ОБЪЕДИНЕННЫЙ
ИНСТИТУТ
ЯДЕРНЫХ
ИССЛЕДОВАНИЙ

Дубна

E12 - 6772

M.H.Mihailov

ЛАБОРАТОРИЯ ЯДЕРНЫХ ПРОБЛЕМ

A CORRELATION BETWEEN THE OVERALL STABILITY CONSTANTS OF METAL COMPLEXES I.

CALCULATION OF THE STABILITY CONSTANTS USING THE FORMATION FUNCTION $\bar{n}$

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Submitted *to Journal of Inorg. Nucl. Chemistry*

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* On leave from Bulgarian Academy of Sciences, Institute of Physics.

Introduction

Since the basical equations related to the stepwise complex formation process were derived [1], a numerous experimental studies of the equilibria in solution have been made. A special attention has been paid to the determination of the stability constants of the metal complexes, which quantitatively characterize the complexity reactions. A description of the mathematical methods used for this purpose could be found in some review articles [2,3] and monographs [4-6]. A large body of data on the stability constants of metal complexes are presented in the compilation of Sillén and Marteil [7].

It had been natural that some mutual stability relationship of the complexes in a given metal-ligand system to be expected. The pioneer work for finding a relation connecting the consequtive stability constants belongs to Bjerrum [1]. Later attempts have been made by Van Panthaleon van Eck [8] and Babko [9]. Yatsimirskii has compared [10] the accuracy with which the relations derived by these three authors could describe the experimental data for the aluminium floride system and has found that best results are obtained when using the Van Panthaleon van Eck's empirical equation. He also demonstrated that this relation is a good approximation for about 17 metal-ligand systems. The stability of metal complexes depends on many factors such as electrostatic, structural, nature of bonding and many others. So it is hard to believe that some relationship with general validity for the whole variety of the metal-ligand system is possible to be derived with our poor knowledge of these factors at present.So a derivation of a relationship valid for less numerous or more numerous class of metal-ligand systems is still of big interest.

Such relationship could contribute to some systematic classification of the metal-ligand systems and to understanding of certain physical and chemical properties. So our interest was focused on a construction of such a mathematical model of the complex formation process in aqueous solution, which could allow the problem as stated above to be solved for as many metal-ligand systems as possible.

In this paper a simplified mathematical model of the equilibrium in aqueous solution is described. This model gives a possibility a relationship connecting the overall stability constants of the metal complexes in a given metal-ligand system to be derived. The validity of that relation was demonstrated on more than 40 metal-ligand systems. Part of them is presented in the present paper. The rest will appear in the next papers of this series.

Theory

Let us consider the complex formation process of the metal M^{m+}(m is the charge number of M) and the univalent ligand L^-, coming from the dissociation of the strong electrolyte CL in an aqueous solution with a constant ionic strength, maintained by adding of the inert electrolyte CL' . Let the system under consideration satisfy the following requirements: i) the concentration of the metal M^{m+} is sufficiently low so the formation of polynuclear complexes could be neglected. ii) the metal M^{m+} does not participate in side reactions with the ligand L'^- and OH^- ions. iii) the ionic strength of the solution is sufficiently low so the formation of outer sphere complexes (ion-pairs) between the anionic complexes and the C^+ - ions could be neglected. iv) the activity coefficients of all species are constants so concentration terms could be used instead to activities in all equations expressing the equilibria in solution.

Then, the formation of stepwise series of metal complexes could be expressed by the following generalized equation

$$M + nL \rightleftarrows ML_n , \tag{1}$$

The stoichiometric stability constant of the ML_n complex is defined as

$$\beta_n = \frac{(ML_n)}{(M)(L)^n}, \tag{2}$$

where ( ) are concentrations, n is the number of ligands, (Here and throughout the paper the charges will be dropped for simplicity).

But the cation M and the ligand L are hydrated in aqueous solution, so the complex formation process may be regarded as a substitution of water molecules from the first coordination sphere of the metal M with negatively charged ligands [11-13], rather than a simple addition reaction as (1). Thus, we could write:

$$MS_N + n\ L \underset{backward}{\overset{forward}{\rightleftarrows}} ML_n\, S_{N-n} + nS\ , \tag{3}$$

where S denotes water molecule, N is the coordination number of M . Here the reaction is restricted to the first coordination sphere of M .For simplicity the water molecules in the second and third hydration spheres [14] are omitted and the hydration sphere of L is not also denoted.

