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Introduction

When the complex formation process is studied in some metal-ligand system traditionally the number of complex species is restricted to the coordination saturated complex [1]. If the complexity reaction is expressed as $M + nL \leftrightharpoons ML_n$ then, the thermodynamic stability constant of the complex ML_n defined as

$$\beta'_{ML_n} = \frac{(ML_n)}{(M)(L)^n} \cdot \frac{f_{ML_n}}{f_M \cdot f_L^n} = \beta_{ML_n} \cdot \frac{f_{ML_n}}{f_M \cdot f_L^n}$$

could be regarded as a product of concentration quotient β_{ML_n} and activity coefficient quotient $\dfrac{f_{ML_n}}{f_M \cdot f_L^n}$. Most experimental methods used for the determination of stability constants are designed for constant ionic strength of the solution, which provides conditions such as the activity coefficient quotient to be considered as a constant. Actually, the activity coefficient quotient expresses the medium effect. The latter is usually estimated by using the Debye–Hückel's expression [2] or some of its modifications [3,4].

Sillén [5] has pointed out that generally there is not always an evidence to ignore the presence of the species formed in the solution as a result of the interaction between the metal complexes ML_n and the ionic medium ions and solvent molecules. The rightness of this opinion was supported by the results reported in a number of papers [6-8]. According to Mironov [9] part of the ionic medium effect could be ascribed to a formation of outer sphere complexes in the solution.

In previous papers [10-16] the validity of a simple relation which connects the overall stability constants of metal complexes was demonstrated for a number of metal-ligand systems. That

relation has been derived on the basis of a mathematical model concerned with a stepwise series of mononuclear metal complexes formed in an aqueous solution with a constant ionic strength[10].

In the present paper an attempt is made to modify this model for metal-ligand systems studied at several constant ionic strengths on the basis of the assumption that the ionic medium effect is mainly due to a formation of outer sphere complexes the number and the concentration of which depend on the ionic strength of the solution.

Theory

The equations which will be derived are based for the most part of earlier paper[10] so here many details will be omitted. The mathematical model constructed in Ref.[10] was concerned with the formation of a series of mononuclear complexes of the type ML_n formed in an aqueous solution with a constant ionic strength. One of the basical assumption was that in the system under consideration no formation of outer sphere complexes of the type C_pML_n occurs, where C denotes the electrolyte cation. For this case the quantity P – the total probability for the distribution of the metal M in the solution has been introduced and defined as

$$P = P_M + \sum_{n=1}^{n=N} P_{ML_n} = 1,$$ (1)

where

$$P_M = \frac{(M)}{C_M}$$ (1')

is the probability of M ion being found in the solution,

$$P_{ML_n} = \frac{1}{C_M} \cdot A \frac{a^n}{n!} (M)(L)^n$$ (1'')

is the probability of ML_n complex being found in the solution,
M is the complex forming metal M^{m+}, L is monovalent ligand,
C_M is the total (analytical) concentration of M in the solution,
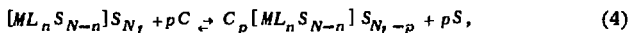n is the number of ligands, ( ) are concentrations, A and a are constants.

The concentration of ML_n in the solution is then given by

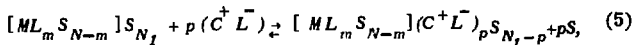$$(ML_n) = C_M P_{ML_n} = A \frac{a^n}{n!} (M)(L)^n .$$ (2)

Now, we shall consider the same metal-ligand system but at a constant ionic strength of the solution at which the formation of outer sphere complexes could not be ignored. The higher the ionic strength of the solution is the higher is C^+ ions concentration. On one hand this could cause ion-pairing of the electrolyte

$$C^+ + L^- \rightleftarrows C^+ L^-$$ (3)

and on the other hand a formation of outer sphere complexes of the type $C_p ML_n$. The latter could be charged as well as neutral ones, and their formation may proceed by different mechanisms. Two conceivable reactions are

$$[ML_n S_{N-n}] S_{N_I} + pC \rightleftarrows C_p [ML_n S_{N-n}] S_{N_I - p} + pS ,$$ (4)

$$1 \leq p \leq N-m \qquad m < n \leq N$$

$$[ML_m S_{N-m}] S_{N_I} + p(C^+ L^-) \rightleftarrows [ML_m S_{N-m}](C^+ L^-)_p S_{N_I - p} + pS ,$$ (5)

$$1 \leq p \leq N_I$$

where S is water molecule, N and N_I is the maximum number of water molecules coordinated to M in its first and second hydration spheres respectively.

Here also, as it was already done in the derivation of the equations in Ref.[10], the hydration of the species which substitute water molecules is not taken into account. It should be pointed out that the proposed reactions (4) and (5) could not represent the actual mechanism. But since the thermodynamic considerations underlying the equilibria in solution are concerned with the initial and final states and not with the path the reaction takes, formally, we could use each of these reactions to express the process and it will not affect the final results.

Depending on the properties of the system as a whole the electrolyte ion-pairing, Eq. (3), and the formation of outer sphere complexes, Eqs. (4) and (5), may proceed to a different degree.

