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Calculation of the Parameters of the Mutual Effect of Ligands the Au(III)–Chloride Ion–Bromide Ion Complexation System

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Abstract—Published experimental curves of spectrophotometric titration of the system Au^{3+}–Cl^-–Br^- under the conditions of stepwise formation of mononuclear mixed-ligand complexes $AuCl_{4-n}Br_n^-$ are analyzed. A new matrix method is applied to calculating the constants of ligand substitution in the inner sphere of the central ion with fixed coordination sites. The suggested approach allows reduction of the number of variables in least-squares optimization of the titration curves, without impairing the accuracy of the description. The model of formation of square-planar complexes $[MY_{4-n}X_n]$ (n = 0–4) includes three independent variables K, ω_{cis}, and ω_{trans} (K is the equilibrium constant of substitution of the first ligand, and ω_{cis} and ω_{trans} are corrections for the mutual effect), instead of four constants of stepwise substitution. The parameters of the substitution of chloride ion by bromide ion in the inner coordination sphere of Au(III) were calculated using the suggested approach.

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There are numerous examples of formation of mononuclear mixed-ligand coordination compounds in a solution containing a metal ion and several different ligands [1]. A traditional way to determine the conditions of formation of definite species in such systems is simulation of changes in the spectal and potentiometric characteristics with variation of the component concentrations [2]. The parameters of the model to be found are step stability constants of the complexes, independent of each other. The number of independent variables is equal to the number of complex species. Differentiation of isomers within the model of stepwise complexation requires introduction of additional microconstants [3]. In mixed-ligand complexation, the presence of a large number of complex species in solution severely complicates the computation and may make the result indeterminate.

If we assume that entering of a ligand into the inner coordination sphere of a central ion is determined by the positions occupied by the already coordinated ligands, it becomes possible to reduce the number of independent variables required for describing an equilibrium.

Inner-sphere substitution of one acido ligand by another formally differs from replacement of a solvent molecule in the inner coordination sphere of a solvated metal ion in stepwise complexation only in that the equilibrium constants are dimensionless. Hence, the equilibrium constants of ligand substitution can be calculated by the matrix method, as I did in the previous paper in which this method was applied to describing the complexation equilibria of Cu(II) with halide ions [4]. The parameters of the matrix method are the intrinsic substitution constant K, similar to the constant of binding of the first ligand with the central ion, and the corrections ω_{cis} and ω_{trans} taking into account interactions in the course of further ligand substitution. These parameters are essentially similar to interaction cooperativity parameters used for describing the polyelectrolytic effect for oligomers [5].

Here I check the applicability of the matrix method to describing equilibrium mixed-ligand complexation, with the system Au^{3+}–chloride ion–bromide ion in solution as example.

The system I chose is of not only theoretical but also practical interest, as gold tetrahalide complexes are active homogeneous catalysts and are used for

preparing supported catalysts. In both cases, the nature of complex species in solution is very important [6].

Calculation of the equilibrium constants by the matrix method. To describe the spectrophotometric titration curves, I used the matrix method. The physical model takes into account mutual effect of ligands in a compound containing a series of fixed coordination sites. Assume that a metal ion can reversibly bind ligands of two types, X and Y. If under the experimental conditions the inner coordination sphere of the metal is fully occupied by ligands Y, mixed-ligand complexes will be formed by replacement of ligand Y by X. In a square-planar complex $[MY_{m-n}X_n]$ (m = 4; n = 1, 2, ..., N), the ligands can occupy coordination sites in different combinations. In the example considered in this study, N = 4, and 16 configurations are possible. Let log $\mathbf{B}_k$, the vector of stability constants of complex species of specific configurations $[MY_{m-n}X_n]$, be the sum of logarithms of the equilibrium constants of substitution of ligand Y by X on a separate site (β_{ki}):

$$\log \mathbf{B}_k = \sum_i^N \log \beta_{ki}, \qquad (1)$$

To calculate β_{ki}, let us introduce the matrix of configurations $\mathbf{M}$ (2^N, N). The matrix of configurations $\mathbf{M}$ is a set of 2^N binary numbers. The matrix row $\mathbf{M}_k$ reflects the possible configuration of the complex with a sequence of zeros in positions where the sites are occupied by ligands Y and a sequence of unities in positions where the sites are occupied by ligands X.

