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NUMERICAL METHODS PERFORMANCE OPTIMIZATION IN ELECTROLYTES PROPERTIES MODELING

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ABSTRACT

A global optimization algorithm for the residual function is considered in application to the cluster model of electrolyte aqueous solutions. A method for finding a set of parameter estimates is developed and criteria for adequate solutions subset identification are proposed. Due to the high computational intensity of the minimization procedure, a performance optimization technique of the proposed method is described.

Keywords: multistart, cluster model, global optimization, model adequacy, modeling.

1. INTRODUCTION

A large number of electrolyte aqueous solution models have now been proposed. Often, the equations of these models contain a large number of empirical parameters the physical meaning of which is not defined, that creates significant difficulties in obtaining their estimates and, as a consequence, in checking the consistency of the solution found with data obtained by other research methods. Therefore, attempts are made to construct new models whose parameters would have a clear physical meaning. In this paper, one of such models is considered: the cluster model of solutions [1]. This model puts into correspondence the molality of the solution m and the osmotic coefficient φ.

Within the cluster model, it is assumed that the non-ideality of electrolytes aqueous solutions is determined by the independent action of electrostatic interactions, hydration and ion association. Electrostatic interactions are accounted for by the second approximation of the Debye-Hückel theory. Hydration of ions and their association are described respectively by concentration dependencies of hydrate and associate distributions by stoichiometric coefficients. The parameters of the model are: B is the Debye coefficient, A_s is the coefficient characterizing the degree of association in solution, h_1, h_2 is the average degree of hydration of cations and anions, respectively, r_1, r_2 are the coefficients characterizing the dispersion of the cation and anion distribution in the solution by degrees of hydration.

The study described in this paper was one of the stages in the author's development of a software package for thermodynamic properties of electrolyte solutions modeling and model adequacy verification [2].

2. MATERIALS AND METHODS

2.1 Least square method

The main method for identifying estimates of model parameters is the least squares method. According to it the parameters of the model equations are chosen in such a way as to minimize the following functional:

$$F = \sum_{i=1}^{N}(\varphi_{exp}(m_i) - \varphi_{model}(m_i))^2, \quad (1)$$

where m_i is the concentration value in the i-th measurement point, φ_{exp} is the experimental data on the osmotic coefficient of the solution, φ_{model} is the osmotic coefficient values predicted by the model equations.

In the overwhelming majority of cases, and in particular in case of the cluster model, the mathematical models describing physicochemical processes are non-linear functions of many variables. In this case, the minimized sum of the squared deviations of the model from the experimental data is also a nonlinear function of the model parameters. Thus it is often impossible to analytically find the minimum of this function, and usually various numerical methods are used. The following optimization methods are provided in the developed software package: quasi-Newtonian method, simulated annealing method [3], method of trusted regions [4].

All of the above algorithms start searching for the minimum of the function from the initial approximation x_0, which is usually specified by the user. The solution of the optimization problem depends heavily on this initial approximation, whose wrong assignment can lead to finding a local minimum, in which the value of the objective function is much larger than the value at the global minimum point. To overcome this problem, random search methods are used.

The main method for randomly searching for a global extremum of multidimensional functions is multistart [5], when a subset of N points is randomly chosen from the set X, from which a local descent to the nearest minimum U_i* is made by any local search method. Then the minimal extremum is considered the global minimum U**. Multistart is a generalized approach: most effective methods of global optimization are based on the idea of a multistart method, i.e. of launching standard local algorithms from a set of points uniformly distributed over set X.

2.2 Optimal model parameters estimation algorithm

When designing a software package for electrolyte thermodynamic properties modeling, special

attention was paid to the autonomy of the optimization problems solution. This means that the user does not enter the initial approximation to start the algorithm. Thus the multistart method was applied, the local search algorithm was started from n = 10 admissible points, chosen at random. The distribution of the probability of choosing a point was taken uniformly in the first step, and then the forbidden areas were added in accordance with the procedure described further in section 3.1.

After generating a random starting point, a method of trusted regions was applied, modified to take into account possible constraints. Given that the optimized function is the sum of the squares of the residuals of the experimental data and the values of the model function at the same points, it is possible to increase the efficiency of the algorithm due to the fact that the second derivatives of the residual functions $f_i(x)$ are not used [6]. Since this algorithm is started several times when using multistart, the execution time is reduced by a factor proportional to n. After finding n = 10 solutions of the problem, the best is chosen from them, after which it is used as the initial approximation for the simulated annealing method.

Finally, the result of the simulated annealing method serves as the starting point for the quasi-Newtonian method, the solution of which is taken as the minimum of the function. Figure-1 shows a block diagram of the algorithm used.

