Unusual Concentration-Distribution of Metal Complexes

I. NAGYPÁL* and M. T. Beck**

*Institute of Inorganic and Analytical Chemistry, and **Institute of Physical Chemistry, Kossuth Lajos University,
4010 Debrecen, Hungary

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The partial molar ratio of metal complexes in general exhibits at most one extremum as a function of free ligand concentration. More than one extremum can be found, however, if the complex formation is accompanied by the change in the medium, or if special competition reactions take place. Examples for both cases can be found in the literature.

Introduction

The partial molar ratio of the mononuclear complexes either changes monotonously or exhibits at most one extremum as a function of free ligand concentration. This is an evident consequence of the correlation between the mass-balance and the equilibrium constants (K_i) or stability products ($\beta_i = \Sigma K_i$) of the stepwise equilibria:

$$M + L \rightleftharpoons ML$$
$$\vdots \qquad \vdots \qquad\qquad (1)$$
$$ML_{N-1} + L \rightleftharpoons ML_N$$

With these, the partial molar ratio of an individual complex could be given as follows:

$$\alpha_n = \frac{\beta_n [L]^n}{\sum\limits_{0}^{N} \beta_i [L]^i} \qquad (2)$$

If $n = 0$, then the molar ratio decreases, in case of $n = N$ it increases monotonously and between these it shows one maximum as a function of free ligand concentration. This statement is also valid if the complex formations are considered as exchange processes:

$$MS_N + L \rightleftharpoons MS_{N-1}L + S$$
$$\vdots \qquad\qquad \vdots \qquad\qquad\quad (3)$$
$$MSL_{N-1} + L \rightleftharpoons ML_N + S$$
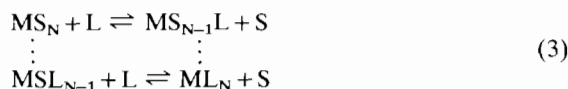
In this case the partial molar ratios could be given by the following general equation:

$$\alpha_n = \frac{\beta_n \left(\frac{[L]}{[S]}\right)^n}{\sum\limits_{i=0}^{N} \beta_i \left(\frac{[L]}{[S]}\right)^i} \qquad (4)$$

Recently, however, experimental investigations[1,2] have been published which showed that plotting α_n versus $[L]$ more than one extremum can be found.
Because of the obvious coordination chemical importance of this phenomenon we have been dealing with this and have come to the following conclusion:
There are two possibilities for the unusual concentration-distribution. In the first case there is a change of the medium accompanying the successive complex formation. The second case is when the unusual concentration-distribution is the consequence of the nature of competition reactions.

The Consequences of the Change of the Medium

Vértes, Gaizer and Beck[1] have recently studied the effect of the dimethylformamide on the SnI_4 dissoluted in carbontetrachloride, registering the Mössbauer spectra of quickly-frozen solutions. On the basis of spectrophotometric and conductometric measurements it had earlier been stated[3], that the dimethylformamide formed a sixcoordinated mixed ligand complex with the weakly solvated SnI_4 in carbontetrachloride:

$$SnI_4 + 2D \rightleftharpoons SnI_4D_2$$

(D = dimethylformamide). The iodide ions bound in the first coordination sphere are exchanged by dimethylformamide at higher dimethylformamide concentration. On the other hand there is a possibility for the formation of penta- and hexa-iodo complexes due to disproportionation reactions:

$$2 SnI_4D_2 \rightleftharpoons SnI_3D_3^+ + SnI_5D^-$$
$$2 SnI_4D_2 \rightleftharpoons SnI_2D_4^{2+} + SnI_6^{2-}$$
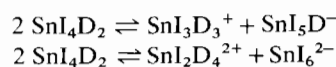
Of course the equilibrium constants of the disproportionation reactions can be expressed by the equilibrium constants of the successive exchange processes. The Mössbauer data unambiguously showed that the sum of the molar ratio of the two six-coordinated parent complexes (SnI_6^{2-} and SnD_6^{4+}) had two extrema in the function of dimethylformamide · concentration. These changes were observed in the $0–12.9$ mol dm^{-3} dimethylformamide concentration range. It is evident,

that when the dimethylformamide concentration is increased, the change in the medium of the reaction have to be considered. This means, that the equilibrium constants depend on the medium, and so the following equation is valid for the change of the partial molar ratios as a function of the ligand (solvent) concentration.

$$\alpha_n = \frac{\beta(L)_n \left(\frac{[L]}{[S]}\right)^n}{\sum\limits_{i=0}^{N} \beta(L)_i \left(\frac{[L]}{[S]}\right)^i} \tag{5}$$

The functions $\beta(L)_i$ in equation (5) are not known, and this system is too complicated for model calculations. Hence the simplest possible model system ($N = 2$) have been choosen for model calculations.