The ligand substitution on a separate site can be described by the equilibrium constant

$$\beta_{ki} = (M_{ki}K\omega_{ki})_{M_{ki}\neq 0}, \qquad (2)$$

where K is the constant of the eqilibrium reaction of the substitution of the first ligand in the inner coordination sphere of the complex $[MY_m]$. In the general case, the correction for the mutual effect ω_{ki} was taken into account, depending on the geometry of the coordination polyhedron, as follows: At square-planar geometry (D_{4h}), for i from 1 to N, if $M_{ki} \equiv 1$ and $M_{ki+1} \equiv 1$, the ligand substitution constant for both sites is multiplied by ω_{cis}, i.e., the mutual effect is due to ligand addition in the cis position; when the ligand is added in the trans position relative to the occupied site, then $M_{ki} \equiv 1$, $M_{ki+2} \equiv 1$, and the ligand substitution constant is multiplied by ω_{trans}.

The formation function, taking into account the determination of the stability constant of the configuration, can be calculated for any equilibrium concentration of ligands by the formula

$$\bar{n} = \frac{C_R - [R]}{N \cdot C_M} = \frac{[R]^S \times S \cdot \mathbf{B}_k}{N(1 + [R]^S \cdot \mathbf{B}_k)}, \qquad (3)$$

where $S = ...M_i$ is the sum of elements of the row; $\times$ and $\cdot$ are the signs of elementwise and common multiplication of the matrices. As follows from Eqs. (1)–(3), $\bar{n}$ depends on N, variable $[R]$, and three parameters: K, ω_{cis}, and ω_{trans}. If the sites are equivalent relative to each other ($\omega_{cis} = \omega_{trans}$), the formation function will be determined by two parameters: K and ω. In each specific configuration $[MY_{4-n}X_n]$, the sites differ in how the other sites are occupied.

Let us introduce the matrix $\mathbf{P}(2^N, 5)$ with the elements equal to the number of free and occupied sites of definite type in the configuration. Then, at a definite equilibrium concentration of a ligand, it is possible to calculate the matrix $\mathbf{C}_{form}$ of concentrations of free sites and occupied sites:

$$\mathbf{C}_{form} = \left[\left(\mathbf{B}_k \times ([R]^S)^{\mathbf{T}}/(1 + [R]^S \cdot \mathbf{B}_k)\right)^{\mathbf{T}} \cdot \mathbf{P}\right]/NC_M . \qquad (4)$$

Analysis of internal correlations in $\mathbf{C}_{form}$ allows us to construct a matrix from sums of correlated rows of $\mathbf{C}_{form}$. In the case of coordination of four ligands, this matrix is a matrix of concentrations of sites occupied by ligand Y, of species in which the sites occupied by ligand X do not have neighbors occupied by ligand X and have one and two neighbors occupied by ligand X, and of sites fully complexes by ligands X.

Summation of columns in matrix $\mathbf{P}$, followed by substitution of the obtained matrix of sums in Eq. (4), gives the matrix $\mathbf{C}_{form}$. For the system Au^{3+}–bromide ion–chloride ion, this is the matrix of the equilibrium concentrations of $AuBr_4^-$, $AuBr_3Cl^-$, $AuBr_2Cl_2^-$, $AuBrCl_3^-$, and $AuCl_4^-$.