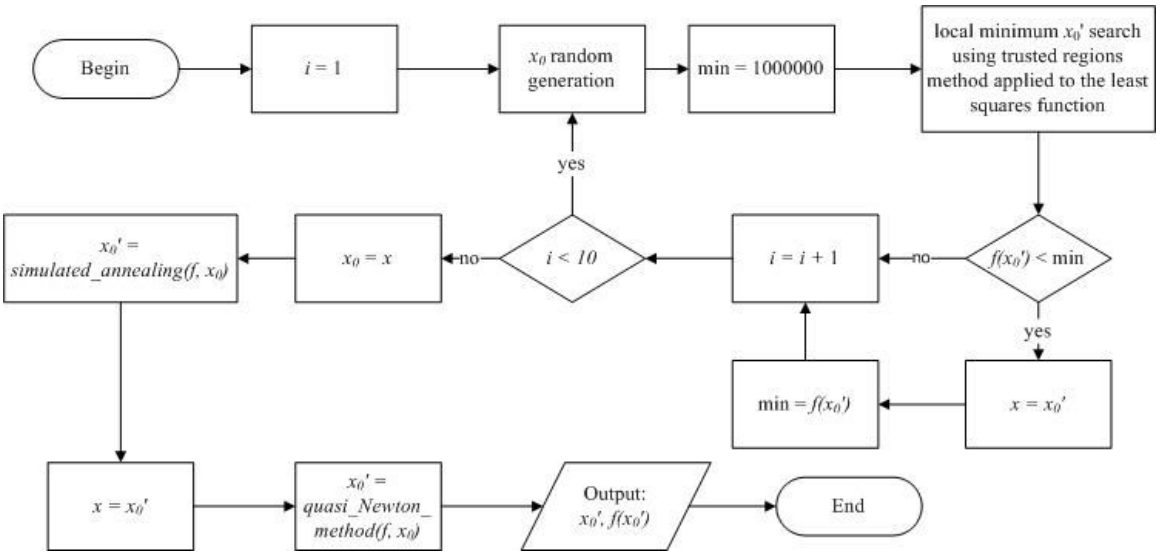

Figure-1. Block diagram of the algorithm used by default in the system.

2.3 Finding the solution set

Global optimization methods can partially overcome the problem of multi-extremality of the residual function, but for most of the solutions considered, the values of this function in their local minima are much less than the error in measuring the experimental data. This means that, although it is preferable to find a global minimum in a purely mathematical sense, from a practical point of view any of the local minima that provide acceptable accuracy can be a solution corresponding to the true values of the parameters, i.e. physically interpreted solution. In this case, the conclusion about the adequacy of the estimates found should be made by the expert, but for that it is necessary to provide him with information about all found local extrema of the function. In case of using the multistart algorithm in its classical form, for some extrema the probability of being detected is very small. In the case of the existence of two extrema, with description accuracy of the concentration dependence of the osmotic coefficient respectively $\sigma_1 = 0.01$ and $\sigma_2 = 0.001$, even if the first of them is found at some iteration, it will most likely be replaced by another during the remaining n-1 iterations of the multistart. Therefore, in order to determine the adequacy of the solutions obtained, the results found at each iteration of the method are preserved in the package developed if they provide an acceptable accuracy from the practical point of view for describing the experimental dependence. An additional criterion for the selection of solutions was their location strictly inside the range of admissible values (that is, solutions in which one of the parameters is at the boundary of its admissible interval are not included in the final set of solutions). To display the set of solutions on a graph (in case of a large number n of model parameters), the parameters are plotted in pairs.

2.4 Adequate sets of parameter estimates selection

When constructing a set of solutions, it is necessary to filter it in order to find adequate ones. In some cases, only an expert can determine the adequacy of the solution, but it is often possible to perform an automated reduction of the found set using check dependencies.

Several criteria can be used to test the sets of parameter estimates for adequacy: consistency between reference and modeled activity values of individual ions (γ_+ and γ_-); the excess of the total amount of water in the electrolyte over the amount of bound water. Also to verify

the adequacy of the solution, functional relationships between the parameters of various modifications of models can be used.

A general algorithm for finding a set of parameter estimates that are adequate from the point of view of the criteria considered above consists of the following stages:

a) finding a set of solutions that provide acceptable accuracy in describing the experimental electrolyte osmotic coefficient values by storing the optimization results at each iteration of the multistart algorithm;

b) optimization using a simplified model which includes only a subset of the parameters of the original model or for which a functional relationship between some parameters of the original model and its modification is known;

c) finding the intersection of the sets obtained in steps 1 and 2 by common parameters (when applying the operation of intersection of sets, the values of the parameters differing by an amount less than the permissible error are considered to represent the same solution);

d) calculation of the individual ions activity coefficients concentration dependences for each set of parameter estimates belonging to the set obtained in step 3;

e) comparison of the obtained dependencies with the reference ones. Discarding decisions that provide an unsatisfactory description of reference data.

f) found solution adequacy verification based on the estimation of the amount of bound water in the electrolyte.

g) Results saving. In case of more than one solution found, their subsequent expert processing.