Let us suppose that by reaction (4) only charged outer complexes are formed. Then, the following unequalities will be hold $m + l < n \leq N$ and $l \leq p < N - (m + l)$. The neutral outer sphere complexes are supposed to be formed by reaction (5) only.

As far as the mathematical model which will be presented in this paper is an extension of that developed in Ref. [10], all initial assumptions made in that paper are hold here also. A similar treatment as that applied in Ref. [10] will be used keeping in mind that: i) In the system treated in Ref. [10] the metal ion M is considered as a central group of the complex series and here this part will be played by the species ML_n ii) In Ref. [10] the complex formation reaction is considered as a substitution of water molecules from the first hydration sphere of M with ligands L, and in the present treatment the water molecules from the second hydration sphere of M are substituted with C^+ ions (or with C^+L^- ion-pairs if reaction (5) is considered). iii) Short range attractive forces will be introduced and defined as follows: a) for reaction (4) $f_{x \to y}$ is the force directed from the species ML_n, CML_n, C_2ML_n... towards C^+ ion, which is assumed to be a constant independent of the type of the complex species. $f_{y \to x}$ is the force directed from C^+ ion towards the complex species ML_n, CML_n, C_2ML_n ..., which is assumed to be constant independent the type of the complex species. $f_{x \to s}$ is the force directed from the species CML_n, C_2ML_n... towards water molecule, which is assumed to be constant independent of the type of the complex species. $f_{s \to x}$ is the force directed from the water molecule towards the complexes CML_n, C_2ML_n... which is assumed to be constant independent of the type of the complex species. b) for reaction (5) $f_{x' \to y'}$ is the force directed from the species CML_m, CML_{m+1}, C_2ML_{m+2}... towards C^+L^- which is assumed to be constant independent of the type of the complex species. $f_{y' \to x'}$ is the force directed from the ion-pair C^+L^- towards the complexes ML_m, CML_{m+1}, C_2ML_{m+2}... which is assumed to be constant independent of the complex species. $f_{x' \to s'}$ is the force directed from the complexes CML_{m+1}, C_2ML_{m+2}... towards a water molecule, which is assumed to be constant independent of the type of the complex species. $f_{s' \to x'}$ is the force directed from a water molecule

towards the complexes CML_{m+1} , $C_2 ML_{m+2}$ ..., which is assumed to be constant independent of the type of the complex species. iv) The number of the complex species which have a suitable energy for the forward reaction of Eq. (4) is given by $K_x (C_p ML_n)$. The following relations are assumed to be hold

$$K_{CML_n} = K_{C_2 ML_n} = \cdots = K_{C_p ML_n} = K_x$$

and

$$K_{ML_n} = B_n K_x \, ,$$

where B_n is a coefficient of parametrization, the index n denotes that this coefficient depends on the number of ligands in the complex ML_n . The number of C^+ ions, which have a suitable energy for the forward reaction of Eq. (4) will be given by $K_c (C)$; By analogy, the number of the neutral complex species, which have a suitable energy for the forward reaction of Eq. (5) will be given by $K_{x'} (C_p ML_{m+p})$. The following relations are assumed to be hold

$$K_{CML_{m+1}} = K_{C_2 ML_{m+2}} = \cdots = K_{x'} \quad \text{and} \quad K_{ML_n} = Q K_{x'} \, ,$$

where Q is a coefficient of parametrization. The number of the $C^+ L^-$ ion-pairs which have a suitable energy for the forward reaction of Eq. (5) will be given by $K_{CL} (C^+ L^-)$.The number of the complex species which have a suitable energy for the backward reaction of Eq. (4) will be given by $K_{x,c}$ $(C_p ML_n)$. Here also as it was already done for the coefficients in the forward reaction of Eq. (4), $K_{x,s}$ coefficient is assumed to be independent of the complex species The number of the water molecules which have a suitable energy for the backward reaction of Eq. (4) will be given by $K_S (S)$ .By analogy, the number of the neutral complex species which have a suitable energy for the backward reaction of Eq. (5) will be given by $K_{x',s'} (C_p ML_{m+p})$ .The number of water molecules which have a suitable energy for the backward reaction of Eq. (5) will be given by $K_{S'} (S)$.

Now let us introduce the total probability for the distribution of the metal M (central group) in a solution with a given ionic strength – P

$$P = P_M + \Sigma P_{ML_n} + \Sigma P_{C_p ML_n} + \Sigma P'_{C_p ML_{m+p}} = 1 , \tag{6}$$

where P_X is the probability of X species being found in the solution; $p + m < n$ is hold for the charged outer sphere complexes.

