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Abstract. A new approach providing a direct calculations of equilibrium constants, parameters of the chemical exchange reactions, and spectral characteristics of complexes on the basis of data of several methods including pH-potentiometry, multi-wavelength electronic spectroscopy, and NMR relaxation within a single computer program was proposed and realized in the program STALABS. Application of the STALABS program has been demonstrated on the example of investigation of the complex nickel(II) - *L*-histidine system by joint usage of the above three methods.

1. Introduction

Determination of thermodynamic and kinetic parameters of equilibria and spectral characteristics of coordination compounds in solutions of complex systems is an important problem of coordination and physical chemistry which cannot be resolved without a computer simulation. In most of the programs intended for these purposes only one additive physico-chemical response dependent on pH or component concentrations of the equilibrium system is modeled [1].

Earlier in the Kazan University two programs, CPESSP [2] and STABLAB [3], for computation of equilibria and physico-chemical properties of coordination compounds were created. The program CPESSP is able to calculate separately data of the methods of pH-potentiometry, spectrophotometry, or spin-lattice NMR relaxation in conditions of "rapid chemical exchange". The program STABLAB is used for the simultaneous calculation of the thermodynamic parameters of equilibria and kinetic characteristics of the proton and ligand exchange reactions from the parallel measurements of the spin-lattice (T_1) and spin-spin (T_2) relaxation times of the solvent nuclei.

The major aim of the present work is to develop a new approach for simultaneous calculation of equilibrium constants, parameters of the chemical exchange reactions, and spectral characteristics of complexes based on the data of several methods including pH-potentiometry, ion-selective potentiometry, multi-wavelength electronic spectroscopy, and NMR relaxation within a single computer program. The approach was implemented in the new program STALABS. The second aim of the work is to demonstrate the applicability of the STALABS program for investigation of the complex system nickel(II) - *L*-histidine.

2. Results and discussion

In the base of thermodynamic calculations of equilibrium system the Brinkley algorithm [4, 5] applied to the matrix algebra is put. A minimum set of components (B_l, $l = \overline{1, m_1}$), called a basis, is selected from all chemical forms (A_j, $j = \overline{1, M}$) participated in the reactions to determine the equilibrium concentrations of all the present species. So the reaction of any form A_j can be written as follows:

$$\sum_{l}^{m_1} \nu_{jl} B_l \xrightleftharpoons{\beta_j} A_j \tag{1}$$

where ν_{jl} is stoichiometric coefficient at the B_l component in j-th reaction and β_j is the equilibrium constant of this reaction. Equilibrium in the system with reactions of the type (1) corresponds to a minimum of the Gibbs potential which satisfies equations of the mass action law and mass balance:

$$[A_{ij}] = \exp(\theta_j + \sum_{l}^{m_1} \nu_{jl} \ln[B_{il}]) \text{ or } [A_{ij}] = \beta_j \prod_{l}^{m_1} [B_{il}]^{\nu_{jl}} \tag{2}$$

$$c_{il} = \sum_{j}^{M} \nu_{jl}[A_{ij}] \tag{3}$$

where $[A_{ij}]$ is equilibrium concentration of the species A_j, $\theta = \ln\beta$, $[B_{il}]$ and c_{il} are respectively equilibrium and total concentrations of the basis species in i-th experiment, $i = \overline{1, N}$, and N is the number of experiments.

For the calculation of the equilibrium concentrations of all the components of the system the first derivatives of the total concentrations of basis species by their equilibrium concentrations are used:

$$\frac{\partial c_{ik}}{\partial \ln[B_{il}]} = \sum_{j}^{M} \nu_{jk} \nu_{jl}[A_{ij}] \tag{4}$$

Symmetric Jacobi matrix **J** is composed from the values of these derivatives.