The interaction between a metal ion and negatively charged ligand in solution depends on their solvation [15,16], the structure of the solvent in the solvation spheres of ions [17,18], and the relative ease with which ion of opposite charge displaces the water molecule from the coordination sphere [19,20]. All these effects as well as others may be important. To make direct calculations for such a complicated system taking into account all these factors is an extremely difficult task. So, for our purpose we felt better to consider the total effects, making some crude simplifying approximations when deriving the main equations.

The assumptions necessary for the validity of the relations which will be derived are as follows: i) The complex formation process (forward reaction) involves substitution of water molecules coordinated to the metal ion M in its first coordination sphere with negatively charged ligands L . ii) The dissociation of the complex ML_nS_{N-n} (backward reaction) is a substitution of the ligands

L coordinated to the metal M in its first coordination sphere with water molecules. iii) The coordination sides of the metal ion M are equivalent. iv) The metal ions M, ligands L, all metal complexes and electrolyte ions are randomly distributed in the solution and undergo random motion. v) The forward reaction proceeds under the action of the short range forces defined as follows: the force directed from the metal ion M towards the ligand L or from the central group M of the complex $ML_n S_{N-n}$ towards L with which M attracts L denoted by $f_{M\to L}$, and the force directed from L towards M or towards the central group M of the complex, $ML_n S_{N-n}$, with which L attracts M denoted by $f_{L\to M}$. We shall assume that these forces remain constant independent of the number of ligands coordinated to the metal ion M in its first coordination sphere. In the most general case: $f_{M\to L} \neq f_{L\to M}$ because the hydration shells of M and L contain different number of water molecules and have a different structure. vi) The backward reaction proceeds under the action of the short range forces defined as follows: the force directed from the central group M of the complex $ML_n S_{N-n}$ towards S with which M attracts the water molecule denoted as $f_{M\to S}$ and the force directed from a water molecule towards the central group M of the complex $ML_n S_{N-n}$ with which the water molecule attracts M denoted by $f_{S\to M}$. We shall assume that these forces also are independent of the number of ligands in the complex species. vii) The proceeding of a reaction (forward or backward) is a result of an effective collision between the interacting particles. We shall define as an effective collision this one at which the colliding species first have a suitable energy to approach within some distance at which the attractive forces act and second have a proper orientation. viii) The number of M ions and complex species $ML_n S_{N-n}$ which have a suitable energy for the forward reaction will be proportional to their concentration in the solution and to the temperature. Thus, for a given temperature the number of metal ions M, which have a suitable energy for the forward reaction will be equal to $K_M(M)$, for the complex ML this number will be: $K_{ML}(ML)$, for the complex ML_n it will be $K_{ML_n}(ML_n)$ and for the ligand L this number will be given by: $K_L(L)$, respectively. By analogy, the number of the complex species which have a suitable energy for the backward reaction at a given temperature will be proportional to their concentrations in the solution with a proportional factors K'_{ML}, K'_{ML_2}, ... K'_{ML_n}, respectively. This number for the water molecules will be $K_S(S)$.

We shall assume that: $K_{ML} = K_{ML_2} = \dots = K_{ML_n} = K_X$, this corresponding to the consideration that the heat effect of the displacement of a water molecule in the complex ML_nS_{N-n} with ligand L is independent of the number of ligands in a given complex. If the same could be assumed for backward reaction we could write: $K'_{ML} = K'_{ML_2} = \dots = K'_{ML_n} = K'_X$. The metal ion M could not be regarded as a member of the complex series, its first coordination sphere being symmetrical and containing only water molecules. So considering the proportional factor K_M we supposed that the following relation is hold: $K_M = A . K_X$, where A is a constant of parametrization. ix) In each complex the domains available to the attractive force of the central group M and to those of each ligand are equivalent. So, a collision between complex species ML_nS_{N-n} and a ligand L will be effective only in the case that L approaches the complex in the domain where the attractive force of the central group $f_{M\to L}$ is dominant. x) The hydrated metal ion M and the hydrated complex ML_nS_{N-n} have approximately equal volumes.

Now, we shall define the probability of ML complex being found in the solution as a difference between the forward and backward reactions probabilities.

If the forward reaction probability is expressed as a product of a numbers of the M ions and L ligands having a suitable energy for reaction and the corresponding attractive forces we get

$$P_{for.} = \frac{1}{C_M} . A . K_X . f_{M\to L}(M) K_L f_{L\to M}(L), \qquad (4)$$

where C_M is the total (analytical) concentration of the complex forming metal M .