To obtain Eq. (6) in an explicit form we have to find relations giving $\Sigma P_{C_p ML_n}$ and $\Sigma P'_{C_p ML_{m+p}}$ as functions of the variable (L). (P_M and ΣP_{ML_n} could be taken from Eqs. (1') and (1'') respectively). For this purpose, we shall first consider reaction (4), starting with the formation of the complex species CML_n which will be given in details. The probability of CML_n complex being formed according to the forward reaction of Eq. (4) will be given by

$$P_{for.} = \frac{B_n}{C_M} \cdot K_x \cdot f_{x \to y} (ML_n) K_c f_{y \to x} (C) = \frac{1}{C_M} \cdot B_n \cdot b_{n,0} (ML_n)(C) , \tag{7}$$

where $b_{n,0} = K_x f_{x \to y} \cdot K_c \cdot f_{y \to x} = const .$

The backward reaction probability will be given by:

$$P_{back.} = \frac{1}{C_M} \cdot K_{x,S} f_{x \to S} B_n \cdot b_{n,0} (ML_n)(C) K_S f_{S \to x} (S) =$$

$$= \frac{1}{C_M} \cdot B_n \cdot b_{n,0} D(ML_n)(C) , \tag{8}$$

where $(S) = const ; \quad D = K_{x,S} f_{x \to S} K_S \cdot f_{S \to x} (S) = const .$

The probability of the CML_n complex being found in the solution will be given by the difference of the forward and backward reactions probabilities

$$P_{CML_n} = P_{for.} - P_{back.} = \frac{1}{C_M} \cdot B_n \cdot b_{n,0} (1-D)(ML_n)(C) = \tag{9}$$

$$= \frac{1}{C_M} \cdot B_n \cdot b_n (ML_n)(C) ,$$

where

$$b_n = b_{n,0} \ (1 - D) = const \ .$$

If Eq. (2) is used to express the term (ML_n) in Eq. (9) the latter will be transformed to

$$P_{CML_n} = \frac{1}{C_M} \cdot A \ \frac{a^n}{n!} \cdot B_n \cdot b_n \ (C)(M)(L)^n \ . \tag{10}$$

In analogous way we can get the following equation for the probability of $C_p ML_n$ complex being found in the solution

$$P_{C_p ML_n} = \frac{1}{C_M} \cdot A \ \frac{a^n}{n!} \ B_n \ \frac{b_n^p}{p!} \ (C)^P (M)(L)^n \ . \tag{11}$$

Here a factor of $p!$ appears in the denominator, which is related to the model consideration of the proper orientation of the interacting species at collision (see Ref. /10/). Summation of Eq. (11) over n and p will give

$$\Sigma \ P_{C_p ML_n} = \frac{1}{C_M} A (M) \sum_{p=1}^{p=N-m-1} \sum_{n=m+2}^{n=N} B_n \frac{a^n}{n!} \ \frac{b_n^p}{p!} (C)^P (L)^n . \tag{12}$$

Let us now consider reaction (5) assuming that it is the main reaction by which the formation of neutral outer sphere complexes proceeds. If an analogous approach to that applied above is used, the following relation for the probability of $C_p ML_{m+p}$ complex being found in the solution will be obtained

$$P'_{C_p ML_{m+p}} = \frac{1}{C_M} \cdot Q \ \frac{q^P}{p!} \ (ML_m)(C^+ L^-)^P =$$

$$= \frac{1}{C_M} \cdot A \ \frac{a^m}{m!} \cdot Q \ \frac{q^P}{p!} \ (M)(L)^m (C^+ L^-)^P , \tag{13}$$

where

$$q = q_0 (1 - D') = K_{x'} \ f_{x' \to y'} \ K_{CL} f_{y' \to x'} [1 - K_{x'S'} f_{x' \to S'} K_{S'} f_{S' \to x'} (S)].$$

9

If the concentration of the electrolyte ion-pairs C^+L^- in Eq. (13) is expressed by using the equilibrium constant β_{CL} of reaction (3) and a summation of Eq. (13) over p is performed it will be transformed to

$$\sum P'_{C_pML_{m+p}} = \frac{1}{C_M} A \cdot Q \frac{a^m}{m!}(M)(L)^m \sum_{p=1}^{p=N_1} \frac{q^p \cdot \beta_{CL}^p \cdot (C)^p}{p!}(L)^p. \quad (14)$$

Expressing now Eq. (6) through Eqs. (1'), (1''), (12) and (14) and multiplying its both sides to $C_M/(M)$ we get the following relation for the complexity function of the system, which will be denoted as F_{gross}

$$F_{gross.} = F_{0,n} + F_{p,n} + F'_{p,m+p} = 1 + A \sum_{n=1}^{n=N} \frac{a^n}{n!}(L)^n +$$

$$+ A \sum_{p=1}^{p=N-m-1} \sum_{n=m+2}^{n=N_1} B_n \frac{a^n}{n!} \frac{b_n^p}{p!} (C)^p (L)^n + \quad (15)$$

$$+ A Q \frac{a^m}{m!}(L)^m \sum_{p=1}^{p=N_1} \frac{q^p \beta_{CL}^p (C)^p}{p!}(L),$$

where $F_{0,n}$ – complexity function of the ML_n complexes plus unity, $F_{p,n}$ – complexity function of the charged outer sphere complexes, $F_{p,m+p}$ – complexity function of the neutral outer sphere complexes.

