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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 salvation 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.

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) catalytical 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 CH_3CN 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)–CH_3CN–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 overspread 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 resolvation 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:

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

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

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

here $S = 1 + m_1 K[X] + m_2 K^2 \omega_2 \cdot [X]^2 + \cdots + m_N K^N \omega_N [X]^N$; $\boldsymbol{K}^s = [1 \quad K \quad K^2 \quad \cdots \quad K^N]$; $\cdot [\boldsymbol{X}]^s = [1 \quad [X] \quad [X]^2 \quad \cdots \quad [X]^N]^T$; $s = [0 \quad 1 \quad 2 \quad \cdots \quad N]$; $\boldsymbol{w} = [1 \quad m_1 \quad m_2\omega_2 \quad \cdots \quad m_N\omega_N]$; $\times$ 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 $\boldsymbol{C_f}$ 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:

$$Cu^{2+} + nX = CuX_n^{2+} \quad (3)$$

one can compute $\boldsymbol{C_{form}}$ by substituting into Eq. (2) the matrix $\boldsymbol{w}$ in the form:

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

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 resolvation 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

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

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 $\boldsymbol{w}$ by a new matrix:

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

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

For a solvent substitution the concentration matrix $\boldsymbol{C_f} = [[Cu(S_x)]^{2+} \quad [Cu(S_{x-1})X]^{2+} \quad \cdots \quad [Cu(S_{x-y})X_N]^{2+}]$ 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 $\boldsymbol{C_f^{exp}}$ with matrices of species concentration which were calculated by the matrix method $\boldsymbol{C_f^{calc}}$.

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

above is used to find minimum of the objective function:

$$S = \sum (C_f^{exp} - C_f^{calc})^2 \quad (7)$$

The sum of squares of deviations of all elements of a concentrations matrix was calculated based on experimental equilibrium model of stepwise complex formation (C_f^{exp}) from the appropriate matrix considered on the current iterative step (C_f^{calc}), which was calculated by using Eq. (2) and was minimized in this case. The optimization is stopped when the relative difference in S between consecutive iterations is below a threshold value. Once convergence of the iterative optimization is achieved, the quality of the data fits can be determined by the expression for the percentage of data lack of fit [23]:

$$lof = \sqrt{\frac{Trace[C_{exp} - C_{calc})(C_{exp} - C_{calc})^T]}{Trace[C_{exp} C_{exp}^T]}} \times 100 \quad (8)$$

here *Trace* is the sum of the diagonal elements. In this paper, to reject the model, the critical level of discrepancy between the calculated and experimental profiles has been set more than ***lof*** 6%.

The test of the matrix method. In order to test the proposed method of calculation, the system Ni(II)–H_2O–NH_3 has been analyzed. All mixed ligand complexes formed in this system have octahedral structure. The distribution diagram of the Ni(II) species retrieved in accordance with the experimental equilibrium constants and computed with help of matrix method is in good agreement. The discrepancy does not exceed the usual experimental error (***lof*** 3.7%); see Supplementary information.

3. Results and discussion

Acetonitrile replacement by DMF. When acetonitrile was mixed with DMF in the presence of Cu(II) ion the coordinated solvent molecules were bonded in the first coordination shell and were substituted by molecules of another solvent molecules. To calculate the parameters of substitution of coordinated solvent molecules CH_3CN by stronger donor DMF we borrowed the results of colorimetric studies, published in [7]. Using the values of stepwise equilibrium constants $\lg \beta_n$ n=1–4, 6 the species distribution has been recovered. These profiles were taken for the calculation of intrinsic binding constants. First the pure association model was tested. The calculation showed that the distribution diagram of the complexes formed according to the pure association model calculated by LS using substitution of Eq. (4) into Eq. (2) differs considerably from the experimental ones. The discrepancy is more than 27%, which far exceeds the usual experimental error.

According to calorimetry [7] and X-ray diffraction [12] in the first stage of the process, one molecule of acetonitrile in the equatorial plane of axially elongated octahedral structure $[Cu(CH_3CN)_6]^{2+}$ is replaced by one DMF molecule. In the second stage the reaction apparently proceeds similarly, but the structure of formed complex is unknown. Perhaps in the third stage the molecules of CH_3CN in the first shell are replaced by DMF forming Cu(II) ion with no molecules along the axis of the plane. Next in accordance with the X-ray diffraction the DMF molecules replace the solvent initially coordinated in the equatorial plane while forming the Cu(II) ion coordinated with four DMF molecules with no solvent molecule along the axis of the plane. With further increase in the concentration of DMF in a solution the complex $[Cu(DMF)_6]^{2+}$ is finally formed. In the proposed structural transformation sequence it is assumed that in the third and fifth steps we see changes in CN and symmetry of the ligand environment; see Scheme 1. It should be noted that square planar $[Cu(CH_3CN)(DMF)_3]^{2+}$ and $[Cu(DMF)_4]^{2+}$ assumed significant distortion that excludes considerable difference in cis and trans influence. Considering the transformations in coordination polyhedron of Cu(II) in this system in a mathematical model in Eq. (2) the matrix $\boldsymbol{w}$ must be replaced by

