibrium	Concentration product
$MX_3Y + 5Y = MY_6 + 3X$	$[MX_3Y][X]$
$3\ MY_6 + 2Y + MX_4 = 4\ MXY_5$	$[MX_4][MXY_5]$
$MXY_5 + Y = MY_6$	$[MXY_5][X]$

The effect of these equilibria can be seen in the Figures almost separately. Between $T_Y/T_X = \frac{1}{3} - \frac{1}{2}$, MY_6 is formed mainly from MX_3Y, through the first equilibrium. In the $T_Y/T_X = 0.5$–0.7 range, however, the second equilibrium becomes important. It is interesting to note that for the formation of MXY_5, the coordinatively saturated MY_6 reacts with further Y; thus, the increase of the free ligand concentration decreases the concentration of the coordinatively saturated parent complex. This is evidently the consequence

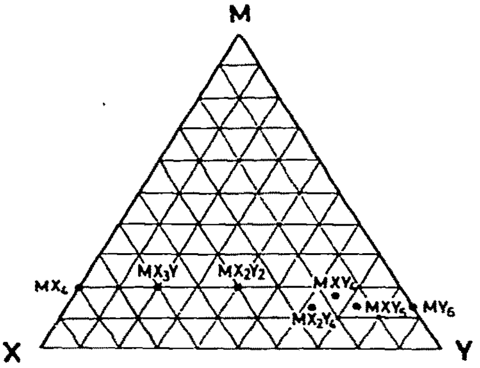


Fig. 9. Representation of the composition of the species formed in the Al(III)–Cl^-–dimethylformamide system.

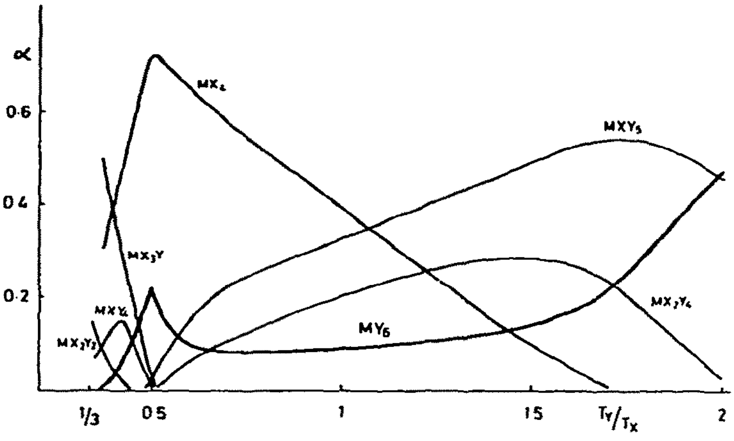


Fig. 10. Concentration distribution of the species formed in the Al(III)$-$Cl$^-$$-$dimethylformamide system as a function of the $T_{\mathrm{DMFA}}/T_{\mathrm{Cl}}$ concentration ratio [4].

of the difference in maximum coordination number of the M$-$Y and M$-$X subsystems, i.e. of the asymmetry.

Finally, the concentration of MY_6 increases, and this complex becomes the only important species at sufficiently high DMFA concentration.

(v) Cl^-–Hg^{2+}–OH^- system

The hydrolysis of the mercury ion in the presence of chloride has been studied by Sjöberg [10]. The triangle diagram and the concentration distribu-

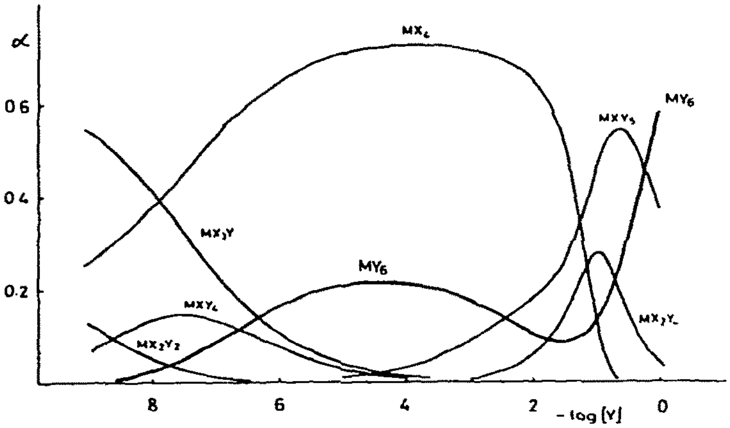


Fig. 11. Concentration distribution of the species formed in the Al(III)$-$Cl$^-$$-$dimethylformamide system as a function of $-$log[DMFA].

tion at a given total concentration are seen in Figs. 12 and 13.