When some metal ligand system is studied at several constant ionic strengths of the solution the constants in Eq. (15) will have definite values. A priori it could be said that the constant A will remain independent on the ionic strength of the solution, while the constants $B_{(n)}$ and Q will be functions of μ. This follows from the fact that A is a coefficient of parametrization for a process concerned with the first hydration sphere of M which is expected to be less sensitive to the presence of electrolyte ions in the solution, while $B_{(n)}$ and Q are coefficients of parametrization introduced for a process which is concerned with the second hydration sphere of M. The structure of the latter is expected to be much more affected by the presence of electrolyte ions in the solution,

e.g., by the ionic strength. The constants a, b and q are products of a number of quantities, the variation of which with the ionic strength is assumed to be neglible.

If the relations $B_n = B_n(\mu)$ and $Q = Q(\mu)$ are known, the problem of finding the values of the complexity function of a given metal-ligand system studied in an aqueous solution with a variable ionic strength will be reduced to getting the solution of the following modification of Eq. (15)

$$F_{gross} = F_{0,n} + F_{p,n(\mu)} + F'_{p,m+p(\mu)} = 1 + A \sum_{n=1}^{n=N} \frac{a^n}{n!}(L)^n +$$

$$+ A \sum_{p=1}^{p=N-m-1} \sum_{n=m+2}^{n=N} B_n(\mu)\frac{a^n}{n!}\cdot\frac{h_n^p}{p!}(L)^{n+p} + AQ(\mu)\frac{a^m}{m!}(L)^m \sum_{p=1}^{p=N_l} \frac{q^p\beta_{CL}^p}{p!}(L)^{2p}, \qquad (16)$$

where the index (μ) indicates that the quantity is a function of μ, (C) is substituted by (L), taking into account the relation $(C) = (L)$, which is hold in the given case.

So we have obtained an expression for the total complexity function at a discrete ionic strength - Eq. (15) and an expression for variable ionic strength - Eq. (16). These two functions show some interesting features which could be summarized as follows:

1) When $B_n(\mu) \to 0$; $Q(\mu) \to 0$; in a certain range of ligand concentrations and ionic strengths no outer sphere complexes are present in the system. Then, Eqs. (15) and (16) are reduced to the following unique form

$$F_{gross} = F_{0,n} = 1 + A \sum_{n=1}^{n=N} \frac{a^n}{n!}(L)^n. \qquad (17)$$

2) When $N_l \gg q$ Eq. (15), where the following relations are hold: $b_n(C) = b_n^* = const$ and $q\beta_{CL} = q^* = const$, is transformed to

$$F_{gross} = 1 + A \sum_{n=1}^{n=N} \frac{a^n}{n!}(L)^n +$$

$$+ A \sum_{p=1}^{p=N-m-1} \sum_{n=m+2}^{n=N} B_n\frac{a^n}{n!}\cdot\frac{b_n^{*p}}{p!}(L)^n + AQ\frac{a^m}{m!}(L)^m(e^{q^*(C)(L)}-1) \qquad (18)$$

and Eq. (16), where the following relations are hold $(C) = (L)$ and $q\beta_{CL} = q^* = const$, is transformed to

$$F_{gross} = 1 + A \sum_{n=1}^{n=N} \frac{a^n}{n!} (L)^n +$$

$$+ A \sum_{p=1}^{p=N-m-1} \sum_{n=m+2}^{n=N} B_n(\mu) \frac{a^n}{n!} \cdot \frac{b_n^p}{p!} (L)^{n+p} + AQ(\mu) \frac{a^m}{m!} (L)^m (e^{q^*(L)^2} - 1).$$

$$(19)$$

3) For the particular case, when $N = 4$ and $m = 2$ (a great number of metal-ligand systems studied belongs to this class), the number of the charged outer sphere complexes is reduced to one. So, if the contribution of $F_{p,n}$ in F_{gross} is neglected Eq. (18) is transformed to

$$F_{gross} \quad 1 + A \sum_{n=1}^{n=4} \frac{a^n}{n!} (L)^n + AQ \frac{a^2}{2!} (L)^2 (e^{q^*(C)(L)} - 1) \qquad (20)$$

and Eq. (19) is transformed to

$$F_{gross} \quad 1 + A \sum_{n=1}^{n=4} \frac{a^n}{n!} (L)^n + AQ(\mu) \frac{a^2}{2!} (L)^2 (e^{q^*(L)^2} - 1). \ (21)$$

Results and Discussion

To check the validity of the relations derived in the previous part of this paper we had to have at our disposal experimental data for a given metal-ligand system studied at several ionic strengths, from which the complexity function for each discrete ionic strength could be gotten, e.g., to have available a family of F-functions. We have focused our attention to families of F-functions, each obtained by one author or working group, using a single experimental method for each ionic strength. This was done to escape the error which could be introduced if the individual F-functions of the family are obtained by different authors [5].