$$\boldsymbol{w} = \begin{bmatrix} 1 & m_1\omega_s^5 & m_2\omega_s^4\omega_l^2 & m_3\omega_r\omega_s^3\omega_l^6 & m_4\omega_r\omega_l^{12} & \omega_l^{30} \end{bmatrix} \quad (9)$$

here ω_r is the coefficient taking into account the inequality of the number of displaced solvent molecules. There was a necessity of introducing an additional factor due to the fact that the third and the fourth ligands attached with anti-cooperative effect which far exceeds the effect expected from the additive scheme. Deviation found from the additive scheme supports the assumption made from calorimetric study that in the third stage of resolvation of Cu(II) the DMF–ligand replaces three bound CH_3CN solvent molecules. In Eq. (9) the number of microstates corresponds to the coordination of the ligand only in the equatorial plane. It should be noted that if the number of microstates is set as 6-vacancy the model falls into the critical region (***lof*** 7.4%). Fig. 1

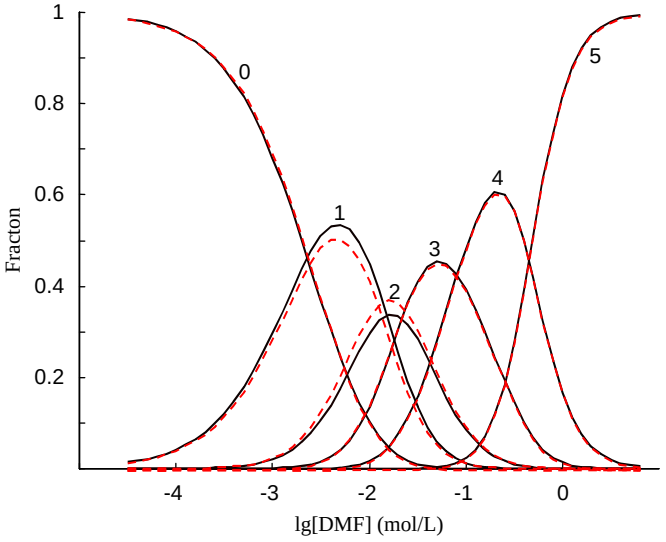
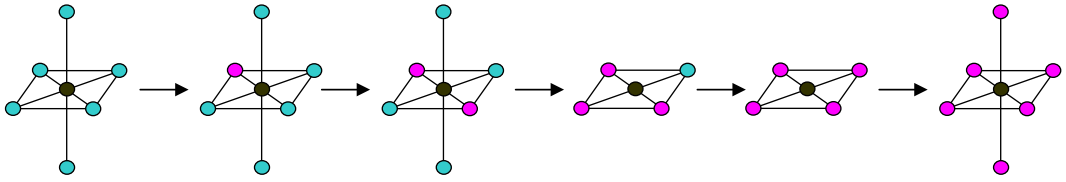


Fig. 1. The distribution plots of Cu(II) between species 0-$[Cu(CH_3CN)_6]^{2+}$; 1-$[Cu(CH_3CN)_5(DMF)]^{2+}$; 2-$[Cu(CH_3CN)_2(DMF)_2]^{2+}$; 3-$[Cu(CH_3CN)(DMF)_3]^{2+}$; 4-$[Cu(DMF)_4]^{2+}$; 5-$[Cu(DMF)_6]^{2+}$; calculated from the equilibrium constants $\lg \beta_{1-4,6}$=[2.64, 4.46, 6.12, 7.21, 7.9] as a function of equilibrium concentration DMF; the dotted lines are distribution calculated with the help of the matrix method (Eqs. (2) and (7)) $\lg K$=3.27; ω_l=0.41; ω_l=0.56; ω_r=0.067; 1 M $(C_2H_5)_4NClO_4$; 25 °C.



Scheme 1. Scheme of the transition from axially elongated octahedral $[Cu(CH_3CN)_6]^{2+}$ to $[Cu(DMF)_6]^{2+}$ in CH_3CN solution via mix-solvated intermediate species (CH_3CN and DMF molecules are depicted as cyan and pink balls correspondingly).

Table 1
The values of stepwise stability constants, intrinsic binding constants and model of coordination number sequence in the process of re-solvation for Cu(II) ion in CH_3CN solution.

The ligand	lg β_n	lg[L]	Sequence of CN	lg K	ω_l	ω_s	ω_r	***lof***
DMF;[a]	2.64, 4.46, 6.12, 7.21, 7.9 [7]	−4.5,…,0.8	6–6–6–4–4–6	3.27	0.41	0.56	0.067	2.8
DMSO[b]	3.0, 5.1, 7.3, 8.9,9.9 [8]	−4,…,0	6–6–6–4–4–6	3.82	0.37	0.50	0.063	5.3

[a] 1 M $(C_2H_5)_4NClO_4$.
[b] 0.2 M $(C_2H_5)_4NClO_4$; 25 °C.