The matrix of equilibrium concentrations was also calculated on the basis of the stepwise complexation model, by solving the system of equations of material balance. Formation of a mixed-ligand complex can be formally described by the following equilibrium constants, similar to constants used for describing stepwise complexation:

$$MY_m + nX = MY_{m-n}X_n + nY,$$

$$K_n = \frac{[MY_{m-n}X_n]\cdot[Y]^n}{[MY_m]\cdot[X]^n}. \quad (5)$$

If we replace the Y/X concentration ratio by a variable R, the model of the equilibrium becomes similar to the model of stepwise ligand addition. The equilibrium concentrations can be calculated by solving the following system of material balance equations:

$$C_M = [M]\sum_{i=1}^{4} b_i[R]^i,$$

$$C_R = [R] + [M]\sum_{i=1}^{4} ib_i[R]^i.$$

Optimization procedure. To calculate optimal parameters of the model, I used in this study the standard Marquardt algorithm of the nonlinear least-squares method [7]. As the function being minimized I chose the matrix $\mathbf{PE}(A_{exp}, A_{calc})$ of deviations of the experimental absorption values at arbitrarily chosen wavelengths A_{exp} from the corresponding values calculated in the course of minimization, A_{calc}. The matrix was calculated by Eq. (6):

$$\mathbf{PE}(A_{exp}, A_{calc}) = \sqrt{\frac{\mathrm{Trace}\{(A_{exp} - A_{calc})\times(A_{exp} - A_{calc})^T\}}{\mathrm{Trace}\{A_{exp}\times A_{exp}^T\}}}, \quad (6)$$

where $A_{calc} = [A_{exp}/\mathbf{C}_f]_{>0}\mathbf{C}_f$; $[...]_{>0}$ is an operator cutting off the negative values having no physical sense, and $\mathbf{C}_f$ is the matrix of concentrations of spectral forms. The adequacy hypothesis was checked by analyzing the homogeneity of the experimental and calculated variance of the absorption [8]. In so doing, we used the tabulated values of the Fisher test F_{tabl} ($\alpha = 0.05$). According to the principle of the maximal likelihood on the condition that the variance is homogeneous, the parameters at which **PE** is minimal correspond to the maximum plausible model of the system.

Example of calculations based on experimental data. As example I used the results of a spectrophotometric study of the system Au^{3+}–Cl^-–Br^-, published in [9]. The equilibrium constants given in that paper were calculated from the kinetic data. The electronic absorption spectra at varied concentrations of chloride and bromide ions were measured after the equilibrium was attained. These data were not directly used for calculating the equilibrium constants. Therefore, for comparison, the step equilibrium constants were initially calculated in this study from variations of the electronic absorption spectra, using the traditional stepwise complexation model. The matrix of absorptions A_{exp} was obtained by computer digitization of the absorption spectra published in [9] using the DIGIT program. Singular decomposition [10] of the matrix A_{exp} shows that the data can be restored with common experimental accuracy (better than 3%) without problems of rank deficiency when five components are considered. Hence, to restore the initial matrix, it is possible to consider five spectral species. From the common chemical standpoint, these are $AuBr_4^-$, $AuBr_3Cl^-$, $AuBr_2Cl_2^-$, $AuBrCl_3^-$, and $AuCl_4^-$.

The step equilibrium constants and the constants calculated in accordance with the matrix model for the system Au^{3+}–Cl^-–Br^- in solution are given in the table. It should be noted that the constants appreciably differ from the values expected statistically if there were no mutual effect of the coordinated ligands (K_0/K_1:K_1/K_2:K_2/K_3 = 2.67:2.25:2.67 [2]). This fact suggests the occurrence of specific interactions betwen coordinated ligands of one kind. Virtually all the known Au(III) complexes are square-planar. In this case, the sites are nonequivalent to each other. Hence, according to the matrix model, the formation function will be determined by the parameters $\bar{K}$, ω_{cis}, and ω_{trans}.

If X and Y in Eq. (5) are permuted, i.e., if the direction of the equilibrium reactions is formally changed, in any case the species having the same chemical composition will participate in the mutual transformations. The physical soundness of the models used is confirmed by coincidence of the calculated spectra for the cases of substitution of chloride ions by bromide ions and, vice versa, substitution of bromide ions by chloride ions. The error arising when the experimental data are described using the matrix method does not exceed the error arising when the stepwise complexation model is applied. Hence, the model constructured on the assumption that the ligand binding is determined by the intrinsic constant and parameters of mutual effect adequately describes the observed changes in the absorption spectra of the system [Au^{3+}]–chloride ion–bromide ion in solution. Figure 1 illustrates the distribution pattern, calculated using the matrix method, of mixed-ligand complexes in relation to the logarithm of the ratio of the ligand concentrations. The distribution corresponding to the stepwise complexation model with K_0 169, K_1 81, K_2 34, and K_3 7 is shown for comparison. The two patterns well coincide at low bromine concentrations, but the equilibrium fractions of the species $AuBrCl_3^-$