Here as an illustrative example the system $Cd^{2+} - Br^-$ studied by Kivalo and Ekari [17] will be given. This system had been studied polarographically at temperature $25°C$ and ionic strengths

0.5, 0.75, 1.0, 2.0 and 3.0 respectively. $NaClO_4$ had been used as an inert electrolyte. At each ionic strength the measurements had been performed to bromide concentration corresponding to the full substitution of ClO_4^- with Br^- ions. The F -function at each ionic strength had been obtained from the experimental data using the De Ford and Hume's method [18] and they are presented in the corresponding tables of Ref. [17] where they are denoted as F_0. In Fig. 1 the $log\ F_0$ vs. the bromide concentration of the solution are plotted, the values taken from Ref. [17]. These curves were the subject of our analysis. As far as Cd^{2+} has a coordination number $N=4$ and charge $m=2$, this family of complexity functions could be described by Eq. (20). To find the values of the corresponding constants A, a, Q and q^* these curves were analysed in the following way: first, the ligand concentration region has been found in which the F -functions at low ionic strengths coincide. This was the bromide concentration 0-0.5 M in which the F -functions at $\mu = 0.5$ and $\mu = 0.75$ lay on one curve as shown in Fig. 2 in a suitable scale. So, according to the idea developed in the previous part of this paper, the absence of an ionic medium effect in this concentration range for these two F -functions was considered as an indication that no outer sphere complexes are formed in the solution at these conditions. So, for this concentration range and for these F -functions the requirements for the application of Eq.(17) are fulfilled. Using the method described in Ref. [10] the constants A and a in Eq. (17) were determined. In Fig. 3 the solid line represents the theoretical F -function calculated by Eq. (17) to bromide concentration 0.5 M, where the experimental points for both the ionic strengths are given too. As could be seen a satisfactory fit is obtained. Then, using the values of A and a constants obtained, the Q and q^* parameters are gotten by solving Eq. (20) for two values of F_0 at each ionic strength. In Table 1-5 the experimental F -functions (F_0) are compared with the F -functions calculated by using the β_n values reported by Kivalo and Ekari [17] and these by using Eq. (20) of the present paper. The fit at each data point is estimated by the quantity ΔF defined as $\Delta F = 1/F_0\ (F_{calc} - F_0)\ 100$. It should be pointed out that irrespective of the fact that Eq. (20) is an approximate equation (the presence of the charged outer sphere complex $NaCdBr_4^-$ is neglected) the F -functions calculated by Eq. (20) show satisfactory fit to the experimental ones. As could be seen from the data presented in Tables 1-5 the constants A, a

and q^* are independent of the ionic strength and only the Q parameter is a function of the ionic strength of the solution, this being in agreement with the theoretical considerations of the mathematical model presented in the previous part. In Fig. 4 the graphical plot of Q vs μ is presented. It gives a straight line: $Q = Q^*_\mu - Q_0$. The constants Q^* and Q_0 could be found as a slope of the curve and an intersect on the x -axis. In this way, the results obtained indicate that for a metal–ligand system to which Eq. (20) could be applied, five constants are necessary to describe the system for an arbitrary number of ionic strengths. When the same system is described by the conventional polynomial expression of the complexity function [19] with the stoichiometric stability constants of the complexes the number of the constants necessary to describe the system is given by the number of the complex species assumed to be present in the solution multiplied to the number of ionic strengths at which the system is studied. So, for the present case 16 free parameters will be necessary to describe the system. The extrapolation to zero ionic strength reduced the number of the constants to nine. But as Sillén has pointed out [5], this procedure is far from being safety. He has given the Gütelberg's investigation [20] as an example showing that by using different equations for the activity coefficients the value for $log\ \beta_1$ ranges from 1.0-1.5. (Note that this will give a difference of about 75% in the values of the theoretical F -function calculated in the ligand range from 1-3 M).

As it has been mentioned above, the last data point in the F_0 at each ionic strength had been obtained with a full exchange of the $NaClO_4$ with $NaBr$. So, if the values of F_0 at these points are taken from each F_0 -function at each ionic strength a new complexity function can be obtained which is actually the complexity function of the system for variable ionic strength of the solution. We have found that this function denoted as $F_{0(var)}$ obeys strictly Eq. (21) and this is visualized in Fig. 5 in a semilogarithm scale, where the full circles represent the experimental $F_{0(var)}$ function as taken from Ref. [17]. They coincide with the open circles, which represent the theoretical $F_{gross(var)}$ function calculated up to $(L) = 8$ M from Eq. (21). As could be seen these points are on a straight line which is an indication that an exponential function $F_{gross(var)} = T \cdot e^{t(L)}$ (T and t are constants) is a sufficiently accurate approximation for the complexity function of the system for variable ionic strength of the solution. Such approximation could be very useful in all case

where Eq. (21) could be applied and the knowledge of the exact values of β_n is not necessary and has already successfully used in two of our earlier publications [21, 22].