Minimization step is calculated by equation (5):

$$\mathbf{\Delta}_i = (\mathbf{J}_i)^{-1} \mathbf{r}_i \tag{5}$$

where $\mathbf{r}_i$ is the residuals vector with the $r_{ik} = c_{ik}^{\text{exp.}} - c_{ik}^{\text{calc.}}$ elements. The next values of the B_{il} components of the **B** vector on (x+1)-th iteration are given by equation (6):

$$\ln[\mathbf{B}]_i^{x+1} = \ln[\mathbf{B}]_i^x + \mathbf{\Delta}_i \tag{6}$$

The Bjerrum function (n_i) used in the pH-potentiometric data processing is calculated in the general form:

$$n_i^{\text{calc.}} = \frac{c_{i\text{H}} - [B_{i\text{H}}]}{c_{i\text{L}}} \tag{7}$$

Experimentally this function is calculated by the equation (8):

$$n_i^{\text{exp.}} = \frac{\dfrac{10^{\lg[B_{i\text{H}}]}(V_0 + \Delta V_i)}{a_{\text{H}}} - c_0^{\text{T}} \Delta V_i - \dfrac{10^{\lg K_w - \lg[B_{i\text{H}}]}(V_0 + \Delta V_i)}{a_{\text{OH}}}}{c_{i\text{L}} V_0} + \alpha \tag{8}$$

where V_0 is the initial volume of solution, ΔV_i is the added volume of titrant, c_0^{T} is the titrant concentration, a_{H} and a_{OH} are the activity coefficients of proton (H$^+$) and hydroxide ion (OH$^-$) respectively, and α is the ligand titration fraction.

To reduce the systematic errors in the program the joint or separate fitting of equilibrium constants with the following independent variables is provided: $c_{i\text{L}}$, c_0^{T}, α, a_{H}, and a_{OH}. Potentiometric methods are the simplest methods for calculation and analytical and numerical derivatives in this case match with great accuracy.

Spectrophotometric method is less accurate but more informative method for calculations of equilibria in solutions. The response function for the spectrophotometric method is written in the following matrix form:

$$\mathbf{D^M} = \mathbf{C^M}\mathbf{E} \tag{9}$$

where $\mathbf{D^M}$ is matrix of the system absorption per unit concentration of the absorbing particles of dimension $N \times W$ (W is number of wavelengths), $\mathbf{C^M}$ is matrix of the mass fractions of the absorbing particles of dimension $N \times S$ (S is number of the absorbing particles), and $\mathbf{E}$ is the molar extinction coefficients matrix of dimension $S \times W$.

Calculations of the molar extinction coefficients and equilibrium constants are performed separately by the variable separation method. The molar extinction coefficients are calculated as follows:

$$\mathbf{E} = (\mathbf{C^M})^{-1}\mathbf{D^M} \tag{10}$$

at $i = w$ or

$$\mathbf{E} = ((\mathbf{C^M})^{\mathbf{T}}\mathbf{C^M})^{-1}(\mathbf{C^M})^{\mathbf{T}}\mathbf{D^M} \tag{11}$$

at $i \neq w$. Such scheme of calculation is correct in the absence of species with negative molar extinction coefficients. Otherwise the method of non-negative linear least-squares should be used. Algorithm FNNLS [6] was applied to solve the problem of finding molar extinction coefficients with non-negative constraints by minimizing the system of equations for the residuals vector $\mathbf{r}$:

$$\mathbf{r} = (\mathbf{C^M})^{\mathbf{T}}\mathbf{D^M} - (\mathbf{C^M})^{\mathbf{T}}\mathbf{C^M}\mathbf{E} \tag{12}$$

Calculations of the analytical derivatives of the response function by the equilibrium constants were performed by the method described [7].

In the case of NMR relaxation method paramagnetic contributions (p) to the measured spin-lattice (T_1) and spin-spin (T_2) relaxation times of the nuclei of the solvent (A_0) from the M chemical forms $\{A_j, j = \overline{1,M}\}$ which are generated in solution and undergo exchange with the dominant state of solvent A_0 (diluted solutions) are given by additive relations [8]:

$$\frac{1}{T_{1p}} = \frac{1}{T_1} - \frac{1}{T_{1(A)}} = \sum_{j=1}^{M} K_{1j}[A_j] \tag{13}$$

$$\frac{1}{T_{2p}} = \frac{1}{T_2} - \frac{1}{T_{2(A)}} = \sum_{j=1}^{M} K_{2j}[A_j] \tag{14}$$