The backward reaction probability will be given by the product of the number of the ML species which have a suitable energy for the reaction and the number of water molecules having a suitable energy for the reaction and the corresponding attractive forces. If the concentration of the ML complexes in the solution is expressed by Eq. (4) we could write

$$P_{back.} = \frac{1}{C_M} \cdot K'_X f_{M\to S} \; A \cdot K_X \; f_{M\to L}(M) K_L f_{L\to M}(L) K_S f_{S\to M}(S). \qquad (5)$$

Then, the probability P_{ML} of finding the ML complex in the solution will be given by

$$P_{ML} = P_{for.} - P_{back.} = \frac{1}{C_M} \cdot A \cdot K_X f_{M \to L}(M) K_L f_{L \to M} (L)[1 - K'_X f_{M \to S} K_S f_{S \to M} (S)] =$$

$$= \frac{1}{C_M} \cdot A \; a_0 (1-d)(M)(L), \qquad (6)$$

where

$$a_0 = K_X f_{M \to L} K_L f_{L \to M} = const.$$

$$d = K'_X f_{M \to S} K_S f_{S \to M}(S) = const.$$

By analogy, the probability of ML_2 species being found in the solution will be given by

$$P_{ML_2} = \frac{1}{C_M} \cdot A \; \frac{a_0^2}{2!} (1-d)^2 (M)(L)^2. \qquad (7)$$

Here a factor of 2 appears in the denominator corresponding to the model consideration under which the domain available to the specific attractive force of M in the complex MLS_{N-1} is twice less than in the simple metal ion MS_N. In analogous way the following relation for the probability of $ML_n S_{N-n}$ complex ($n > 2$) being found in the solution can be derived

$$P_{ML_n} = \frac{1}{C_M} \cdot A \frac{a_0^n}{n!} (1-d)^n \; (M)(L)^n \;, \qquad (8)$$

or

$$P_{ML_n} = \frac{1}{C_M} \cdot A \frac{a^n}{n!} (M)(L)^n \;, \qquad (8')$$

where $a = a_0 (1-d)$.

If we define the total probability as

$$P = P_M + \sum_{n=1}^{n=N} P_{ML_n} = 1 \qquad (9)$$

then

$$P_M = \frac{(M)}{C_M} \tag{10}$$

will be the probability of M ion to be found in the solution.

Expressing P_M and P_{ML_n} through Eqs. (10) and (8'), respectively, we get the following expression for Eq. (9):

$$P = \frac{1}{C_M}(M)\left[1 + A\sum_{n=1}^{n=N}\frac{a^n}{n!}(L)^n\right] = 1. \tag{11}$$

Multiplying both the sides of Eq. (11) by C_M, the following expression for the distribution of M (central group) in the solution is obtained

$$C_M = (M)\left[1 + A\sum_{n=1}^{n=N}\frac{a^n}{n!}(L)^n\right]. \tag{12}$$

Obviously, if Eq. (12) is equaled to the conventional expression for the distribution of M (central group) in the solution /[illegible]/ we get the following equation for the stability constant β_n of the complex ML_n:

$$\beta_n = A\frac{a^n}{n!}. \tag{13}$$

Then, the complexity function as defined by Froneous /21/ will be transformed to

$$F = 1 + A\sum_{n=1}^{n=N}\frac{a^n}{n!}(L)^n, \tag{14}$$

and the degree of formation or the formation function of the system $\bar{n}$ will be given by:

$$\bar{n} = A\sum_{n=1}^{n=N}\frac{a^n}{(n-1)!}(L)^n\left[1 + A\sum_{n=1}^{n=N}\frac{a^n}{n!}(L)^n\right]^{-1}. \tag{15}$$

Calculation of the Overall Stability Constants Using the Formation Function of the System $-\bar{n}$.

