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Calculation of equilibrium binding constants and cooperativity of Cu(II) mixed solvated complexes formation

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ABSTRACT

A new extension of matrix approach is proposed to calculate the equilibrium constants of coordinated solvent substitution in a metal ion first solvation shell in the mixed solvent system. The proposed method allows reducing the number of independent variables, necessary to calculate the fractions of species in solution. The equilibrium model of MeCN substitution with DMF and DMSO in the presence of Cu(II) ion for the assessment of structure of intermediate species is presented and verified. The distribution diagrams of Cu(II) species in mixed organic solvents have been analyzed using the modified matrix method. The intrinsic equilibrium constants K of the first solvent molecule replacement in the Cu(II) coordination shell and the correction for the mutual influence between the solvent molecules as ligands in the successive complex formation (cooperativity parameter w) in acetonitrile solution have been calculated from the fitting procedure. It is shown that anticooperative substitution of MeCN by donor ligands in the first coordination shell of the Cu(II) ion is always governed by the change of coordination number during the stepwise process.

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1. Introduction

The copper(II) ion behavior in pure and mixed solvents systems is governed by an intricate balance of solvated complexes. The better understanding of these phenomena is considerable for the theory of coordination compounds and also has practical value [1]. Acetonitrile solutions are of particular interest because in this solvent, Cu(II) exhibits catalytic properties [2,3]. The use of acetonitrile as the reaction solvent proved to be crucial for catalysis, both to function as a labile ligand for copper, as well as an agent to minimize hydrolytic catalyst poisoning [4]. The study of mixed solvents systems was performed for the development of an a priori criterion of choice of the best solvent's composition for Cu(II) catalytic activities in Cu(II)-catalyzed reactions [5]. To fully exploit these properties, however, we need to better understand the interactions of the constituents. The problem appears because addition of donor ligands or solvents in CH₃CN solutions containing Cu(II) ion leads to the formation of numerous species. It was assumed that molecules of these solvents coordinate to the metal ion to form mononuclear complexes [1,6]. But, it is not always possible to determine stability constants precisely and even the correct number of mixed-solvate complexes [7,8]. In previous papers [9,10] isolation of those interactions and gaining insight into the complexation behavior

by performing computational studies of the simplified models for those composites based on the matrix method have been proposed. The variability of species structure with stepwise filling of the first coordination shell was discussed for cadmium and copper ions [1]. On the basis of spectral data for compounds of copper(II) it was concluded that the structure of complexes varies in different solvents [11]. In particular, it is interesting to analyze systems Cu(II)–CH₃CN–DMF for which solvation structure of Cu(II) ion has been investigated by the X-ray diffraction in solution [12]. The matrix method has not been previously over-spread to describe the filling of the inner coordination sphere in mixed solvent solution, accompanied by changes in the geometry of the coordination polyhedron.

The aim of this work is to analyze the distribution of species during successive resolution of Cu(II) in non-aqueous solutions, and to calculate the equilibrium parameters and cooperativity of the selective binding of a solvent from solvent's mixture using the matrix method.

2. Computational details

It is well known that in the simplest case, the addition of a ligand to the central ion or neutral molecule in inert solvents, as well as in the gas phase, is pure association. For these systems, using the nearest neighbor interaction approximation allows reduction of the dimensionality of the space of independent

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variables required to describe titration curves and species distribution for successive mononuclear homoleptic complexes formation [13]. For instance, provided that addition of a ligand follows an additive scheme and that complexes have tetrahedral structures, two independent parameters K and ω (K is the intrinsic binding constant for a first ligand and ω is a correction for mutual influence) are sufficient for the description of ligand coordination instead of four constants required in a traditional modeling of independent stepwise complexation [14]. The thermodynamic description of ligands binding to an ion in solution is the same as adsorption of ligands onto a one-dimensional homogeneous lattice as described in [15–19]. The central concept for a ligand binding on a matrix of vacancies is that an expression describing the change in free energy of a system as a function of the equilibrium concentrations is given by

$$\Delta F/RT = \ln([MX_n]/[M]) - \ln m_n - n^2 \ln K[X] + \omega \quad (1)$$

here $[MX_n]$, $[M]$, $[X]$ are the equilibrium concentrations of the complex with n coordinated ligands, and complexing components in solution; K is the binding constant; ω is a parameter of mutual influence; R is the universal gas constant, T is the temperature; $m_n = N!/n!(N-n)!$ is the number of microstates which is equal to the number of combinations of N on n , related with the number of possible ways of coordinating N ligands to the central ion having N vacant sites $\sum_{n=0}^N m_n = 2^N$.

The mathematical basis of the matrix method differs from the traditional model of independent stepwise complexation. Instead of stepwise equilibrium constants first the ligand binding intrinsic constant and the parameter of the ligands' mutual influence are calculated. The assumption that the addition of another ligand to the central ion is determined by the location of previously joined ligands allows us to calculate the ratio between the stepwise equilibrium constants. Let us consider that the coordination polyhedron geometry does not get altered in the process of stepwise complexation i.e. the location of coordination vacancies is fixed. In applying this approach the model presented allows to calculate the concentrations matrix of all equilibrium species in the system by the equation:

$$\mathbf{C}_{form} = \frac{(\overline{\mathbf{K}}^s \cdot \mathbf{w})^T \cdot [\mathbf{X}]^s}{\overline{\mathbf{K}}^s \cdot \mathbf{w} \times [\mathbf{X}]^s} \cdot C_{Me}$$