where $T_{1(A)}$ и $T_{2(A)}$ are spin-lattice and spin-spin relaxation times of the nuclei in pure solvent A_0; $[A_j]$ is equilibrium concentration of the A_j form, and K_{1j} и K_{2j} are the molar coefficients of spin-lattice and spin-spin relaxation respectively. For each A_j form with q nonequivalent positions of the nuclei including the outer coordination sphere the relaxation coefficients K_{1j} and K_{2j} take the generalized form [9, 10]:

$$K_1 = \sum_{n=0}^{q-1} \frac{P'_{(n)}}{\tau_{(n)} + T_{1(n)}} \tag{15}$$

$$K_2 = \sum_{n=0}^{q-1} \frac{P'_{(n)}}{\tau_{(n)}} \cdot \frac{T_{2(n)}^{-2} + T_{2(n)}^{-1} \times \tau_{(n)}^{-1} + \Delta\omega_{(n)}^2}{(T_{2(n)}^{-1} + \tau_{(n)}^{-1})^2 + \Delta\omega_{(n)}^2} \tag{16}$$

where n is number of the nonequivalent position, $P'_{(n)} = P_{(n)}/[A_j]$, $P_{(n)}$ is probability of presence of the solvent nuclei in n-th position of the A_j form; $\tau_{(n)}$ is the nuclei lifetime in corresponding position; $T_{1(n)}$ и $T_{2(n)}$ are spin-lattice and spin-spin relaxation times of the nuclei in this position, $\Delta\omega_{(n)}$ is difference of the Larmor precession frequency of nuclei between A_0 and n-th position of the A_j form (the j index of each element in the formulas (15) and (16) is omitted). Lifetime $\tau_{(n)}$ is defined by the solvent nuclei chemical exchange between the n-th position in the coordination sphere of the A_j form and free states in the bulk solution as following [11]:

$$\tau_{(n)}^{-1} = k_0^{(n)} + \sum_{m=1}^{M_{(n)}} k_m^{(n)}[A_{m(n)}] \tag{17}$$

where $k_0^{(n)}$ and $k_m^{(n)}$ are the rate constants of the chemical exchange reactions of first and second kinetics orders respectively without and with activation by certain chemical forms which are selected in subsets $\left\{ A_{m(n)}, m = \overline{1, M_{(n)}} \right\}$ for each n value. When $\Delta \omega_{(n)} = 0$ equation (16) is similar to equation (15).

If $T_{1(n)} \gg \tau_{(n)}$ then the molar relaxation coefficients are calculated similarly to the molar extinction coefficients in spectrophotometry. The analytical derivatives of the response function by the equilibrium constants in the NMR relaxation method are approximately calculated as in spectrophotometry. Physico-chemical parameters of the NMR relaxation method are assumed to be independent of each other, the equilibrium concentrations, equilibrium constants, and other system parameters. Data calculations using numerical and analytical derivatives are in good agreement with each other.

Joint processing of the experimental data on the s properties measured by several methods with the simultaneous determination of physico-chemical parameters can be carried out by non-linear methods via minimization of the objective function.

$$\Phi(\eta, \theta) = \sum_{k=1}^{s} \sum_{i=1}^{N_k} r_{ki}^2 \tag{18}$$

where η is set of the spectral, NMR relaxation, and kinetics parameters, r_{ki} is normalized i-th residual for k-th property (Y_k) having the form $r_{ki} = (Y_{ki}^{\text{exp.}} - Y_{ki}^{\text{calc.}}) \sqrt{w_{ki}} \left(\sqrt{N_k} \right)^{-1}$, N_k is number of experimental points by the k-th method data, w_{ki} is statistical weight giving by relation $w_{ki} = 1 / (\sigma_0^2 Y_{ki}^{\text{exp.}} Y_{ki}^{\text{calc.}})$, σ_0 is the method error. The generalized residuals vector $\mathbf{r}$ of dimension $N = \sum_{k=1}^{s} N_k$ and the generalized Jacobian $\mathbf{J}$ of dimension $N \times d$ (d is number of fitted parameters) are introduced. Thus, to find the equilibrium constants by the several method data the following system of equations should be solved:

$$\mathbf{J}^{\mathrm{T}} \mathbf{J} \Delta \boldsymbol{\theta} = \mathbf{J}^{\mathrm{T}} \mathbf{r} \tag{19}$$

