A mathematical method for calculation of the stability constants of complexes by spectrophotometric data is represented. The program algorithm SQCONS is developed based on the method of nonlinear squares. As a test example, a calculation of the constant and the molar coefficients of extinction of the monosulfate complex CuSO₄ is presented.

Key words: absorption spectra, molar extinction coefficient, method of least squares, copper aquaion, copper monosulfate.

The calculation of stability constants from spectrophotometric data is carried out presently by various mathematical methods implemented, as a rule, in the form of computer programs. Among those several general-purpose programs such as SQUAD [1], DALSFEK [2], and PSEQUAD [3] should be noted. The use of matrix algebra allows these programs to be extended to calculation of a given chemical system based on solutions with an arbitrary number of optically active structures. To use them for the calculation of stability constants, it is necessary to specify the absorption spectra of a series of solutions with different initial concentrations and molar coefficients of extinction of all optically active structures present in the solution. Based on the algorithms implemented in the programs under consideration, namely, of the iteration procedure for seeking stability constants whose values could satisfy the minimum sum of squares of deviation of the calculated spectrum from the experimental spectrum, the author has developed an alternative method for the calculation of stability constants implemented in the form of the computer program SQCONS. The basic difference of the proposed algorithm from those used in DALSFEK and SQUAD is the fact that instead of the molar coefficients of extinction use is made, as the initial data, of the absorption values of the chosen optically active structures obtained experimentally or separated with the aid of a preliminary procedure of spectrum decomposition into components. An advantageous feature of the program SQCONS lies in the possibility of calculation of thermodynamic stability constants by calculation of the activity coefficients and results of measurements on solutions with different ionic strengths in a large concentration range. A disadvantage is the impossibility of calculation by the proposed algorithm for spectra containing one absorbing structure.

The practical applicability of the proposed method of processing of electronic spectra is demonstrated by calculating, as an example, the stability constant of the copper sulfate (II) complex at room temperature. In forming the initial absorption model the necessity arises of determination of the number of optically active structures represented in the spectrum. To solve this subproblem, the author has employed the method [4] and algorithm TRIANG [5].

Absorption for a jth solution in a cell of unit length at some wavelength \( \lambda \) can be written as

\[
D_j^{\text{obsr}}(\lambda) = \sum_{k=1}^{n} x_{kj} c_k^{(j)},
\]

(1)
where \( n \) is the number of optically active structures in the solution on the considered spectrum fragment; \( \varepsilon_k^{(2)} \) is the molar (molal) coefficient of extinction of the \( k \)th absorbing structure in the solution; \( x_{kl} \) is the equilibrium concentration of absorbing particles in a solution of a given series. In matrix form this equation acquires the form \( D = EX \). Since in the general case the number of wavelengths at which measurements are made is not equal either to the present structures or to the number of measured solutions, the matrix \( D \) is, as a rule, rectangular. After symmetrization by multiplying it by the transposed matrix \( D^T \) we obtain \( A = DD^T \), i.e., a symmetrical matrix of the order \( m \) (the number of measured wavelengths) and rank \( n \) (the number of optically active structures) [4]. As the matrix \( A \) is symmetrical and real, it can be expressed linearly in terms of its eigenvalues and eigenvectors:

\[
A = \alpha_1 P_1^{**} P_1 + \alpha_2 P_2^{**} P_2 + \ldots + \alpha_n P_n^{**} P_n
\]  

(2)

and will contain as many summands or linearly independent variables as there are nonzero eigenvalues of the matrix \( A \). Here, *P_1, *P_2 ... are the column eigenvectors; \( P_1^*, P_2^* \ldots \) are the row eigenvectors; \( \alpha_1, \alpha_2 \ldots \) are the corresponding eigenvalues of the matrix \( A \). From this point of view the number of nonzero eigenvalues is the rank \( n \) of the matrix \( A \).

Thus, the problem is reduced to determination of the rank of the matrix \( A \), which determines the number of linearly independent variables and, consequently, the number of independently absorbing chemical structures. For this, the eigenvalues of the matrix \( A \) calculated by the Jacobi method were arranged in a decreasing series and then they were compared with the corresponding standard deviations. The rank of the matrix was determined by the number of significant eigenvalues of the matrix \( A \) that exceed the standard deviations. For verification purposes the statistical criterion \( \chi^2 \) was used. One more refinement of the obtained rank of the matrix was made using the statistical criterion of rule 3\( \sigma \), where the calculation by the algorithm TRIANG was based on the fact that the matrix of absorptions is reduced to triangular form and compared with the matrix of absorption errors, which is reduced also to triangular form. The rank of the matrix was determined by the number of significant elements on the diagonal exceeding triple the value of the diagonal elements of the matrix of errors of light absorption [6]. For reducing the matrices to triangular form the Gauss elimination method was adopted.

On the basis of the calculated number of spectrum structures an absorption model was specified and the main problem of determination of the stability constants was determined. Let us represent the observed solution absorption \( D^{\text{obs}}(\lambda) \) as the sum of the absorption components of the optically active structures at the wavelength \( \lambda \):

\[
D^{\text{obs}}(\lambda) = \sum_{k=1}^{n} D_k^{(1)} \; ,
\]

(3)

Then to solve the problem of determination of the stability constants of the complex structures existing in the solution, it is necessary to know both the absorption \( D^{\text{obs}}(\lambda) \) of a series of solutions with different initial concentrations and the absorptions \( D_k^{(1)} \) chosen from the total number of optically active structures obtained experimentally or separated using the procedure of spectrum decomposition into components. The number of specified optically active structures \( q \) must be sufficient for "determination" of the problem proceeding from the rule \( q \geq n - 1 \) [4]. The unknown stability constants can be determined by the nonlinear method of least squares by minimizing the sum of the squares of the deviations:

\[
U = \sum_{k=1}^{q} \sum_{i=1}^{m} (D_k^{\text{exper}}(\lambda) - D_k^{\text{calc}}(\lambda))^2 \; ,
\]

(4)

where \( m \) is the number of points with respect to wavelengths; \( D_k^{\text{exper}}(\lambda) \) are the absorptions of the chosen optically active structures obtained experimentally or after decomposition into components.

The calculated absorption \( D_k^{\text{calc}}(\lambda) \), provided that Beer's law is fulfilled, is found as

\[
D_k^{\text{calc}}(\lambda) = C_k \varepsilon_k^{(1)} \; l \; ,
\]

(5)

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