It was interesting to see how efficiently the relations derived in the previous part of this paper will describe the complex formation process in aqueous solution. For this purpose we have turned our attention to the metal halogenide systems as the most exhaustively studied part of the metal-ligand systems. For example, in the compilation of Sillén and Martell [7] they represent 1/3 of all listing for inorganic ligands. Thus, in this group it was not difficult to find systems which satisfy the requirements encountered in the first part of this paper. We have selected only systems for which more than three stability constants are reported. We have not include systems for which only the first two stability constants β_1 and β_2, respectively, are reported because for such systems always two constants a and A, respectively, could be found to satisfy Eq. (13). But this fact could not serve as a firm support for the validity of the relation previously derived. We wanted to see how the model will work out for systems for which at least three of the stability constants are reported. The calculations have been performed as follows: from the values of β_n reported in the literature [7] for a given metal-ligand system the formation function $\bar{n}$ was calculated using the conventional expression [1]. Then, from two values of $\bar{n}$ taken at two ligand concentrations, the constants A and a were determined using Eq. (15). From the constants A and a determined the corresponding β_n were calculated using Eq. (13). To check the correctness of the values of a and A constants determined, the formation function $\bar{n}$ was now recalculated using the set of stability constants derived according to Eq. (13). The formation functions $\bar{n}$ for the systems: $Cu^{2+}-Cl^-$ [22], $Zn^{2+}-Cl^-$ [23], $Cd^{2+}-Cl^-$ [24], $In^{3+}-Cl^-$ [25,26], $Ca^{3+}-Cl^-$ [27], $Pb^{2+}-Cl^-$ [28], $Zn^{2+}-Br^-$ [23] and $Cd^{2+}-Br^-$ [29] were analyzed in the way described above. In Tables 1-9 the formation functions $\bar{n}^{**}$ which were calculated using the β_n values obtained by the present method and correlated according to Eq. (13) are compared with the $\bar{n}^{*}$, calculated using the β_n values reported in Ref. [7] for the corresponding systems. The discrepancies at each ligand concentration were estimated by the quantity $\Delta n = 1/\bar{n}^{*}(\bar{n}^{*}-\bar{n}^{**})\ 100$.

For the most part of the systems the representative values of the formation functions were calculated for ligand concentration up to a value close to that of the ionic strengh of the solution. Only for the $Cu^{2+} - Cl^-$ system, which had been studied at constant ionic strength equal to 0.69, the formation functions were calculated up to $(L) \sim 4$ M. Irrespective of the fact that the results in Table 1 show a satisfactory coincidence of both the formation functions in the whole ligand region, we consider such extrapolation as not quite correct because at higher ionic strengths side reactions could take place, which are not taken into account in the present model. Gallium chloride and cadmium chloride are the other exception, which had not been studied at a constant ionic strength of the solution and so for these systems the conditions for a constancy of the activity coefficients are not fulfilled. Nevertheless, the stability constants which were found by the present method obey Eq. (13).

In a conclusion it must be said that in all systems studied a satisfactory fit between the formation functions calculated by using the β_n values reported in the compilation of Sillen and Martell /7/ and those obtained when using the β_n values of the present method was achieved. So, the results presented in Tables 1-9 could serve as a support for the validity of the relations derived in this paper for all systems analyzed.

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Received by Publishing Department
on October 31, 1972.

Table 1.
Comparison of calculated formation functions for the cupric-chloride system

(L) M	$\bar{n}$ *	$\bar{n}$ **	$\Delta\bar{n}$ in %
0.050	0.337	0.319	5.34
0.075	0.444	0.427	3.83
0.100	0.512	0.515	-0.59
0.200	0.771	0.764	0.91
0.300	0.922	0.936	-1.52
0.400	1.054	1.075	-1.99
0.500	1.173	1.198	-2.13
0.600	1.281	1.312	-2.42
0.690	1.384	1.400	-1.16
1.000	1.700	1.712	-0.71
1.500	2.133	2.124	0.42
2.000	2.467	2.449	0.73
2.500	2.718	2.700	0.66
3.000	2.907	2.893	0.48
3.500	3.037	3.043	-0.20
4.000	3.163	3.167	-0.13

*- calculated by using the β_n values reported in Ref. /22/ : $\beta_1 = 9.55$; $\beta_2 = 4.90$; $\beta_3 = 3.55$; $\beta_4 = 1.00$.
**- calculated by using the β_n values obtained by the present method: $\beta_1 = 8.60$; $\beta_2 = 6.10$; $\beta_3 = 2.89$; $\beta_4 = 1.03$.
$A = 6.056$ and $a = 1.42$.

Table 2
Comparison of calculated formation functions for the zinc-chloride system

(L) M	$\bar{n}$ *	$\bar{n}$ **	$\Delta\bar{n}$ in %
0.05	0.2I9	0.2I9	0.00
0.I0	0.379	0.38I	-0.53
0.I5	0.503	0.509	-I.25
0.20	0.606	0.6I6	-I.65
0.25	0.695	0.709	-2.0I
0.30	0.774	0.792	-2.33
0.35	0.848	0.867	-2.24
0.40	0.9I7	0.937	-2.I8
0.45	0.983	I.002	-I.93
0.50	I.048	I.064	-I.53
0.55	I.II2	I.I24	-I.08
0.60	I.I75	I.I8I	-0.5I
0.65	I.239	I.236	0.24
0.69	I.290	I.297	0.85

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* - calculated by using the β_n values of Ref. /13/ : $\beta_1 = 5.25$ $\beta_2 = 3.09$; $\beta_3 = 0.65$; $\beta_4 = 1.51$.