It is assumed that ML and ML_2^- parent complexes are formed in the inert solvent from the M^+ metal ion and L^- ligand. When the second solvent (S) is present, then MS^+, MS_2^+ and MLS complexes are also formed. It is assumed moreover, that ideal mixing occurs between the two solvents, both has a density of 1 $kgdm^{-3}$. Finally it is assumed, that each formation constant is a linear function of the reciprocal value of dielectric constant, as it was experimentally found in a number of examples:

$$\lg\beta = \lg\beta_0 + \gamma'/\varepsilon \tag{6}$$

The concentration-distribution curves have been calculated with a method published earlier[4]. Unusual concentration-distribution curves have been found for example using the data given in Table I.

The change of the $\lg\beta$ values as a function of $-\lg[S]$ is shown on Figure 1 (the x axis of the Figure also shows the $1/\varepsilon$ values and the molar fraction x_2 of the "donor" solvent). The concentration-distribution of the complexes is shown on Figure 2.

TABLE 1. The Data Used for Model Calculations.

Dielectric Constant Molar Volume (cm₃)	"Inert" Solvent	"Donor" Solvent
	2	40
	154	78

Equilibrium	$\lg\beta_0$	γ
$M + L \rightleftharpoons ML$	7.0	15.0
$M + 2L \rightleftharpoons ML_2$	9.1	28.0
$M + S \rightleftharpoons MS$	5.8	4.25
$M + 2S \rightleftharpoons MS_2$	5.9	7.0
$M + L + S \rightleftharpoons MLS$	5.5	18.0

Although the data of the Table do not belong to any real chemical system, the functions given are in accordance with chemical considerations. The formation of ML and ML_2^- complexes is generally accompanied by charge-compensation, and so the corresponding constants are much more dependent on the dielectric constant than the formation constants of MS^+ and MS_2^+ complexes. At the same time the relation of the formation constants of complexes containing L^- and S ligands have been selected on such a way that they have concentrations of similar magnitude in a relatively wide concentration range. These chemically expected relations are reflected in the data of Table 1.

It can be seen on Figure 2 that with decreasing and increasing $-\lg[S]$ values the concentration of MS^+ complex asymptotically reaches zero, and in the medium concentration range it has two maxima and one minimum. It is noticeable moreover that the concentration-distribution for each complex is somewhat "unusual" in the $1.5 > -\lg[S] > 0$ range. The explanation could be that the increase of the concentration may be compensated or overcompensated by the decrease of
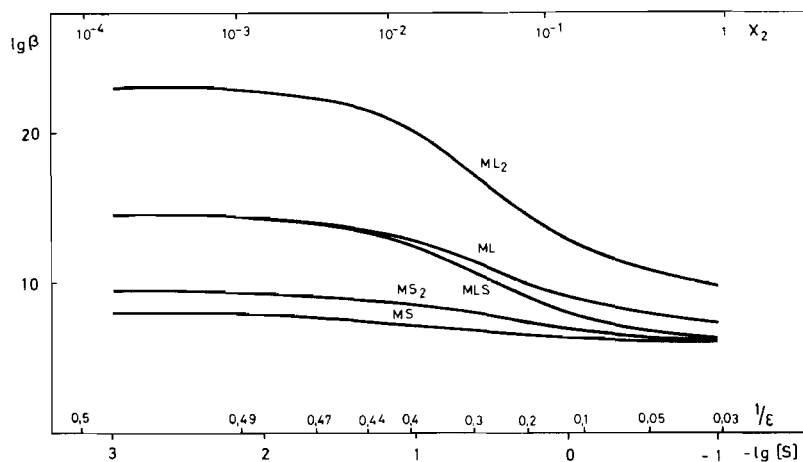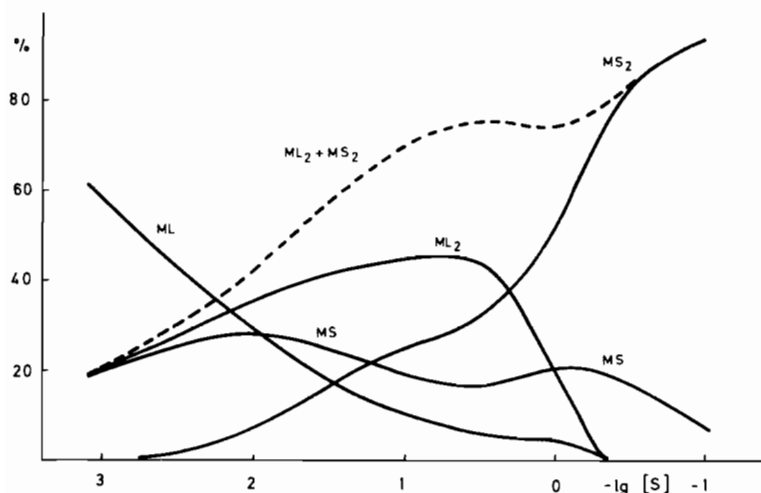

