UDC 519.876:544.6
DOI: 10.15587/1729-4061.2026.352348

DETERMINING THE IDENTIFICATION OF PARAMETERS FOR THE MATHEMATICAL MODEL OF ELECTRICAL CONDUCTIVITY IN CONDUCTOMETRIC MODELS

Using an aqueous solution of acetic acid an example, this study has investigated a mathematical model of the electrical conductivity of weak electrolyte dilute solutions.

To resolve the issue of identification and reliability in determining the parameters for the mathematical model of the electrical conductivity of dilute solutions of weak electrolytes, the determinant of the Fisher information matrix was calculated.

The issues related to determining the association constants and the limiting molar electrical conductivity of weak electrolytes under different conditions of experimental experiments were identified and explained.

This paper reports results of mathematical processing of conductometric data for aqueous solutions of acetic acid.

It was established that for weak, associated electrolytes, when determining the association constants and the limiting molar coefficients, it is necessary to take into account the existence of a correlation between them.

It is proven that at large values of the association constant (5.58 * 10^4 mol/L) the determinant of the Fisher information matrix is close to zero and there is a structural non-identification of parameters for the mathematical model of electrical conductivity of dilute solutions of weak electrolytes.

It is shown that the results of mathematical processing of conductometric data for aqueous solutions of acetic acid indicate the presence of structural non-identification. This is confirmed by the values of the determinant of the Fisher information matrix, which is equal to 5.5 * 10^{-8}, and the normalized index of 0.988.

Analysis of the shape of the surface of the objective functions of the studied mathematical models and the form of the average error ellipse reveals the existence of a canyon with an almost flat bottom, which complicates the interpretation and reliability of parameters for the mathematical model of electrical conductivity.

The results confirm the possibility of structural non-identification of parameters for the mathematical model of the electrical conductivity of dilute solutions of weak electrolytes

Keywords: conductometry, Fisher matrix, parameter non-identification, weak electrolytes, association constant, electrical conductivity

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Received 04.12.2025
Received in revised form 22.01.2026
Accepted date 13.02.2026
Published date 26.02.2026

How to Cite: *Chumak, V., Maksymiuk, M., Kopanytsia, A. (2026). Determining the identification of parameters for the mathematical model of electrical conductivity in conductometric models. Eastern-European Journal of Enterprise Technologies, 1 (6 (139)), 16–24. https://doi.org/10.15587/1729-4061.2026.352348*

1. Introduction

The theory of electrolyte solutions currently does not allow for a single description of the concentration dependence of the conductivity of an electrolyte solution in the entire concentration range. The conductivity of solutions is one of the basic parameters that characterizes ion mobility and the interaction of ions in the environment. Conductivity measurements are used in analytical chemistry to determine ion concentrations; conductometric methods for controlling the quality of water and industrial solutions; biotechnologies for monitoring processes; energy systems (batteries, fuel cells); medical diagnostics (electrolyte balances).

Conductometry is also used to determine the equilibrium constants of chemical reactions in solutions, dissociation constants of weak electrolytes.

For modern mathematical models of the conductivity of dilute solutions, a key problem may exist: the model parameters may be unidentified, i.e., they cannot be estimated unambiguously from the available data and may also be strongly correlated. This poses a challenge to practical applications of the model as it is unclear to what extent the resulting parameters reflect actual properties of the system.

Conductometric models often use a narrow range of concentrations. Under such conditions, the sensitivity of the model to parameters becomes similar or almost linearly dependent; the Fisher information matrix may lose its certainty. This could lead to practical non-identification of the parameters, the inability to separate the influence of individual physical processes; uncertainty in the predictions made on the basis of the model.

Thus, without identifiability analysis, the use of electrical conductivity models could lead to incorrect conclusions in applied problems, for example when measuring the composition of solutions; controlling technological processes; in the process of modeling complex real solutions.

Modern mathematical modeling is not limited to the search for the best parameters but includes an assessment of the stability of estimates; identification of parameter correlations; analysis of structural and practical identifiability.

These approaches are important in many modern fields of science and technology (chemical modeling, systems biology, energy); their application in the context of conductometry helps reduce the uncertainty of models and increase confidence in the results of analysis.

The study of non-identifiability in electrical conductivity models makes it possible to devise methods for numerical parameter estimation, apply modern statistical methods, analyze the Fisher information matrix, error ellipses, and correlation indices.