** - calculated by using the β_n values obtained by the present method: $\beta_1 = 5.20$; $\beta_2 = 3.38$; $\beta_3 = 1.46$; $\beta_4 = 0.48$ $A = 4.0$ and $a = 1.3$.

Table 3.
Comparison of calculated formation functions for the cadmium-chloride system

(L) M	$\bar{n}$ *	$\bar{n}$ **	$\Delta \bar{n}$ in %
0.0010	0.091	0.096	-4.35
0.0050	0.344	0.353	-2.62
0.0075	0.449	0.456	-1.56
0.010	0.530	0.535	-0.94
0.050	1.020	0.993	2.65
0.075	1.161	1.125	3.10
0.10	1.276	1.237	3.06
0.50	2.494	2.518	-0.96
0.75	2.931	2.944	-0.44
1.00	3.201	3.202	-0.03
1.50	3.496	3.478	0.51
2.00	3.643	3.618	0.68
2.50	3.727	3.700	0.72
3.00	3.781	3.753	0.74

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* - calculated by using the β_n values reported in Ref. /24/ : $\beta_1 = 100$; $\beta_2 = 400$; $\beta_3 = 504$; $\beta_4 = 1008$.

** - calculated by using the β_n values obtained by the present method: $\beta_1 = 105$; $\beta_2 = 312$; $\beta_3 = 619$; $\beta_4 = 920$; $A = 17.68$ and $a = 5.94$.

Table 4.
Comparison of calculated formation functions for the indium-chloride system

(L) M	$\bar{n}$ *	$\bar{n}$ **	$\Delta \bar{n}$ in %
0.005	0.57I	0.60I	-5.25
0.007	0.700	0.705	-0.7I
0.0I	0.849	0.820	3.42
0.03	I.354	I.223	8.5I
0.05	I.596	I.477	7.46
0.07	I.753	I.676	4.39
0.I0	I.9I5	I.907	0.42
0.20	2.2I2	2.339	-5.74
0.30	2.370	2.452	-3.4
0.40	2.473	2.649	-7.I2
0.50	2.545	2.7I8	-6.80
0.60	2.600	2.765	-6.35
0.69	2.639	2.796	-5.95

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*- calculated by using the β_n values reported in Ref. /25/ : $\beta_1 = 186$; $\beta_2 = 4677$; $\beta_3 = 13800$.

**- calculated by using the β_n values obtained by the present method: $\beta_1 = 250$; $\beta_2 = 2750$; $\beta_3 = 20166$; $A = 11.36$ and $a = 22.0$.

Table 5.
Comparison of calculated formation functions for the indium-chloride system

(L) M	$\bar{n}$ *	$\bar{n}$ **	$\Delta\bar{n}$ in %
0.001	0.193	0.193	0.00
0.003	0.443	0.430	2.93
0.005	0.607	0.575	5.27
0.007	0.721	0.676	6.24
0.01	0.851	0.785	7.76
0.03	1.278	1.151	9.94
0.05	1.491	1.375	7.78
0.07	1.676	1.556	7.16
0.10	1.788	1.773	0.84
0.20	2.081	2.217	-6.54
0.30	2.245	2.441	-8.73
0.40	2.354	2.570	-9.18
0.50	2.434	2.653	-9.00
0.60	2.496	2.710	-8.57
0.70	2.545	2.751	-8.09

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*- calculated by using the β_n values reported in Ref. /26/ : $\beta_1 = 229$; $\beta_2 = 4266$; $\beta_3 = 8913$.

** calculated by using the β_n values obtained by the present method: $\beta_1 = 234$; $\beta_2 = 2083$; $\beta_3 = 12356$; $A = 13.15$ and $a = 17.80$.

Table 6.