Step equilibrium constants and constants calculated in accordance with the matrix model for the system Au^{3+}–Cl^-–Br^- in solution

Parameter	$AuCl_{4-n}Br_n^- + Br^- = AuCl_{3-n}Br_{n+1}^- + Cl^-$			$AuBr_{4-n}Cl_n^- + Cl^- = AuBr_{3-n}Cl_n^- + Br^-$
K_0	169	243±40 [9]	288 [11]	
K_1	81	98±20 [9]	135 [11]	–
K_2	34	49±10 [9]	65 [11]	
K_3	7	17±5 [9]	23 [11]	
	PE 1.2	–	–	
K_0/K_1	2.1	2.5	2.1	
K_1/K_2	2.4	2.0	2.1	–
K_2/K_3	4.9	2.9	2.8	
$\bar{K}$	48.5			0.018
ω_{cis}	1.18 (0.90)	–	–	1.19 (0.90)
ω_{trans}	0.78 (1.32)			0.77 (1.34)
	PE 1.2			**PE** 1.2
$\bar{K}$	55.7	61.2	76.9	
ω	0.92	1.03	1.04	–
	PE 1.4	**PE** 0.2	**PE** 0.3	

and $AuCl_4^-$, calculated by different methods, differ more appreciably.

Calculation in accordance with the matrix model leads to two peer solutions with different parameters of the cis and trans effect (see table). It is impossible to determine directly from the spectrophotometric data measured for the system in the equilibrium state what pair of quantities is true. It is necessary to use additional data, e.g., to perform quantum-chemical calculations. A specific feature of our system is that the *cis* and *trans* isomers are formed at different rates. This fact allowed calculation of the microconstants for the formation of the isomers [9]:

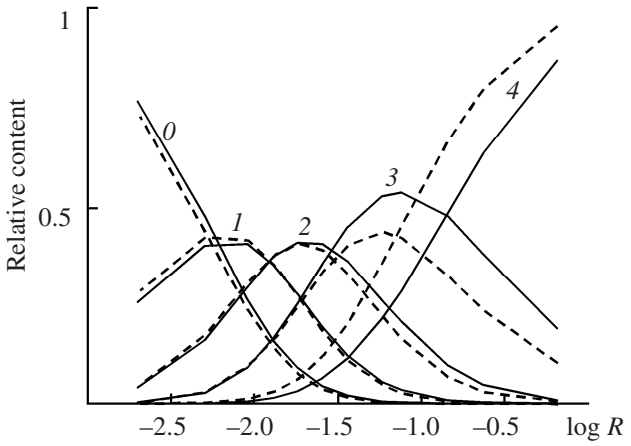

Fig. 1. Calculation from data for solutions at an equilibrium. Relative content of mixed-ligand complexes vs. logarithm of the ligand concentration ratio $R = C_{Br}/C_{Cl}$ [(*0*) $AuCl_4^-$, (*1*) $AuBrCl_3^-$, (*2*) $AuBr_2Cl_2^-$, (*3*) $AuBr_3Cl^-$, and (*4*) $AuBr_4^-$] calculated in accordance with the stepwise complexation model (K_0 169, K_1 81, K_2 34, K_3 7); dashed lines show the equilibrium fractions of the species, calculated using the matrix model ($\bar{K}$ 48.5, ω_{cis} 1.18, ω_{trans} 0.78); C_{Au} 1.71×10^{-4} M, 1 M $NaClO_4$, 25°C.