Thus, the issue of non-identifiability of parameters for the mathematical model of electrical conductivity in conductometric models is relevant because of its direct impact on the quality of parameter estimation, the reliability of predictions, and the practical applicability of models in actual applied problems. Analysis of this issue meets the modern requirements of statistical and mathematical modeling and is of great importance both in theoretical and applied aspects.

2. Literature review and problem statement

It is shown in [1–3] that situations often arise when model parameters cannot be reliably estimated from experimental data.

The authors of work [1] considered the issues of parametric identification of models, covering the problems of experimental data processing.

In [2], software for analyzing real data is described; however, the lack of instructions for using the programs complicates their use.

In paper [3], issues of parametric identification of models are considered, moving from simple to more complex, but even in this case it takes a lot of effort to understand the argumentation.

Despite the fact that the results reported in [1–3] are theoretically justified, they were not used to process experimental data from conductometric studies for the purpose of parametric identification of the electrical conductivity model of weak electrolytes. The two most common manifestations of this problem are multicollinearity in linear models and non-identifiability of parameters for linear and nonlinear models.

Multicollinearity is a phenomenon in which independent variables in a regression model are highly correlated with each other. Parameter non-identification is a more general concept and means the impossibility of unambiguously determining parameters for the model from experimental data. There are two possible cases of non-identification: structural non-identification is the impossibility of determining parameters for the model, which is due to the form of the model itself, while practical non-identification arises due to limited informativeness of the data, noise (errors) of measurements, or an unsuccessful experimental design.

The disadvantage of studies [1–3] is the failure to resolve issues related to the task of processing experimental data; if practical non-identification is observed – the model is theoretically identified, but real experimental data do not allow for reliable estimation of parameters.

From a mathematical point of view, the phenomenon of parameter non-identification is associated with the degeneracy of the Fisher information matrix [4], which is manifested in the strong correlation of the estimated parameters and the presence of “flat valleys” on the surface of the error function.

The Fisher information matrix is a central tool for analyzing parameter identifiability. Its degeneracy or poor conditionality indicates structural or practical non-identifiability of parameters and is a mathematical analog of multicollinearity in linear models.

Geometric signs of non-identifiability: the surface of the error function has an elongated narrow “valley” and along this valley the error function does not change or practically does not change.

In paper [5] it is shown that the least squares method, based on a large but finite set of observations determined by initial parameter estimates, provides a unified approach to local identifiability.

Study [6] considers illustrative examples of structural non-identifiability and its consequences using mechanistically derived models.

Thus, the main and most unpleasant manifestation of non-identifiability is the uncertainty of model parameter estimates [5, 6].

Works [4–6] are theoretical in nature and do not have clear recommendations for overcoming the non-identification of parameters for mathematical models used in chemical research.

In paper [7], the Fisher information matrix for two-factor panel data models with random effects is analyzed; computational issues are also discussed.

In paper [8], it is proven that the increase in computing power has led to an increase in interest in the Fisher criterion in the social sciences.

In paper [9], the quantum Fisher information matrix is analyzed as a fundamental quantity in quantum physics.

In paper [10], a comprehensive review of achievements in the systematic use of mathematical models in chemical engineering is given.

A proposed approach from [11] uses the likelihood function, which makes it possible to detect structural non-identification in functionally related model parameters.

The use of the Fisher information matrix has been used to describe the parameters of various models [7–11] but has not been used to estimate the parameters of conductometric models.

An option for overcoming the difficulties of uncertainty in the estimates of model parameters is to change the experimental design or conduct the experiment in a different range of values of variable x. This is the approach that could be used in chemistry; for example, when determining parameters for the Shyshkovsky equation or the equation of the kinetics of first-order chemical reactions.

Such cases correspond to practical non-identifiability. Naturally, in examples it is not the values of model parameters that are important but their relationship with the values of variable x. Eliminating the issue of practical non-identifiability in such cases is solved by conducting an experiment in a different range of x values. However, there are cases, for example, mathematical models of the electrical conductivity of dilute electrolyte solutions that can be used only in a certain range of electrolyte concentrations [12].

Construction of a truly successful universal electrolyte model (for example, the equation of state) should include consideration of all available data on electrolytes when estimating parameters and checking the model [13].

In paper [14], based on the influence of the number of free ions and ion mobility on conductivity, a semi-empirical model of electrical conductivity was proposed. The disadvantage of the model is the large number of parameters for correlating data on electrical conductivity, concentration, and temperature of electrolyte solutions at medium and high concentrations.

Modern electrical conductivity models [15] take into account various interactions at the molecular level within the framework of chemical physics to calculate the transport properties of the electrolyte with minimal computational costs.