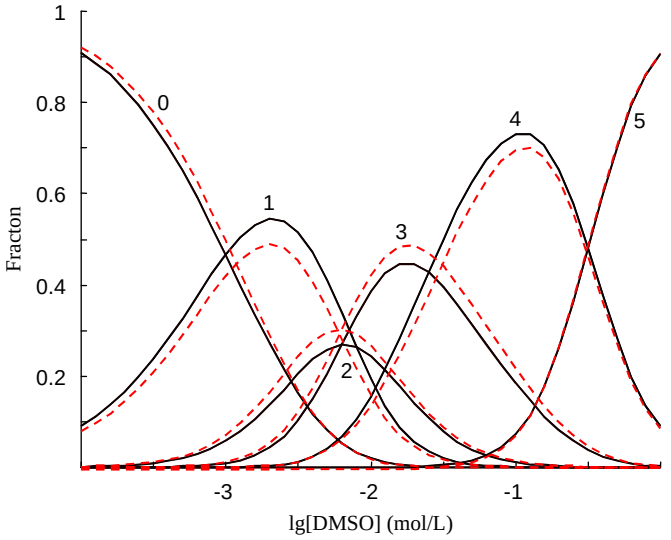


Fig. 2. The distribution plots of Cu(II) between species 0-$[Cu(CH_3CN)_6]^{2+}$; 1-$[Cu(CH_3CN)_5(DMSO)]^{2+}$; 2-$[Cu(CH_3CN)_2(DMSO)_2]^{2+}$; 3-$[Cu(CH_3CN)(DMSO)_3]^{2+}$; 4-$[Cu(DMSO)_4]^{2+}$; 5-$[Cu(DMSO)_6]^{2+}$; calculated from the equilibrium constants lg $\beta_{1-4,6}$=[3.0, 5.1, 7.3, 8.9, 9.9] as a function of equilibrium concentration DMSO; the dotted lines are distribution calculated with the help of the matrix method (Eq. (4)) lg K=3.82; ω_l=0.37; ω_s=0.5; ω_r=0.063; 0.2 M $(C_2H_5)_4NClO_4$; 25 °C.

shows the distribution diagram of the Cu(II) complexes calculated in accordance with the experimental equilibrium constants and corresponding to the matrix model. As can be seen the calculated profiles are close to the experimental ones. The difference between calculated and experimental profiles is 3.3%, which is in the tolerance level explained by an experimental error. Therefore, we may say that the model calculated by the matrix method has adequately recovered the experimental species distribution for the system Cu(II)–CH_3CN–DMF. The intrinsic binding constants are given in Table 1.

Acetonitrile replacement by DMSO. For the system Cu(II)–CH_3CN–DMSO experimental concentration profiles were recovered from the values lg β_n of equilibrium constants published in [8]. Although structural transformations in this system are not described, the performed calculations have shown that the Cu(II) complexation with DMSO in CH_3CN is similar to those described above for DMF. Acetonitrile solvates Cu(II) ion much more weakly than DMSO does, and thus in small excess of DMSO in solution it mainly exist as $[Cu(DMSO)_4]^{2+}$ and $[Cu(DMSO)_6]^{2+}$ species. A performed calculation suggests the substitution of coordinated CH_3CN solvent with a decrease in coordination number in the third stage of the process; see Scheme 1. Fig. 2 shows copper species fraction vs. lg[DMSO] recovered from the values of experimental equilibrium constants and calculated in accordance with the matrix method. As one can see the calculated profiles are close to the experimental ones. The ***lof*** value is about 5%, which fits into the acceptable experimental error. The model parameters are given in Table 1. The obtained values of intrinsic parameters for the CH_3CN substitution by donor ligands indicate that complexation with a stronger donor such as DMSO is somewhat more anticooperative character. The binding of a stronger donor leads to more anticooperative mutual influence between the same ligands and between ligands and coordinated solvent molecules. However, the difference in the anticooperativity is not very significant which is consistent with similar donor numbers of DMSO and DMF.

4. Conclusions

In summary the proposed method allows to reduce the number of independent variables, necessary to calculate the fractions of species in mixed solvent system which facilitated the modeling of acetonitrile substitution by DMF and DMSO in the presence of Cu(II) ion. The coordinated solvent molecules were bonded in the first coordination shell substitution by molecules of another solvent molecule which are governed by the change in coordination number during the stepwise process. Applying this approach the model presented allows for the prompt assessment of the impacts of structural transformation of an ion in solution, thus providing for facilitated design of composition of mixed solvent with more deterministic catalytic properties of the Cu(II) ion.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.09.014.

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