There are two distinct features of this system. The system seems to be apparently symmetric, yet a concentration minimum occurs in $[HgCl_2]$. In all of the preceding examples, the species having concentration minimum contained that component whose total concentration has changed along the distribution curve. This system is an exception. The concentration products, the appropriate equilibrium processes, and the x values given from the mathematical analysis of the $d\log[HgCl_2]/d\,pH$ function are as follows:

No.	Concentration product	Equilibrium	x
1.	$[HgCl][Hg(OH)]$	$2\,HgCl + OH \rightleftharpoons Hg(OH) + HgCl_2$	$+1$
2.	$2[HgCl][Hg(OH)_2]$	$2\,HgCl + 2\,OH \rightleftharpoons Hg(OH)_2 + HgCl_2$	$+2$
3.	$-[Cl][Hg(OH)]$	$Hg(OH) + 2\,Cl \rightleftharpoons HgCl_2 + OH$	-1
4.	$-2[Cl][Hg(OH)_2]$	$Hg(OH)_2 + 2\,Cl \rightleftharpoons HgCl_2 + 2\,OH$	-2
5.	$-[Cl][Hg(OH)Cl]$	$Hg(OH)Cl + Cl \rightleftharpoons HgCl_2 + OH$	-1
6.	$-2[Hg][Hg(OH)Cl]$	$2\,Hg(OH)Cl \rightleftharpoons HgCl_2 + Hg + 2\,OH$	-2
7.	$-[Hg(OH)][Hg(OH)Cl]$	$2\,Hg(OH)Cl \rightleftharpoons HgCl_2 + Hg(OH) + OH$	-1

It is seen that during the hydrolysis of the system, $[HgCl_2]$ may be increased by increasing pH only if equilibrium No. 1 or 2 is dominating. The equilibrium-pairs No. 1–6 and No. 2–7, respectively, must take place in the same pH range, because the concentration products can be expressed by the same

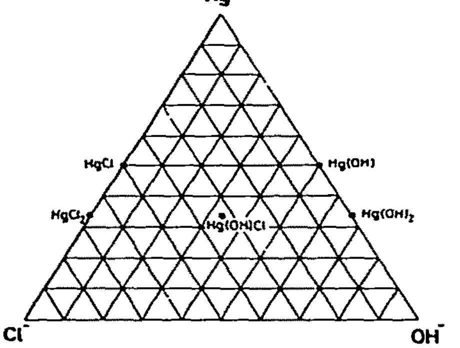


Fig. 12. Representation of the composition of the species formed in the Cl^-–Hg(II)–OH^- system.

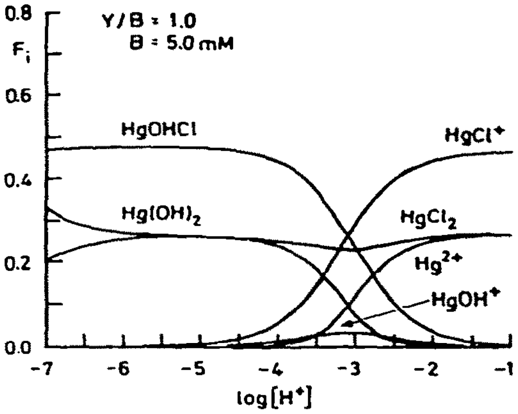


Fig. 13. Concentration distribution of the species formed in the Cl^-–Hg(II)–OH^- system [10]. $Y = Cl^-$, $B = Hg(II)$, $F_i = [S_i]/T_{Hg}$.

power of the free concentrations. Thus, the increase of $[HgCl_2]$ may happen only if the

$$[HgCl][Hg(OH)] > 2[Hg][Hg(OH)Cl]$$

i.e. $K_1^{Cl} \cdot K_1^{OH} > 2\beta_{11}$, or

$$2[HgCl][Hg(OH)_2] > [Hg(OH)][Hg(OH)Cl]$$

i.e. $2K_1^{Cl} \cdot K_2^{OH} > \beta_{11}$, relation is valid.

Introducing the $\lambda_{Cl} = K_1^{Cl}/K_2^{Cl}$, $\lambda_{OH} = K_1^{OH}/K_2^{OH}$, and $K_M = [Hg(OH)Cl]^2/([HgCl_2][Hg(OH)_2])$ notations, then these relations may be rearranged into the following form:

$$\lambda_{Cl}\lambda_{OH} > 4K_M$$

or

$$\lambda_{Cl}/\lambda_{OH} > K_M/4$$

In the statistical case both the ratios of the constants of the stepwise formation of the parent complexes and the value of K_M are equal to 4. It is clear from the obtained relations that no extremum can occur on the distribution curves if the mixed ligand complex formation takes place statistically, and the ratios of the constants of the stepwise formation of parent complexes are the same.