Mathematical electrical conductivity models [12–15] contain parameters calculated during the processing of experimental data; however, there were no stability estimates, no parameter correlation detection; structural and practical identifiability analysis was not conducted.

3. The aim and objectives of the study

The purpose of our study is to identify the correlation of parameters; identify and analyze the structural and practical non-identification of parameters for the mathematical model of electrical conductivity of electrolyte solutions based on nonlinear regression methods and using the Fisher information matrix. This could make it possible to compile recommendations that would determine conditions for the emergence or reduction of the non-identification of parameters for the mathematical model of electrical conductivity, in particular by choosing a concentration range or modifying the mathematical model.

To achieve the goal, the following tasks were set:

– to construct a Fisher information matrix for the mathematical model of the electrical conductivity of electrolyte solutions and investigate its properties;

– to analyze the mathematical models of electrical conductivity of electrolyte solutions and consider conditions for the emergence of non-identification of parameters for the mathematical model of electrical conductivity of electrolyte solutions;

– to develop a program that uses the Excel Solver add-in to compute parameters for the mathematical model of electrical conductivity and calculate the Fisher information matrix;

– to conduct a numerical evaluation of parameters for the electrical conductivity model, the determinant of the Fisher information matrix, the normalized indicator, and construct the dependences of the error function and the confidence ellipse.

4. The study materials and methods

The object of our study is mathematical models of electrical conductivity of electrolyte solutions used in conductometry.

The principal hypothesis assumes the possibility of the phenomenon of non-identification of parameters for the mathematical model of electrical conductivity of weak electrolytes.

The paper assumes that for weak electrolytes the influence of interionic interactions on the mobility of ions could be neglected.

The second assumption is that the random error of the experimental values of electrical conductivity has a normal distribution, the average error is zero.

To simplify the study, in the equation for the association constant, instead of the values of the ion activities, the values of concentrations were used.

The paper uses a set of theoretical, numerical, and applied methods, in particular mathematical analysis, linear algebra, nonlinear regression, Newton's methods, Fisher information matrix analysis, statistical processing of experimental data.

The listed methods were applied to process experimental conductometric data by developing programs in the VBA (Visual Basic for Applications) environment in the MS Excel application (Microsoft Corporation, USA), and subsequent analysis of the results.

5. Results of research on the characteristics of the mathematical model of electrical conductivity of electrolyte solutions

5. 1. Construction of a Fisher information matrix for the mathematical model of electrical conductivity and analysis of properties of the Fisher matrix

In most cases, the mathematical model of electrical conductivity of dilute electrolyte solutions contains two unknown quantities, which are calculated during the processing of experimental data according to certain theoretical equations.

To assess the non-identification of parameters for the mathematical model of electrical conductivity of electrolyte solutions, a numerical calculation of the Fisher information matrix is required.

The equivalent electrical conductivity of dilute electrolyte solutions can be described by a nonlinear regression containing two parameters ($a = \lambda_0, b = K_a$)

$$y_i = f(x_i, a, b) \pm \varepsilon_i, \quad (1)$$

where ε_i is the random error of determining the experimental data, i = 1,....., n is the number of measurements, λ_0 is the limiting equivalent electrical conductivity, K_a is the ionic association constant, y is the equivalent electrical conductivity. Let us assume that it obeys a normal (Gaussian) distribution, i.e., the random variable ε follows a normal distribution, the mathematical expectation and measurement errors are symmetric, the average error is zero ($E[\varepsilon] = 0$), the variance is $\mathrm{Var}(\varepsilon) = \sigma^2$, and the standard deviation is equal to σ.

Under such conditions, the probability density is

$$p(\varepsilon) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{\varepsilon^2}{2\sigma^2}\right). \quad (2)$$

For a vector of parameters $\theta = \begin{pmatrix} a \\ b \end{pmatrix}$, the likelihood function takes the form

$$L((a,b) = \prod_{i=1}^{n} \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{\left[y_i - f((x_i,a,b)\right]^2}{2\sigma^2}\right), \quad (3)$$

a logarithmic probability function

$$\ell(a,b) = -\frac{n}{2}\ln\left(2\pi\sigma^2\right) - \frac{1}{2\sigma^2}\sum_{i=1}^{n}\left[y_i - f(x_i,a,b)\right]^2. \quad (4)$$