In Ref. [17] Kivalo and Ekari had compared the values of the stability constants obtained by them with those reported by Leden [23] and Eriksson [24] for the same system studied at $\mu = 3$. The following β_n values are reported by

	β_1	β_2	β_3	β_4
Kivalo and Ekiri [17]	45	250	1890	3170
Leden [23]	57	220	2100	5000
Eriksson [24]	58	275	1600	5400

Here we think that one can get a better impression about the complexity of the system if not the β_n values are compared but the corresponding F_0 functions. We have made such comparison and found that the F_0 functions obtained by Leden [23] and Eriksson [24] lay nearly on one curve, while the F_0 function obtained by Kivalo and Ekari [17] is somewhat lower. Nevertheless, all the three functions strictly obey Eq. (20) with the following values of the coefficients

	A	a	Q	q^*
Kivalo and Ekari [17]	6.80	5.3	42.00	0.25
Leden [23]	7.27	5.5	52.74	0.25
Eriksson [24]	7.27	5.5	52.74	0.27

In calculation the constants for the data reported by Leden and Eriksson the values of A and a constants obtained in the course of the analysis of Kivalo and Ekari's data were used as initial guesses and they were then refined by successive approximations. As could be seen, there is a small difference between the corresponding parameters A , a , Q and q^* found for the system studied by the authors of the three above cited papers. The observed discrepancies in the values of the corresponding β_n could be ascribed to some small systematic error, which further in the course of the graphical extrapolation applied is accumulated and causes these differences especially high for β_4 .

References

1. J.Bjerrum. Metal Amine Formation in Aqueous Solution, P.Haase and Son, Copenhagen, 1941.
2. P.Debye, E.Huckel quoted by C.W.Davies, Ion Association, Butterworth and Co Ltd., London, 1962.

3. E.A.Guggenheim. Phil. Mag., 19, 588 (1935).
4. V.P.Vasilev. Zhur. neorg. Khim., 7, 1788 (1962).
5. L.G.Sillen. J. Inorg. Nucl. Chem., 8, 176 (1958).
6. V.E.Mironov, Y.I.Rutkovskii. Zhur. neorg. Khim., 10, 1069 (1965).
7. V.E.Mironov, N.P.Lastovkina. Zhur. neorg. Khim., 10, 1082 (1965).
8. V.E.Mironov, F.J.Kulba, Y.I.Rutkovskii, E.I.Ignatenko. Zhur. neorg. Khim., 11, 1786 (1966).
9. V.E.Mironov. Uspehi Khimii, 35, 1102 (1966).
10. M.H.Mihailov. JINR Preprint E12-6772, Dubna (1972).
11. M.H.Mihailov, V.Ts.Mihailov, V.A.Khalkin. JINR Preprint E12-6773, Dubna (1972).
12. M.H.Mihailov, V.Ts.Mihailov, V.A.Khalkin. JINR Preprint E12-6774, Dubna (1972).
13. M.H.Mihailov, V.Ts.Mihailova, V.A.Khvkin. JINR Preprint E12-6775, Dubna (1972).
14. M.H.Mihailov, V.Ts.Mihailova, V.A.Khalkin. JINR Preprint E12-6776, Dubna (1972).
15. M.H.Mihailova, V.Ts.Mihailova, V.A.Khalkin. JINR Preprint E12-6777, Dubna (1972).
16. M.H.Mihailov, V.Ts.Mihailova, V.A.Khalkin. JINR Preprint E12-6778, Dubna (1972).
17. P.Kivalo, P.Ekari. Suomen Kem., 30B, 116 (1957).
18. D.D.DeFord, D.N.Hume, J.Am. Chem. Soc., 73, 5321 (1951).
19. S.Froneus. Thesis, Lund, 1948.
20. E.Guntelberg. Thesis, Copenhagen, 1938, quoted by L.G.Sillén in Ref. /5/ .
21. M.H.Mihailov, V.Ts.Mihailova, V.A.Khalkin. VI Intern. Symposium on Chromatography and Electrophoresis, Bruxelles, 1970, Presses Academiques Europeemnes S.C. Bruxelles, 1971, p.141.
22. M.H.Mihailov, V.Ts.Mihailova, V.A.Khalkin. VI Intern. Symposium on Chromatography and Electrophoresis, Bruxelles, 1970, Presses Academiques Europeennes S.C. Bruxelles, 1971, p.165.
23. I.Leden. Z. phys. Chem., A188, 160 (1941).
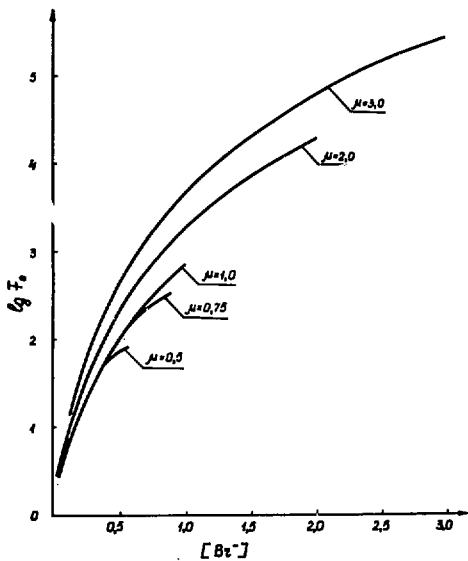24. L.Eriksson. Acta Chem. Scand., 7, 1146 (1953).