3. RESULTS

3.1 Performance optimization when using multistart

A characteristic feature of the multistart method is the independence of the local optimization procedures launched from different starting points. Therefore, algorithms based on this method are easily parallelized. However, the complete independence of these procedures means that the algorithm does not use the results obtained at previous iterations in any way. Nevertheless, the use of such information can give an additional efficiency increase. Consider an arbitrary objective function of one argument. Its values at the points of local minima can differ substantially. When using the least squares method, only minima close to zero are usually of interest whereas when choosing a starting point, located in the area of attraction of a local minimum with a large value (point x_0 in Figure-2), the algorithm will eventually converge to it.

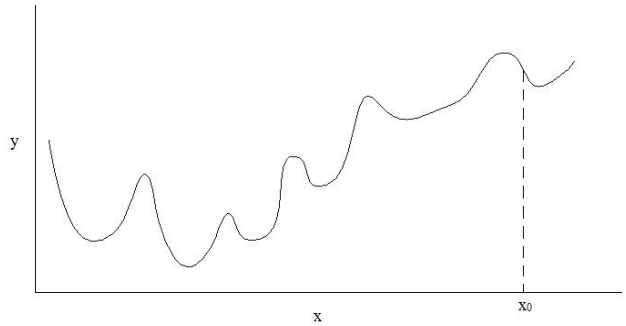

Figure-2. Point x_0 is lies in the attraction area of a local minimum.

For the initial starting point selection it is impossible to predict the value of the minimum that will be found. Nevertheless, after finding a minimum that clearly exceeds the allowable limits it is possible to keep information about this so that in subsequent steps the probability of the starting point getting into this region would be small. In addition, even if an acceptable minimum is found at certain iteration, its area of attraction should be excluded from the possible starting point selection areas. This is achieved by changing the probability distribution of the potential starting points. At the very beginning of the algorithm, the probability distribution is uniform across the entire range of valid values of the argument. If a point x_0 is found, from which the local minimum is reached, the probability distribution is modified as illustrated in Figure-3.

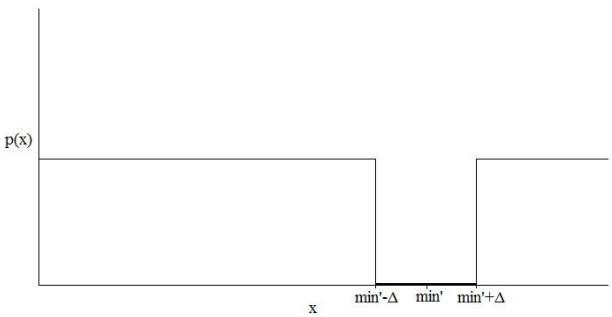

Figure-3. Starting points selection probability distribution change after the first iteration of the modified multistart algorithm.

The value Δis determined by the following expression:

$$\Delta = |x_0 - \arg(\min' f(x))\,| \,, \qquad (2)$$

where x_0 is the starting point of the search, *min'(f(x))* is the local minimum found.

It is also necessary to adjust the probability distribution in other areas.

This approach considered for functions of one argument is also applicable in case of functions of several variables. In that case, each extremum found is put in a spherical region with a radius equal to the distance from the search starting point to this extremum. The recalculation of the probability distribution and the generation of a new random point from it are much faster than repeated local optimization from the region considered. The problem has low impact on algorithms using few starting points, however in case of the algorithm for finding the solution set used in the adequacy verification of the models discussed above, approximately 250 starting points are generated. In this case, the number of areas of inadequate local minima is growing fast; as a result the program uses resources less and less efficiently.

The size of forbidden areas, i.e. areas from which points for subsequent multistart iterations are not selected, can be different. Below the results of modeling the concentration dependence of aqueous NaCl electrolyte using the multistart method are presented. As the radius of forbidden regions, the distance from the initial point of search to the corresponding extremum found was taken, and also as an alternative - half of that distance. These two methods were compared with the classical multistart method. In Figure-4 the results for the first method are marked with round markers, for the second method - with cross markers of white color on a black background. Finally, the black cross markers correspond to the classical multistart.