The first derivatives of the logarithmic probability function by parameters a and b are:

$$\frac{\partial \ell}{\partial a}=\frac{1}{\sigma^2}\sum_{i=1}^{n}\left(y_i-f\left(x_i,a,b\right)\right)\frac{\partial f\left(x_i,a,b\right)}{\partial a}, \tag{5}$$

$$\frac{\partial \ell}{\partial b}=\frac{1}{\sigma^2}\sum_{i=1}^{n}\left(y_i-f\left(x_i,a,b\right)\right)\frac{\partial f\left(x_i,a,b\right)}{\partial b}. \tag{6}$$

Second derivatives (elements of the Hesse matrix):

$$\frac{\partial^2 \ell}{\partial a^2}=-\frac{1}{\sigma^2}\sum_{i=1}^{n}\left(\frac{\partial f\left(x_i,a,b\right)}{\partial a}\right)^2+ +\frac{1}{\sigma^2}\sum_{i=1}^{n}\left(y_i-f\left(x_i,a,b\right)\right)\frac{\partial^2 f\left(x_i,a,b\right)}{\partial a^2}, \tag{7}$$

$$\frac{\partial^2 \ell}{\partial b^2}=-\frac{1}{\sigma^2}\sum_{i=1}^{n}\left(\frac{\partial f\left(x_i,a,b\right)}{\partial b}\right)^2+ +\frac{1}{\sigma^2}\sum_{i=1}^{n}\left(y_i-f\left(x_i,a,b\right)\right)\frac{\partial^2 f\left(x_i,a,b\right)}{\partial b^2}, \tag{8}$$

$$\frac{\partial^2 \ell}{\partial a\partial b}=-\frac{1}{\sigma^2}\sum_{i=1}^{n}\frac{\partial f\left(x_i,a,b\right)}{\partial a}\frac{\partial f\left(x_i,a,b\right)}{\partial b}+ +\frac{1}{\sigma^2}\sum_{i=1}^{n}\left(y_i-f\left(x_i,a,b\right)\right)\frac{\partial^2 f\left(x_i,a,b\right)}{\partial a\partial b}. \tag{9}$$

Considering the definition of the Fisher information matrix as the mathematical expectation: $\mathbf{F}_{jk}=-\mathbb{E}\left[\frac{\partial^2 \ell}{\partial\theta_j\partial\theta_k}\right]$ (where j, k = 1, 2), the elements of the Fisher information matrix for two parameters were obtained:

– $F_{aa}=\frac{1}{\sigma^2}\sum_{i=1}^{n}\left(\frac{\partial f\left(x_i,a,b\right)}{\partial a}\right)^2$ characterizes the accuracy in determining parameter a;

– $F_{bb}=\frac{1}{\sigma^2}\sum_{i=1}^{n}\left(\frac{\partial f\left(x_i,a,b\right)}{\partial b}\right)^2$ characterizes the accuracy in determining parameter b;

– $F_{ab}=\frac{1}{\sigma^2}\sum_{i=1}^{n}\frac{\partial f\left(x_i,a,b\right)}{\partial a}\frac{\partial f\left(x_i,a,b\right)}{\partial b}$ indicates a possible correlation between the parameters.

In cases where $F_{ab}\approx\sqrt{F_{aa}F_{bb}}$ there is a strong correlation of parameters and their unstable estimates.

Then the matrix form of Fisher information for a 2 × 2 matrix will be

$$\mathbf{F}(a,b)=\begin{pmatrix}F_{aa} & F_{ab}\\ F_{ba} & F_{bb}\end{pmatrix}=\frac{1}{\sigma^2}\begin{pmatrix}\sum_{i=1}^{n}\left(\frac{\partial f}{\partial a}\right)^2 & \sum_{i=1}^{n}\frac{\partial f}{\partial a}\frac{\partial f}{\partial b}\\ \sum_{i=1}^{n}\frac{\partial f}{\partial a}\frac{\partial f}{\partial b} & \sum_{i=1}^{n}\left(\frac{\partial f}{\partial b}\right)^2\end{pmatrix}, \tag{10}$$

or $\mathbf{F}=\frac{1}{\sigma^2}\mathbf{J}^{\mathrm{T}}\mathbf{J}$, where $\mathbf{J}$ is the Jacobi matrix.

Determinant of the matrix: $\det(\mathbf{F})=F_{aa}F_{bb}-F_{ab}^2$.

If det(**F**) = 0, then this indicates the structural non-identification of quantities a and b. If det(**F**) ≈ 0, there is a practical non-identification of quantities a and b. As the degree of non-identification, the normalized indicator of the Fisher information matrix is used [3] (analog to the correlation coefficient for parameters) $\rho_F=\frac{F_{ab}}{\sqrt{F_{aa}F_{bb}}}$.