$$= \frac{\left(\left[\begin{array}{cccc} 1 & K & K^2 & \dots & K^N \end{array} \right] \cdot \left[\begin{array}{cccc} 1 & m_1 & m_2 \omega_2 & \dots & m_N \omega_N \end{array} \right]^T \cdot \left[\begin{array}{c} 1 \\ [X] \\ [X]^2 \\ \vdots \\ [X]^N \end{array} \right]^T \right)}{\left(\left[\begin{array}{cccc} 1 & K & K^2 & \dots & K^N \end{array} \right] \cdot \left[\begin{array}{cccc} 1 & m_1 & m_2 \omega_2 & \dots & m_N \omega_N \end{array} \right] \times \left[\begin{array}{c} 1 \\ [X] \\ [X]^2 \\ \vdots \\ [X]^N \end{array} \right] \right)} \cdot C_{Me}$$

$$= \left(\frac{1}{S} \frac{m_1 K [X]}{S} \frac{m_2 K^2 \omega_2 [X]^2}{S} \dots \frac{m_N K^N \omega_N [X]^N}{S} \right) \cdot C_{Me} \quad (2)$$

here $S = 1 + m_1 K [X] + m_2 K^2 \omega_2 [X]^2 + \dots + m_N K^N \omega_N [X]^N$; $\mathbf{K}^s = [1 \ K \ K^2 \ \dots \ K^N]$; $[\mathbf{X}]^s = [1 \ [X] \ [X]^2 \ \dots \ [X]^N]^T$; $s = [0 \ 1 \ 2 \ \dots \ N]$; $\mathbf{w} = [1 \ m_1 \ m_2 \omega_2 \ \dots \ m_N \omega_N]$; \times indicates the signs of array multiplication, matrices multiplication and T denotes the matrix transpose; C_{Me} is the total concentration of central ion. Using Eq. (2) one can calculate augmented concentrations matrix \mathbf{C}_f of species formed in a system at all concentrations of ligand. In the simplest case of six ligand binding (association) with equivalent sites around central ion:

$$\text{Cu}^{2+} + nX = \text{CuX}_n^{2+} \quad (3)$$

one can compute \mathbf{C}_{form} by substituting into Eq. (2) the matrix \mathbf{w} in the form:

$$\mathbf{w} = [1 \ 6 \ 15\omega^2 \ 20\omega^6 \ 15\omega^{12} \ 6\omega^{12} \ \omega^{30}] \quad (4)$$

here exponent ω is calculated as $(n-1)n$, n is the number of coordinated ligands. Eqs. (2)–(4) formally do not take into account the fact that the complexation in a solution is actually replacement of the solvent molecules in the first coordination shell. Nevertheless for the process in a solution, we may assume that the first and the subsequent ligand's binding are governed by the same energetic effect of resolution plus the change of the free energy due to mutual ligand's influence. The equilibrium constants of the first and the subsequent ligands binding in this case (when each incoming ligand replaces one molecule of solvent) are the same, as in the adsorption. Consequently in such a case the introduction of an additional parameter does not change the shape of species distribution diagrams, since the number of linearly independent parameters does not change. For a mixed solution system the equation of the mixed complex formation can be written as

$$\text{Cu}(S_x)^{2+} + nX = \text{Cu}(S_{x-y})X_n^{2+} + yS \quad (5)$$

To describe solvent displacement in the mathematical model in Eq. (2) the coefficients ω of mutual influence between ligands should be replaced with the products of coefficients of initially coordinated solvent influence ω_s and mutual influence between incoming solvent molecules ω_l with the exponents corresponding to the structure of complex. When necessary, to allow for the energy effect due to a changed number of displaced solvent molecules a coefficient ω_r should be introduced. A new equation appears in accordance with the hypothesis about structure and coordination mode of compounds formed in a stepwise process. This hypothesis is accepted if the difference between the calculated and the experimental profiles is less than the established experimental noise. The successive formation of six coordinated (for instance, octahedral or distorted octahedral D_{4h}) complexes obeys Eq. (2) after substitution of \mathbf{w} by a new matrix:

$$\mathbf{w} = [1 \ 6\omega_s^5 \ 15\omega_s^8 \omega_l^2 \ 20\omega_s^9 \omega_l^6 \ 15\omega_s^8 \omega_l^{12} \ 6\omega_s^5 \omega_l^{20} \ \omega_l^{30}] \quad (6)$$

here exponent ω_s is calculated as $(6-n)n$, n is the number of coordinated ligands and exponent ω_l is calculated as $(n-1)n$.

For a solvent substitution the concentration matrix $\mathbf{C}_f = [[\text{Cu}(S_x)]^{2+} \ [\text{Cu}(S_{x-1})X]^{2+} \ \dots \ [\text{Cu}(S_{x-y})X_N]^{2+}]$ having a graphical representation as species distribution diagram, may be used for finding the binding parameters. Deviations from a regular change in the species concentrations corresponding to the additive (association) scheme may be due to a change in the coordination number (CN) or in the structure of the coordination sphere during the stepwise process, for instance, as a result of transition from axially elongated octahedral structure to tetrahedral geometry. A huge number of physical experimental methods allow determining the distribution of the central metal ion or molecule between the species that coexist in equilibrium. The experimental data obtained by these methods are suitable to find the parameters of the matrix model. For the recovery of the experimental model (row of binding constants $\lg \beta_n$) which governs the concentration profiles we have to fit \mathbf{C}_f^{exp} with matrices of species concentration which were calculated by the matrix method \mathbf{C}_f^{alc} .

The optimization procedure: The Levenberg–Marquard algorithm of non-linear least square (LS) fitting is used for refinement of parameters [20,21]. This algorithm has been proven to be successful in calculations of equilibrium constants from data of spectrophotometric titrations [22]. Iterative procedure described

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