Figure 1. $\lg\beta$ values of the complexes as a function of "donor" solvent concentration. For comparison the change of mole fraction of S and that of $1/\varepsilon$ is also shown on the abscissa.

Figure 2. Concentration-distribution of the complexes as a function of "donor" solvent concentration.

β values in this range, depending on the γ values. This phenomenon cannot be observed out of the above concentration range, because there is no significant change in the $1/\varepsilon$ values in the upper and lower regions. It is worth to mention that in analogy with the experimental results for the $Sn(IV)–I^-–$dimethylformamide system, the sum of the concentration of ML_2^- and MS_2^+ complexes exhibits one minimum and one maximum.

The exact determination of the maximum number of possible extrema, and of the range of parameters resulting in unusual concentration-distribution leads to unsurmountable mathematical and chemical difficulties. The reason of this is that even in this system there are sixteen parameters affecting the concentration-distribution (the total concentration of the M^+ metal ion and L^- ligand, the dielectric constant and molar volume of the two solvents, the β_0 and γ values of the complexes). On the other hand the chemically real range of the parameters can only be roughly estimated.

In spite of this it is probable that the unusual concentration-distribution can only be observed in that concentration range, where the change of the formation constants as a function of the concentration is the steepest, where the above mentioned compensation effect could play important role in determining the concentration. At the same time it is also likely, that— assuming the validity of the $lg\beta = lg\beta_0 + \gamma/\varepsilon$ or any other monotonous function—only one minimum could be observed in this range.

The Effect of Competition Equilibrium Processes

There is an example for the unusual concentration-distribution resulted by the competition equilibria in the case of copper(II)–glycine–diglycine system. Agar-

wall and Perrin[2] have calculated the concentration-distribution in this system at (Cu^{2+}): (gly): (digly) $= 10^{-5}: 2 \times 10^{-3}: 2 \times 10^{-3}$ mol dm^{-3} concentration ratio. One minimum and two maxima have been found for the concentration-distribution of $Cu(glycine)_2$ complex (Figure 3).

Let us consider the change of the concentration of components $(Cu^{2+}, L^-, A^-, OH^-)$, in the function of pH to interpret this unusual distribution. Ignoring the total concentration of copper beside that of the ligands, it is easy to realize, that the concentration of L^- and A^- change according to a saturation curve in the function of pH. The $\partial pL/\partial pH$ and $\partial pA/\partial pH$ agree with the $-n_H$ values concerning the appropriate proton complexes. The $\partial pOH/\partial pH$ value however is always -1, which evidently means that at high pH some of the deprotonated (or hidroxo) complex becomes dominant.