The interpretation of values for the normalized indicator of the Fisher information matrix according to [1–4] can be represented in the form of Table 1.

Table 1

Numerical thresholds of values for the normalized indicator of the Fisher information matrix

ρ_F	Interpretation
< 0.7	Weak correlation
0.7–0.9	Moderate correlation
0.9–0.95	Strong correlation
> 0.95	Practical non-identification
≈ 1	Fisher matrix degeneracy

Comparison of the intervals of values of the normalized indicator of the Fisher information matrix given in Table 1 with those calculated from experimental data makes it possible to identify the degree of correlation between the model parameters.

5. 2. Analysis of mathematical models of electrical conductivity of electrolyte solutions and conditions for the occurrence of non-identification of parameters

The experimental data on the conductometric method, which is one of the simplest and most accurate methods of research and analysis of substances, were used in the study. With the help of this method, solutions can be studied in a wide range of temperatures, concentrations, pressures, and practically any solvents [12–15].

On the basis of conductometric measurements, a large number of properties of solutions can be determined, for example the limiting equivalent electrical conductivity (λ_0), ion association constants (K_a), thermodynamic characteristics $\left(\Delta H_a^0, \Delta S_a^0\right)$ of ion migration and association processes. Issues with the reliability of the initial experimental values are sufficiently studied; in addition, modern devices for measuring electrical conductivity make it possible to determine conductometric data with an accuracy of up to ± 0.01%.

There are various theories of the electrical conductivity of electrolyte solutions that describe the dependence of equivalent electrical conductivity on the concentration and properties of the solute and solvent [12–15]. These equations describe the experimental data for strong electrolytes well; however, as practice shows, for weak electrolytes there are uncertainties in the calculations of the ionic association constant and the limiting equivalent electrical conductivity.

To derive reliable λ_0 and K_a values, not only a reasonable choice of the theoretical equation is important but also a mathematical approach to solving it. All equations of the dependence of molar electrical conductivity on the concentration (C) and the physicochemical properties of the solvent and electrolyte can be given in the form

$$\lambda=f(\mathrm{C},\ \varepsilon,\ \eta,\ \mathrm{T},\ \lambda_0,\ K_a), \tag{11}$$

where ε, η – dielectric permittivity and viscosity of the solvent at temperature T; λ_0, K_a – unknown coefficients of the equation. Thus, the task is reduced to finding such λ_0, K_a values that the dependence $\lambda=f(C)$ constructed on the basis of the theoretical equation of electrical conductivity best coincides with the experimental ones. Finding the λ_0, K_a values of parameters for equation (11) is reduced to finding the minimum of the objective function

$$F_{\text{goal function}} = \sum_{i=1}^{n} \left(\lambda_i^{\text{calculated}} - \lambda^{\text{experimental}} \right)^2, \tag{12}$$

or

$$F_{\text{goal function}} = \sum_{i=1}^{n} w_i \left(\lambda_i^{\text{calculated}} - \lambda^{\text{experimental}} \right)^2, \tag{13}$$

where $\lambda_i^{\text{calculated}}$ is the calculated value of the equivalent electrical conductivity according to equation and (11), $\lambda_3^{\text{experimental}}$ is the experimental value of equivalent electrical conductivity, n is the number of measurements, w_i is the weighting factor. Since the justification of w_i is quite complicated, equation (12) is mostly used.

The calculated value of equivalent electrical conductivity according to equation (11) depends on the degree of dissociation of electrolyte (α), which is determined from the following equation

$$K_a = \frac{1-\alpha}{\alpha^2 C}. \tag{14}$$

Practical non-identification is possible in the case of ionic association of very weak electrolytes (α <<< 1). In this case, equation (14) can be written as

$$K_a = \frac{1-\alpha}{\alpha^2 C} = \frac{\left(1-\frac{\lambda}{\lambda_0}\right)}{\left(\frac{\lambda}{\lambda_0}\right)^2 C}, \tag{15}$$

where $\alpha = \frac{\lambda}{\lambda_0}$. Then the solution to this equation will take the form

$$\lambda = \frac{2\lambda_0}{1+\sqrt{1+4K_a C}}, \tag{16}$$

and the derivatives required for the calculation of the Fisher information matrix are equal to

$$\frac{\partial \lambda}{\partial \lambda_0} = \frac{2}{1+\sqrt{1+4K_a C}},$$

$$\frac{\partial \lambda}{\partial K_a} = -\frac{4C\lambda_0}{\sqrt{1+4K_a C}\left(1+\sqrt{1+4K_a C}\right)^2}. \tag{17}$$