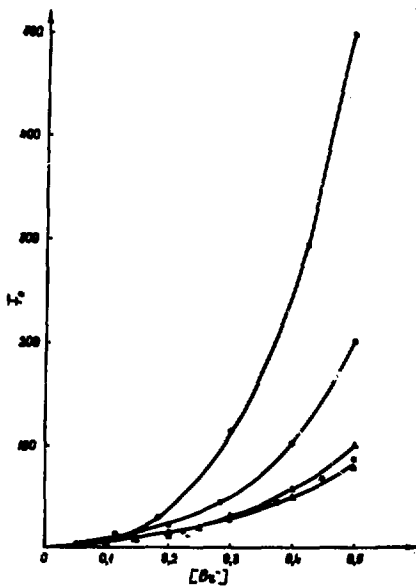Fig. 1. *Log.* F_0 as a function of the bromide concentration of the solution.

Fig. 2. F_0 as a function of the bromide concentration of the solution.

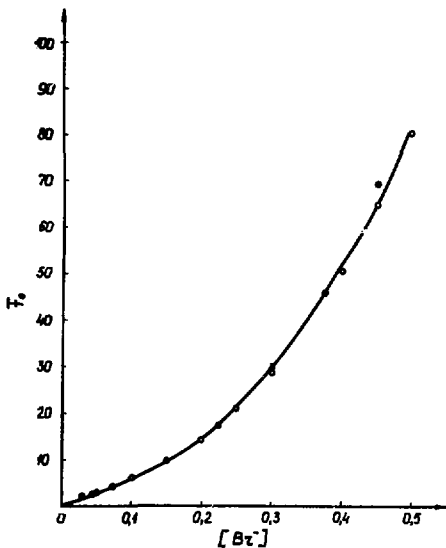Fig. 3. F_0 as a function of the bromide concentration of the solution. The theoretical F -function, calculated by using Eq. (17) is presented as a solid line. The experimental values of F_0 obtained at $\mu = 0.5$ are presented as $\circ$. The experimental values of F_0 obtained at $\mu = 0.75$ are presented as $\bullet$.
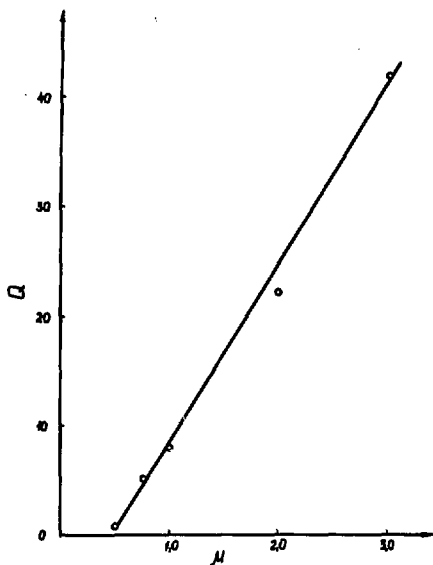
Fig. 4. The variation of the constant Q with the ionic strength of the solution.
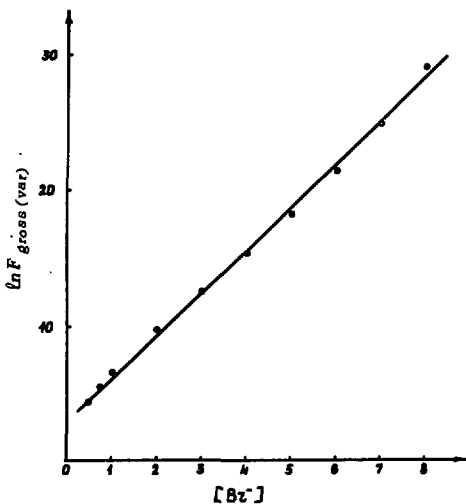
Fig. 5. Logarithm of the complexity function vs. the bromide concentration of a solution with non-constant ionic strength. The open circles are representative values of $F_{gross(var)}$ calculated by using Eq. (21) up to a concentration 8 M. To a concentration of 3 M they coincide with the experimentally obtained values denoted as full circles. The solid straight line is an exponential function.

Table 1
Comparison of the experimental and calculated complexity functions
for $\mu = 0.5$.

| (L) M	F_0	This work	
		F_{calc}^{**}	$_\Delta F^{**}$ in %
0.05	3.271	3.060	-6.45
0.10	6.442	5.750	-10.74
0.15	10.00	9.23	-7.70
0.20	14.62	13.72	-6.16
0.25	21.24	19.46	-8.38
0.30	28.48	26.75	-6.07
0.40	50.32	47.16	-6.28
0.45	64.69	61.03	-5.66
0.5	79.84	77.87	-2.47

F_{calc}^{*} is not calculated because only β_1 value is reported
in Ref. /17/ $\beta_1 = 40$;
F_{calc}^{**} is calculated by using Eq. (17) of the present paper,
where $A = 6.8$ and $a = 5.3$.