The change of the free copper ion concentration cannot be given so simply. In case of mononuclear complex formation however, the change of it has identical effects on the concentration of each complex. Hence, it is not necessary to know the $[Cu^{2+}] = f(pH)$
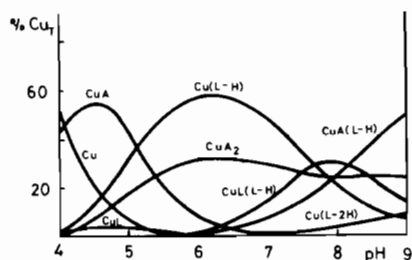

Figure 3. The pH-dependence of the computed distribution of copper(II) species in the presence of glycine (HA) and diglycine (HL). Total copper $Cu_T = 10^{-5}M$, total glycine $= 2 \times 10^{-3}M$, total diglycine $= 2 \times 10^{-3}M$.
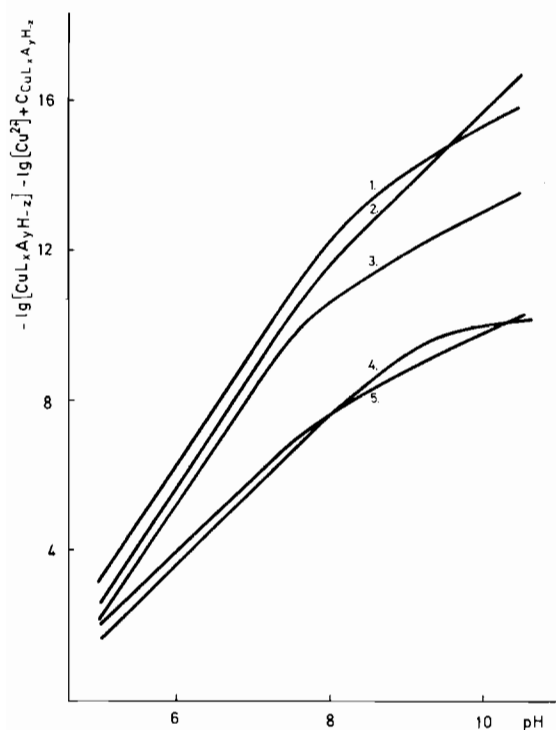
Figure 4. The relative change of the concentration of complexes formed in Cu(II)–glycine–diglycine system, as a function of pH. Notations:

	x	y	z
1:	1	1	-1
2:	1	0	-2
3:	2	0	-1
4:	0	2	0
5:	1	0	-1

function for estimating the *relative* change of the concentration of complexes.

The concentration of a complex could be given as follows:

$$\lg[CuL_xA_yH_{-z}] = \lg\beta_{xy-z} + \lg[Cu^{2+}] + x\lg[L^-] + \\ + y\lg[A] - z\lg[H]$$

The $\lg[CuL_xA_yH_{-z}] = f(pH)$ functions could be constructed with correct relative slopes, without the knowledge of the constants and the $\lg[Cu^{2+}] = f(pH)$ functions. These curves show correctly the relative concentration-distribution of the complexes.

The curves constructed for the copper(II)–glycine–diglycine system from the protonation constants and the stoichiometric compositions are shown on Figure 4. The curves are given on the y axis on arbitrary units, their position depends on the constants. It can be seen, that by parallel shift more than one intersection could be constructed between two curves, which evidently means that a minimum *i.e.* unusual concentration-distribution may occur in the system. Whether it occurs or not, it depends on the stability constants.

In the system studied, the unusual concentration-distribution is the consequence of the deprotonated (hidroxo) complex formation. The increasing pH always increases their concentration, while in the case of L^- or A^- containing complex, the pH effect depends on the pH range.*

Finally it is worth noticing, that unusual concentration-distribution could be found in the literature[5] even in such cases when no chemical (and mathematical) reason could be found for that. However, using the set of evaluated stability constants, the calculated distribution curves are normal. In these cases, the unappropriate calculations and/or experimental errors could result in an unusual concentration-distribution. Hence no chemical meaning is to be attributed to those "unusual" distributions.

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* After submitting this paper for publication, Rabenstein *et al.*[6] published unusual concentration-distribution in the methyl-mercury–acetate–OH$^-$ system. In this case also the *competition* between two ligands *and* the binuclear complex formation are responsible for the unusual concentration-distribution.

References

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