If (α <<< 1), then if $\sqrt{1+4K_a C} >>> 1$ equation (16) takes the form

$$\lambda = \left(\frac{\lambda_0}{\sqrt{K_a}} \right) \frac{1}{\sqrt{C}}. \tag{18}$$

Meeting the condition $\sqrt{1+4K_a C} >>> 1$, which can be observed during the ionic association of weak electrolytes under condition that $4K_a C >> 1$. Thus, there are possible cases of practical non-identifiability and uncertainty of the λ_0 and K_a parameters. Theoretical analysis of equation (18) reveals that if the linearity of the dependence in the coordinates $\lambda = F\left(\frac{1}{\sqrt{C}}\right)$, is observed, difficulties will arise in interpreting the calculated λ_0 and K_a values; therefore, the study of the association of weak electrolytes requires an analysis to determine the presence of practical non-identifiability.

5. 3. Development of a program for calculating parameters for the mathematical model of electrical conductivity and the Fisher information matrix

Calculations of the K_a, λ_0 parameters and the components of the Fisher information matrix were performed using the VBA (Visual Basic for Applications) application in the MS Excel environment using the developed program:

```
Sub Solver_FIM()
  Dim ws As Worksheet
  Set ws = ThisWorkbook.Sheets("Sheet1")
  Dim i As Integer
  Dim n As Long
  n = 18  ' number of experimental points
  For i = 2 To n + 1
  ws.Cells(i, 7).Formula = _
  "=2*$E$2/(1+SQRT(1+(4*$F$2)*A" & i & "))"
  Next i
  '  Sum of squares of the residues (Solver)
  ws.Range("H1").Value = "SSE="
  ws.Range("H2").Formula = _
  "=SUMXMY2(B2:B" & n + 1 & ",G2:G" & n + 1 & ")"
   ' Solver
  Application.Run "Solver.xlam!SolverReset"
  Application.Run "Solver.xlam!SolverOk", _
  ws.Range("H2"), 2, 0, ws.Range("E2:F2")
  Application.Run "Solver.xlam!SolverSolve", True
  ' ws.Range("I1").Value = "d λ/d λ0"
  'ws.Range("J1").Value = "d λ/dKa"
  For i = 2 To n + 1
  ws.Cells(i, 9).Formula = _
  "=2/(1+SQRT(1+(4*$F$2)*A" & i & "))"
  ws.Cells(i, 10).Formula = _
   "=-4*A" & i & "*$E$2/((1+SQRT(1+4*$F$2*A" & i & "))^2*SQRT(1+4*$F$2*A" & i & "))"
  Next i
   '  Fisher Information Matrix F = JTJ
  ws.Range("L1").Value = "Fisher Information Matrix"
  ws.Range("L2").Formula = "=SUMSQ(I2:I" & n + 1 & ")" 'F11
  ws.Range("M2").Formula = "=SUMPRODUCT(I2:I" & n + 1 & ",J2:J" & n + 1 & ")" 'F12
  ws.Range("L3").Formula = "=M2"
  ws.Range("M3").Formula = "=SUMSQ(J2:J" & n + 1 & ")" 'F22
  '  Determiner FIM
  ws.Range("L5").Value = "det(F)="
  ws.Range("M5").Formula = "=L2*M3-M2^2"
   ' Verification F12 / sqrt(F11*F22)
   Dim F11 As Double, F12 As Double, F22 As Double
   F11 = ws.Range("L2").Value
   F12 = ws.Range("M2").Value
   F22 = ws.Range("M3").Value
  Dim Fcrit As Double, relErr As Double
  Fcrit = Sqr(F11 * F22)
  relErr = Abs(F12 / Fcrit)
  ws.Range("L7").Value = "sqrt(F11*F22)="
  ws.Range("M7").Value = Fcrit
  ws.Range("L8").Value = "F12/sqrt(F11*F22)="
  ws.Range("M8").Value = relErr
  ws.Range("L9").Value = "Conclusion"
  If relErr > 0.95 Then
  ws.Range("M9").Value = "Strong correlation of parameters, practical non-identification"
```

```
Else
   ws.Range("M9").Value = "Parameters identified"
End If
End Sub.
```

5. 4. Calculation of parameters for the electrical conductivity model, Fisher matrix, normalized index, and analysis of the error function and confidence ellipse

We have carried out mathematical processing of experimental conductometric data on the example of ionic association of aqueous solutions of acetic acid using experimental conductometric data [16].