Comparison of calculated formation functions for the gallium-chloride system

(L) M	$\bar{n}^{*}$	$\bar{n}^{**}$	$\Delta \bar{n}$ in %
0.5	0.114	0.106	7.02
1.0	0.208	0.196	5.77
1.5	0.287	0.275	4.18
2.0	0.356	0.346	2.81
2.5	0.416	0.409	1.68
3.0	0.469	0.466	0.64
3.5	0.517	0.519	-0.39
4.0	0.561	0.568	-1.25
4.5	0.601	0.613	-2.00
5.0	0.637	0.656	-2.98
5.5	0.671	0.696	-3.73
6.0	0.703	0.734	-4.41
6.5	0.733	0.771	-5.18
7.0	0.761	0.806	-10.25
7.5	0.787	0.839	-6.61
8.0	0.812	0.872	-7.39
8.5	0.836	0.904	-8.01
9.0	0.860	0.933	-8.49
9.5	0.882	0.963	-9.18
10.0	0.903	0.992	-9.86

* – calculated by using the β_n values reported in Ref. /27/ : $\beta_1 = 0.251$; $\beta_2 = 5.01 \times 10^{-3}$; $\beta_3 = 3.16 \times 10^{-5}$; $\beta_4 = 1.58 \times 10^{-6}$.

** – calculated by using the β_n values obtained by the present method: $\beta_1 = 0.2288$; $\beta_2 = 6.59 \times 10^{-3}$; $\beta_3 = 12.65 \times 10^{-5}$; $\beta_4 = 1.80 \times 10^{-6}$; $A = 3.97$ and $a = 0.0576$.

Table 7.
Comparison of calculated formation functions for the lead-chloride system

(L) M	$\bar{n}$ *	$\bar{n}$ **	$\Delta\bar{n}$ in %
0.1	0.563	0.531	5.68
0.2	0.892	0.922	-3.36
0.3	1.169	1.228	-5.05
0.4	1.412	1.470	-4.11
0.5	1.623	1.664	-2.53
0.6	1.804	1.821	-0.94
0.7	1.956	1.950	0.31
0.8	2.083	2.055	1.34
0.9	2.190	2.143	2.15
1.0	2.279	2.218	2.68

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* - calculated by using the β_n values reported in Ref. /28/ : $\beta_1 = 9.3$; $\beta_2 = 7.1$; $\beta_3 = 22.4$.

**- calculated by using the β_n values obtained by present method: $\beta_1 = 6.50$; $\beta_2 = 12.67$; $\beta_3 = 16.50$; $A = 1.67$ and $a = 3.9$.

Table 8.
Comparison of calculated formation functions for the zinc-bromide system

(L) M	$\bar{n}$ *	$\bar{n}$ **	$\Delta\bar{n}$ in %
0.10	0.155	0.155	0.00
0.15	0.226	0.226	0.00
0.20	0.293	0.293	0.00
0.25	0.357	0.358	-0.28
0.30	0.418	0.419	-0.24
0.35	0.477	0.479	-0.42
0.40	0.534	0.537	-0.56
0.45	0.588	0.592	-0.68
0.50	0.642	0.647	-0.78
0.55	0.694	0.700	-0.86
0.60	0.744	0.751	-0.94
0.65	0.794	0.801	-0.88
0.69	0.833	0.841	-0.96

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* - calculated by using the β_n values reported in Ref. /23/ : $\beta_1 = 1.88$ $\beta_2 = 0.794$; $\beta_3 = 0.182$; $\beta_4 = 0.100$.

** - calculated by using the β_n values obtained by the present method: $\beta_1 = 1.65$; $\beta_2 = 0.792$; $\beta_3 = 0.253$; $\beta_4 = 0.061$; $A = 1.72$ and $a = 0.96$.

Table 9.

Comparison of the calculated formation for the cadmium-bromide system

(L) M	$\bar{n}$ *	$\bar{n}$ **	$\Delta \bar{n}$ in %
0.050	0.796	0.766	3.77
0.075	0.970	0.941	2.96
0.10	1.106	1.081	1.90
0.20	1.532	1.541	-0.61
0.30	1.883	1.915	-1.72
0.40	2.231	2.271	-1.80
0.50	2.448	2.479	-1.27
0.60	2.665	2.683	-0.67
0.70	2.744	2.734	0.36
0.80	2.990	2.982	0.26

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*- calculated by using the β_n values reported in Ref. /29/ : $\beta_1 = 36.31$; $\beta_2 = 126$; $\beta_3 = 145$; $\beta_4 = 339$.

**- calculated by using the β_n values obtained by the present method: $\beta_1 = 34$; $\beta_2 = 100$; $\beta_3 = 195$; $\beta_4 = 283$; $A = 6.0$ and $a = 5.6$.