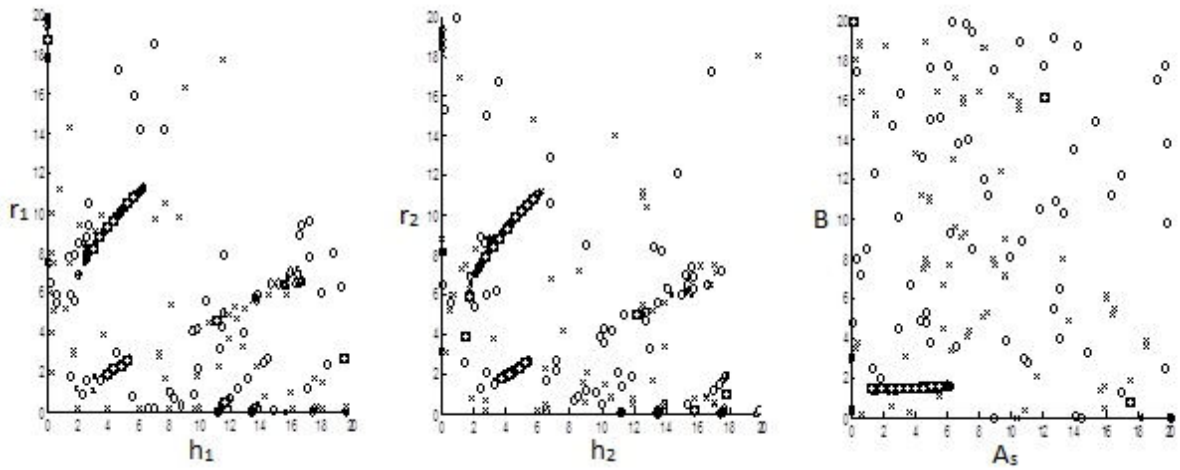

Figure-4. Multistart modification modeling results 1) without using forbidden areas (x); 2) using forbidden areas with radius equal to half of the distance between starting point and the local minimum found (o); 3) using forbidden areas with radius equal to the distance between starting point and the local minimum found (+)

It can be seen from the figure that modification 2 does not give advantages over the usual multistart. The dispersion of the extrema found is large in both cases, and most of them do not provide acceptable accuracy. The number of iterations in both cases was set to 250. In contrast, the solutions obtained with the third modification of the algorithm do not have such a big spread. Only a small number of solutions do not fall into clearly defined clusters in the set and do not provide acceptable accuracy in describing the experimental data. In addition, it should be noted that despite setting the number of iterations equal to 250, the actual number of iterations was 27, because by that time the entire search area had turned into a forbidden one. Here it is necessary to say about the implementation of the algorithm for choosing a random point from a distribution with forbidden areas. Probability distribution recalculation in the case of multidimensional random vectors is a complex operation. In addition, the time of generation of a random point (in case of using a classical multistart) is much less than the optimization time. Therefore, it is more efficient to generate points in a loop until one is found which does not belong to forbidden regions. Such a procedure initially requires a small amount of resources, but as the number of forbidden areas increases, its execution time increases as well. Therefore, a timeout of one second was applied to the starting point generation procedure.

In the method described, it is implicitly assumed that the regions corresponding to the extrema of the function are symmetric and therefore, by finding the initial point in the region of attraction of a given extremum, one can surround it with a spherical forbidden area. However, the method can also be applied in case of asymmetry. Even in case when some potential starting points fall into a forbidden area corresponding to a different extremum, there still remains the possibility of descent from other sides, so on average the main extrema will be found. Taking into consideration a significant reduction in the number of necessary iterations or, with an equal number of them, a better convergence to the main extrema of the objective function, the third modification was chosen for use in the developed software package.

4. DISCUSSIONS

The study presented in this paper was one of the stages in the author's development of a software package

for electrolyte aqueous solutions thermodynamic properties modeling and models adequacy verification. The main method for identifying estimates of model parameters is the least squares method. In case of complex equations the residual function becomes multi-extremal, and to find the global extremum, random search methods can be used. In this paper, we have described the global optimization algorithm used in the developed software package, which consists of using multistart of trusted regions method as the local optimization algorithm, followed by simulated annealing and quasi-Newton method.

Often a physically interpreted solution is a local, but not a global minimum. Thus, the problem transforms into finding a set of solutions with the subsequent choice of a subset of adequate ones. It can be solved by modifying the multistart algorithm and checking the sets of parameter estimates using several criteria: the consistence between reference and model-calculated data on the activity coefficients of individual ions (γ_+ and γ_-), excess of the total amount of water in the electrolyte over the amount of bound water. Also, to verify the adequacy of the solution, functional relationships between the parameters of various modifications of models can be used.

Due to the high resource intensity of the minimization procedure, a performance optimization of the proposed multistart method based on an iterative modification of the potential starting points' probability distribution has been proposed. When applying the electrolytes cluster model to the experimental data for the aqueous NaCl electrolyte, the execution time of the proposed algorithm was reduced by a factor of 9.

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