The correction vector to the approximated parameters, $\Delta \boldsymbol{\theta}$ (minimization step), results from equation (19). For these systems of equations the program provides two solution ways:

1) The subspace trust-region method based on the interior-reflective Newton method [12, 13]. This is a large-scale algorithm with variation of minimization step in each iteration by the approximate solution of a large linear system of equations using the preconditioned conjugate gradient method. This algorithm is able to optimize a large number of parameters in a small number of iterations and can converge from initial values far from the minima. It solves equilibrium problems better than many other classical minimization methods using first derivatives. It works with continuous functions and the number of data points must be greater than the number of parameters. Increment $\Delta \boldsymbol{\theta}_k = \boldsymbol{\theta}_{k+1} - \boldsymbol{\theta}_k$ is an approximate solution of the quadratic subproblem

$$\min \left\{ f_k(\Delta \boldsymbol{\theta}) = \mathbf{g}_k^{\mathrm{T}} \Delta \boldsymbol{\theta} + \frac{1}{2} \Delta \boldsymbol{\theta}^{\mathrm{T}} \mathbf{B}_k \Delta \boldsymbol{\theta} \right\}$$

where $\mathbf{g} = \mathbf{J} \mathbf{r}$, $\mathbf{B} = \mathbf{g} \mathbf{g}^{\mathrm{T}}$, and k is the iteration number. Then the following function is computed:

$$p_k^Y = \frac{(Y(\boldsymbol{\theta}_k + \Delta \boldsymbol{\theta}_k) - Y(\boldsymbol{\theta}_k))}{f_k(\Delta \boldsymbol{\theta}_k)}$$

If $p_k^Y > \mu$ (μ is the validity criterion) then $\boldsymbol{\theta}_{k+1} = \boldsymbol{\theta}_k + \Delta \boldsymbol{\theta}_k$, otherwise $\boldsymbol{\theta}_{k+1} = \boldsymbol{\theta}_k$ and calculation continues.

2) The method of the Jacobian matrix singular values decomposition [14, 15]. This method converges even when $\mathbf{J}^{\mathrm{T}} \mathbf{J}$ matrix is poor conditioned (having determinant close to zero). Poor conditionality occurs when initial parameters are far from real values or when two or more parameters are highly correlated. Firstly singular values decomposition of the weighted Jacobian matrix is performed:

$$\mathbf{J} = \mathbf{U} \boldsymbol{\Sigma} \mathbf{V} \tag{20}$$

where $\mathbf{U}$ is the unitary matrix of dimension $N \times N$, $\boldsymbol{\Sigma}$ is rectangular diagonal matrix of dimension $N \times d$ (d is number of fitted parameters), $\mathbf{V}$ is the unitary matrix of dimension $d \times d$. Then error

$\tau = \sigma_0 \max(\Sigma)$ is computed and vector **p** is composed from indexes of the **diag(Σ)** elements which are greater than τ. After that minimization step is calculated as follows:

$$\Delta\theta_i = \sum_{j=1}^{P} \frac{V_{ip_j}(\sum_{k}^{N} U_{kp_j} r_k)}{\Sigma_{p_j p_j}} \tag{21}$$

where $j = \overline{1, P}$ is index of the vector **p** element, $k = \overline{1, N}$ is number of experimental points, $i = \overline{1, D}$ is number of fitting parameters. This algorithm often converges in less iteration than the previous one when initial estimates are near the local minima, additionally it requires less computer time according to simplicity of calculation. Disadvantages of the algorithm are poor convergence by the initial approximations far from minima and forever loop in some cases.

Both of the minimization algorithms can work with analytical or numerical first derivatives.

The program calculates the following statistical information:

sum of weighted squared residual errors $SSE = \mathbf{r^T\, r}$,

confidence intervals $\boldsymbol{\delta\theta} = \sqrt{\dfrac{\mathbf{diag}(\left|(\mathbf{J^T\, J})^{-1}\right|) \cdot SSE}{N - D}}$,

and the Hamilton's *R*-factor.

Program was written in Qt Development Environment [16] with use of Eigen mathematical library [17]. Calculation data can be loaded in the form of formatted text or inserted into special dialog window.