In the present system $\lambda_{Cl} = 2.75$, $\lambda_{OH} = 0.15$, and $K_M = 3.16$, therefore the second relation is valid, permitting the occurrence of concentration minimum. The reason of the exceptional behaviour of the Hg^{2+}–Cl^-–OH^- system is that the ratio K_1^{OH}/K_2^{OH} is so small.

Strictly speaking, a three-component system can be regarded symmetrical only if its triangle diagram has a C_{2v} symmetry and the ratios of the formation constants of the corresponding parent complexes are the same. The asymmetry of the triangle diagram itself may be called stoichiometric asymmetry, while the considerable difference in the ratios of the formation constants referring to the corresponding parent complexes may be termed as thermodynamic asymmetry. Obviously, stoichiometric asymmetry is the limiting case of the thermodynamic one.

E. CONCLUDING REMARKS

As already mentioned, the metal ion–ligand–proton systems are almost always stoichiometrically asymmetric; this type of asymmetry also seems to be quite common in cases of heteropolyacid formation. Therefore all these systems are suspicious that more than one extremum may occur in the concentrations of some of the species. In cases of mixed-ligand complex formation there are two possibilities for stoichiometric asymmetry. Either there is a difference in the maximum coordination number for the two ligands due to steric reasons, or there is a difference in the dentateness of the two ligands. There are two reasons why these unusual distributions were not found more frequently earlier and, besides the analyzed ones, we found only a few more [11–14] among the published systems. First, they were not looked for. In many cases the distribution curves were not calculated at all or were restricted to the metal-containing species. As was shown in the earlier considerations, such types of distribution may occur in the concentration of protonated ligands. Secondly, both types of asymmetry indicate only the necessary but not the sufficient conditions. The appearance of the concentration minimum requires a fairly high degree of asymmetry. In the case of symmetric systems the distribution curves of all the intermediary complexes are bell-shaped. Any deviation from the symmetry results in a distortion of these curves and if the asymmetry reaches a critical level, more than one extremum appears on the curve(s). Unfortunately this critical level cannot be given in explicit form. From the analysis of equilibria outlined in the paper, the reactions responsible for the concentration minimum can be identified. Qualitatively it is evident that for the appearance of the minimum, the effect of these equilibria should be dominating in the system. Whether these equilibria become dominating in the real concentration range can only be learned from the numerical calculations. A quantitative analysis requires some more effort and will be published later.

Although evidently there is a much greater chance that any three-component system may be asymmetric than symmetric, the term "unusual concentration distribution" may be retained. With increasing number of components the probability of unusual distribution increases.

REFERENCES

1 R.P. Agarwall and D.D. Perrin, in E. Högfeldt (Ed.), Coordination Chemistry in Solutions. Berlingska Boktryekeriet, Lund, 1972.
2 M.L.D. Rouche and D.R. Williams, J. Chem. Soc., Dalton Trans., (1976) 1355.
3 I. Nagypâl and M.T. Beck, J. Phys. Chem., 84 (1980) 722.
4 E. Schippert, Inorg. Chim. Acta, 21 (1977) 35.
5 I. Nagypâl, I. Pâka and L. Zékâny, Talanta, 25 (1978) 549.
6 Th. Kaden and A. Zuberbühler, Helv. Chim. Acta, 54 (1971) 1361.
7 I. Nagypâl, M.T. Beck and A. Zuberbühler, to be published.
8 D.L. Rabenstein, R. Ozubko, S. Libich, G.A. Evans, M. Fairhust and C. Suwanprakorn, J. Coord. Chem., 3 (1974) 263.
9 P. Gans, A. Mota and L.D. Pettit, to be published.
10 S. Sjöberg, Acta Chem. Scand., Ser. A, 31 (1977) 705.
11 L. Harju, Talanta, 22 (1975) 1029.
12 I. Nagypâl and F. Debreczeni, Inorg. Chim. Acta, 57 (1982) 125.
13 A. Gergely and T. Kiss, Inorg. Chim. Acta, 16 (1976) 51.
14 K.S.N. Iyer, S. Lau, S.H. Laurie and B. Sarkar, Biochem. J., 169 (1978) 61.