The experimental data are given in Table 2.

Calculations of the K_a, λ_0 parameters, the determinant of the Fisher information matrix and the normalized index were performed using the developed program. The results of all calculations are shown in Fig. 1.

The calculated characteristics of parameters for the conductivity model, the Fisher matrix, and the normalized index (Fig. 1) provide the opportunity to conduct an analysis of reliability of the association constants and the equivalent conductivity of acetic acid.

To analyze the proposed conductivity model (18) in different concentration intervals, the dependences of equivalent conductivity on $1/C^{0.5}$ were constructed for the 7 largest values of acetic acid concentrations and for the entire interval of acetic acid concentrations (Fig. 2, 3).

Table 2

Experimental conductometric data on aqueous solutions of acetic acid at a temperature of 298.15 K [16]

C, mol/dm^3	λ , S·cm^2·mol^{-1}
0.000028	210.32
0.000111	127.71
0.000153	112.02
0.000218	96.47
0.001028	48.13
0.001316	42.22
0.002414	32.21
0.003441	27.19
0.005912	20.99
0.009842	16.37
0.012829	14.37
0.02	11.563
0.05	7.356
0.052303	7.2
0.1	5.2
0.119447	4.759
0.2	3.65
0.230785	3.391

	A	B	C	D	E	F	G	H	I	J	K	L	M
1	C	λ	1/C^0,5		λ₀=	K_a=	λ₀ calculate	SSE=	∂λ/∂λ₀	∂λ/∂/K_a		Fisher Information Matrix	
2	0,000028	210,32	188,982237		**388,341**	**55844,83**	210,286884	0,4588	0,541500546	-0,00118		0,593492387	-0,001523526
3	0,000111	127,71	94,9157996				127,767125		0,32900753	-0,00092		-0,001523526	4,00416E-06
4	0,000153	112,02	80,8452083		K$_d$=	**1,79E-05**	112,058788		0,288557679	-0,00083			
5	0,000218	96,47	67,7285461				96,4871809		0,248459915	-0,00074		det(F)=	5,53081E-08
6	0,001028	48,13	31,1891431				47,9829171		0,123558709	-0,0004			
7	0,001316	42,22	27,5658923		**HAc**		42,7344582		0,110043632	-0,00036		sqrt(F11*F22)=	0,00154157
8	0,002414	32,21	20,3531375				32,0373561		0,082497993	-0,00027		F12/sqrt(F11*F22)=	**0,988294741**
9	0,003441	27,19	17,0473808				27,0220445		0,069583284	-0,00023		**Conclusion**	**Strong correlation**
10	0,005912	20,99	13,0056717				20,7924336		0,053541685	-0,00018			**of parameters, practical**
11	0,009842	16,37	10,0799486				16,2150563		0,041754682	-0,00014			**non-identification**
12	0,012829	14,37	8,828839		**SOLVER+FIM**		14,2401033		0,036669067	-0,00013			
13	0,02	11,563	7,07106781				11,4474699		0,029477879	-0,0001			
14	0,05	7,356	4,47213595				7,27993421		0,01874624	-6,5E-05			
15	0,052303	7,2	4,37256929				7,1193549		0,018332739	-6,3E-05			
16	0,1	5,2	3,16227766				5,16197659		0,01329238	-4,6E-05			
17	0,119447	4,759	2,89342598				4,72580119		0,012169204	-4,2E-05			
18	0,2	3,65	2,23606798				3,65722856		0,009417569	-3,3E-05			
19	0,230785	3,391	2,08159488		λ₀/(Ka)^0,5	**1,643319**	3,40569109		0,008769846	-3E-05			

Fig. 1. Results of calculating conductometric parameters, Fisher information matrix, and normalized index

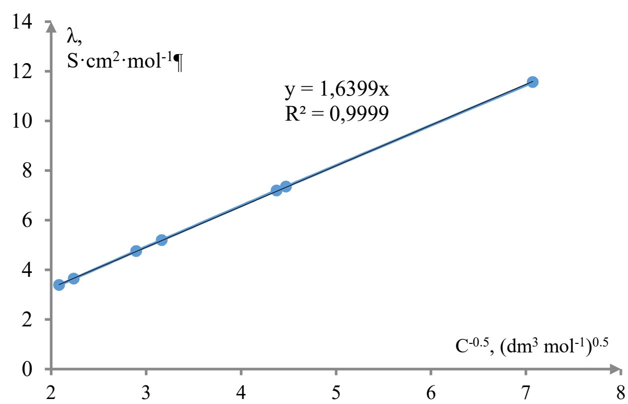

Fig. 2. Dependence of equivalent electrical conductivity on $1/C^{0,5}$ for the 7 largest values of acetic acid concentrations