Table 2
Comparison of the experimental and calculated complexity functions
for μ = 0.75

(L) M	F_o	Kivalo and Ekari		This work	
		F_{calc}^*	ΔF^* in %	F_{calc}^{**}	ΔF^{**} in %
0.03	2.226	2.197	-1.31	2.182	-1.95
0.045	2.856	2.887	1.07	2.828	-0.98
0.075	4.449	4.473	0.55	4.339	-2.46
0.15	9.952	9.859	-0.93	9.546	-4.07
0.225	17.46	17.19	-1.53	17.51	0.26
0.30	29.63	29.50	-0.43	29.33	-1.01
0.375	45.98	45.95	-0.06	46.27	0.63
0.45	69.02	68.67	-0.51	69.84	1.18
0.525	100.1	99.36	-0.74	101.0	0.91
0.60	144.2	137.0	-2.94	143.5	-0.51
0.75	265.6	259.9	-2.15	265.4	-0.07

$*$ – calculated by using the β_n values reported in Ref. [17]
$\beta_1 = 36$; $\beta_2 = 125$; $\beta_3 = 143$; $\beta_4 = 340$;
calculated by using Eq.(20) of the present paper, where
$A = 6.8$; $a = 5.3$; $Q = 5.18$; $q^* = 0.25$.

Table 3
Comparison of the experimental and calculated complexity functions
for $\mu = 1.0$

(L) M	F_o	Kivalo and Ekari		This work	
		P_{calc}^{x}	ΔP^{x} in %	P_{calc}^{xx}	ΔP^{xx} in %
0.04	2.489	2.617	5.15	2.612	4.94
0.06	3.636	3.578	-1.58	3.581	-1.49
0.1	5.801	5.865	1.10	5.943	2.45
0.2	14.48	14.52	0.31	15.29	5.57
0.3	29.56	29.70	0.48	32.10	8.60
0.4	55.26	55.22	-0.07	59.98	8.54
0.5	98.86	96.00	-2.89	103.25	4.44
0.6	157.2	158.1	0.55	166.8	6.11
0.7	253.0	248.5	-1.77	255.8	1.11
0.8	383.2	375.6	-1.98	376.6	-1.73
0.9	545.8	548.6	0.52	536.1	-1.77
1.0	749.9	775.0	3.75	732.9	-2.27

* – calculated by using the β_n values reported in Ref. /17/
$\beta_1 = 36$; $\beta_2 = 104$; $\beta_3 = 179$; $\beta_4 = 458$;
** – calculated by using Eq. (20) of the present paper, where
$A = 6.8$; $a = 5.3$; $Q = 8.00$; $q^* = 0.25$.

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Table 4
Comparison of the experimental and calculated complexity functions
for μ = 2.0

(L) N	F_e	Kivalo and Ekari		This work	
		F_{calc}^{*}	ΔF^{*} in %	F_{calc}^{**}	ΔF^{**} in %
0.08	5.492	5.536	0.80	5.146	-6.30
0.12	9.436	9.206	-2.44	9.204	-2.46
0.2	22.20	22.17	-0.14	22.67	2.12
0.28	44.45	44.98	1.19	48.71	9.59
0.4	102.7	108.7	5.85	123.2	19.99
0.6	354.7	346.6	-2.27	390.2	10.02
0.8	924.7	860.2	-6.97	938.3	1.47
1.0	1893	1812	-4.28	1896	0.16
1.2	3457	3403	-1.57	3455	-0.05
1.4	5992	5871	-2.01	5787	-3.42
1.6	9412	9495	0.88	9134	-2.95
1.8	13880	14590	5.11	13758	-0.88
2.0	21470	21509	0.18	19995	-6.87

/17/

* – calculated by using the β_n values reported in Ref.
β_1 = 38; β_2 = 180; β_3 = 597; β_4 = 996;
** – calculated by using Eq. (20) of the present paper, where
A = 6.8; a = 5.3; Q = 22.30; q^* = 0.25.

Table 5
Comparison of the experimental and calculated complexity functions
for μ = 3.0

(L) M	P_0	Kivalo and Skari		This work	
		P_{calc}^{*}	ΔP^{*} in %	P_{calc}^{**}	ΔP^{**} in %
0.12	13.32	13.93	4.58	12.74	-4.32
0.18	28.39	31.55	11.12	30.53	7.53
0.3	116.70	113.70	-2.56	117.73	0.88
0.42	294.00	302.68	2.95	313.90	6.77
0.6	914.1	937.1	2.51	941.6	3.00
0.9	3736	3702	-0.92	3509	-6.08
1.2	10486	10254	-2.21	9361	-10.73
1.5	22240	23058	3.68	20721	-6.83
1.8	46380	45192	-2.56	40792	-12.05
2.1	73720	80352	8.99	74077	0.48
2.4	135400	132848	-1.88	129255	-4.54
2.7	205100	207612	1.22	208061	1.44
3.0	308900	310186	0.42	329694	6.73

* — calculated by using the β_n values reported in Ref. /17/
β_1 = 45; β_2 = 250; β_3 = 1890; β_4 = 3170;
calculated by using Eq. (20) of the present paper, where
A = 6.8; a = 5.3 Q = 42.0; q^* = 0.25.