$$AuCl_3Br^- + Br^- = cis\text{-}AuCl_2Br_2^- + Cl^-;\ K_c\ 64\pm13,$$

$$AuCl_3Br^- + Br^- = trans\text{-}AuCl_2Br_2^- + Cl^-;\ K_t\ 34\pm7.$$

It follows from these data that the formation of the *cis* form is more favorable compared to the *trans* form. The relationship between the interaction parameters, $\omega_{cis}(Br^-) > \omega_{trans}(Br^-)$, is in agreement with this scheme. The pair of quantities meeting this relationship is apparently true. As noted in the introduction, the parameters of the mutual effect are similar to the cooperativity parameters used for describing interactions with polymers and oligomers. In our case, replacement of chloride ion with bromide ion in the *cis* position is of so-called cooperative nature ($\omega_{cis} > 1$), whereas the replacement in the *trans* position is anticooperative ($\omega_{trans} < 1$). A combination of the cooperativity and anticooperativity in interactions was discussed previously, with protonation of polycytidylic acid as example [12]. For inorganic molecules, this

character of interactions was not considered previously, and it is an interesting specific feature of the system under discussion.

In connection with the above-described uncertainty, it is interesting to calculate the parameters of the mutual effect without taking into account the nonequivalence of ligand coordination in the *cis* and *trans* positions relative to each other. To check the hypothesis that the titration curves can be adequately described with this assumption, we chose as the function to be minimized the matrix $\mathbf{PE}(n_f, n_{calc})$ of deviations of the values of the formation function [Eq. (3)] calculated for a given model from the values calculated in the course of minimization, n_{calc}. In so doing, the minimization was performed in the space of two independent variables K, ω ($\omega_{cis} = \omega_{trans}$). We tested three functions calculated from the kinetic data and from the spectrophotometric data for solutions at the equilibrium. The results show that the matrix model described most adequately the formation functions found from the kinetic data (see table). As seen from Fig. 2, the distribution diagrams of Au^{3+} complex species in solution essentially coincide for both models. The somewhat larger discrepancy in the description of the formation function calculated for the solutions at the equilibrium is within the admissible experimental error. Thus, the models using only two complexation parameters can also be used as alternative models accounting for relationships in formation of Au(III) halide complexes.

It should be noted in conclusion that the calculation scheme considered in this study not only allows description of the titration curves but also gives insight into the mechanism of mixed-ligand complexation. We showed that the matrix model allows the set of constants required for describing the equilibrium to be reduced. The possibility of reducing the dimension of space of independent variables by relatively simple modification of the model gives grounds to expect that we will be able to reformulate the problem of mixed-ligand complexation in a simpler form if the the matrix method will be applicable to other systems also.

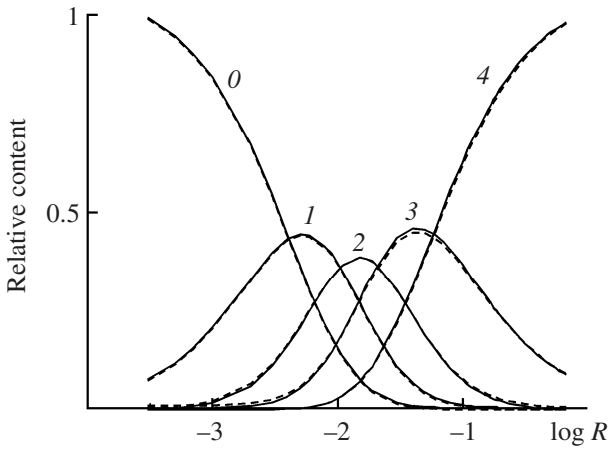

Fig. 2. Calculation from kinetic data. Relative content of mixed-ligand complexes vs. logarithm of the ligand concentration ratio $R = C_{Br}/C_{Cl}$ [(*0*) $AuCl_4^-$, (*1*) $AuBrCl_3^-$, (*2*) $AuBr_2Cl_2^-$, (*3*) $AuBr_3Cl^-$, and (*4*) $AuBr_4^-$] calculated in accordance with the stepwise complexation model (K_0 243, K_1 98, K_2 49, K_3 17 [9]); dashed lines show the equilibrium fractions of the species, calculated using the matrix model (K 61.2, ω 1.03).

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