Applicability of the STALABS program was tested on the example of investigation of the complex nickel(II) – *L*-histidine system by joint usage of the pH-potentiometry, multiwavelength spectrophotometry, and NMR relaxation methods. The computed species distribution diagram and reconstructed electronic absorption spectra of all the revealed species are given on Figures 1 and 2 as examples.
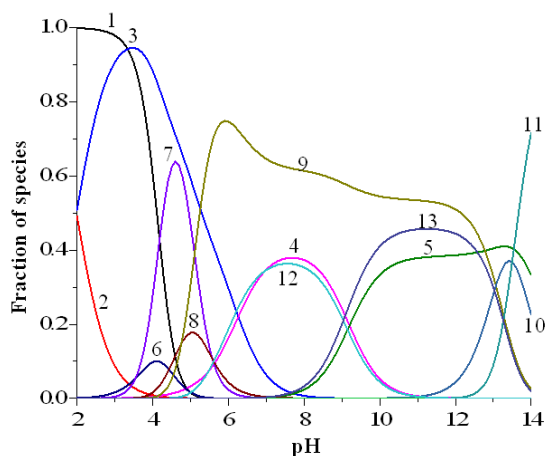

Figure 1. Species distribution as a function of pH for the Ni(II) − *L*-HisH system at a 1:4 metal:ligand ratio and $T = 298$ K with 1.0 M KNO$_3$ as background, $c_{\text{Ni(II)}} = 0.01$ M; 1 − Ni^{2+}, 2 − HisH$_3^{2+}$, 3 − HisH$_2^+$, 4 − HisH, 5 − His$^-$, 6 − Ni(HisH)$^{2+}$, 7 − Ni(His)$^+$, 8 − Ni(His)(HisH)$^+$, 9 − Ni(His)$_2$, 10 − Ni(His)(HisH$_{-1}$)$^-$, 11 − Ni(HisH$_{-1}$)$_2^{2-}$, 12 − Ni(His)$_2$(HisH), 13 − Ni(His)$_3^-$.
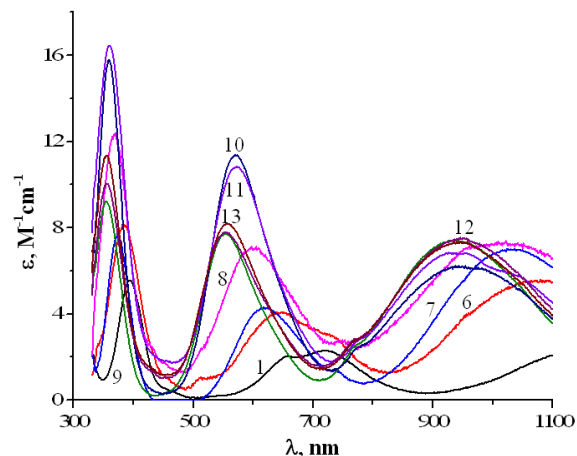

Figure 2. Reconstructed electronic absorption spectra of species in the Ni(II) − *L*-HisH system at $T = 298$ K with 1.0 M KNO$_3$ as background (numeration is given as on Figure 1).

Only four complexes ($Ni(HisH)^{2+}$, $Ni(His)^{+}$, $Ni(His)(HisH)^{+}$, and $Ni(His)_2$) have been described previously in the nickel(II) – *L/DL*-histidine systems [18]. The joint use of the above three methods in wide pH range (2-14) enables us to reveal and characterize four new complexes, $Ni(His)_2(HisH)$, $Ni(His)_3^{-}$, $Ni(His)(HisH_{-1})^{-}$, and $Ni(HisH_{-1})_2^{2-}$ (see Figure 1), and to establish the relaxation, chemical exchange kinetic, and spectral parameters for all the found species (Figure 2).

3. Conclusions

New computer program STALABS for a calculation of equilibrium constants, kinetic, relaxation, and spectral parameters of coordination compounds by the data of several physico-chemical methods including pH-potentiometry, multi-wavelength electronic spectroscopy, and spin-spin and spin-lattice NMR relaxation was elaborated.

Application of the STALABS program for investigation of the nickel(II) – *L*-histidine system by joint usage of the above methods allows one to achieve the most complete description of complex formation thermodynamics, ligand exchange reaction kinetics, and NMR relaxation and spectral characteristics of the eight complexes in this system.

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