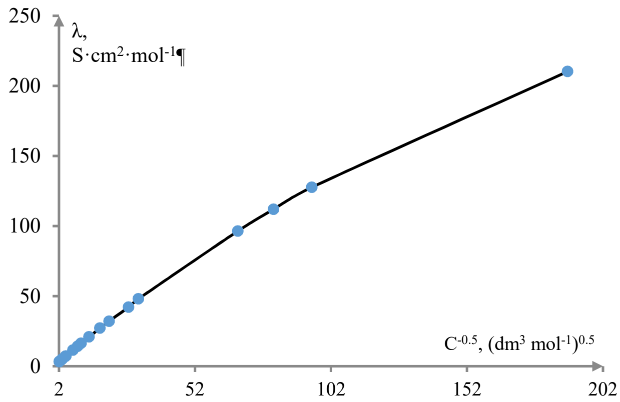

Fig. 3. Dependence of equivalent electrical conductivity on $1/C^{0.5}$ for the entire range of acetic acid concentrations

In addition to analyzing the Fisher information matrix and the normalized indicator, the dependence of objective function ($F(a,b) \cong F(K_a, \lambda_0)$) was constructed (Fig. 4).

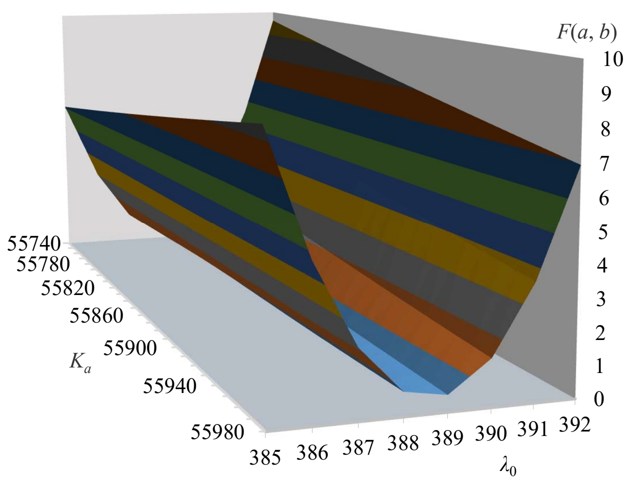

Fig. 4. Dependence of objective function on the values of constants of ion association and equivalent electrical conductivity

Another indicator of the presence of non-identifiable model parameters is the form of the average error ellipse (Fig. 5).

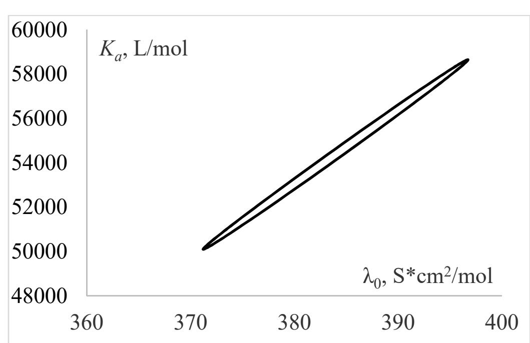

Fig. 5. Average confidence ellipse of the conductometric model

Our results based on determining the non-identification of parameters for the studied mathematical model of the electrical conductivity of aqueous solutions of acetic acid in conductometric models make it possible to analyze reliability of the model parameters.

6. Discussion of results based on the study on determining the non-identification of parameters for the mathematical model of electrical conductivity

As a result of data processing (Table 2), the following results were obtained: $\lambda_0 = 388.3 \pm 11.5$ S*cm^2*mol^{-1}, $K_a = 55{,}844.8 \pm 3{,}910$ L/mol. An additional check of the use of different methods for calculating unknown values of the coefficients (λ_0, K_a) in the case of practical non-identification of the parameters was also carried out.

Comparison of the results from calculating values of the λ_0, K_a coefficients by the Gauss-Newton method [17] and using the Excel Solver add-in shows that both methods find one point on the surface of the valley of the objective function. This is explained by the fact that the curvature of the surface of the valley of the objective function in the minimum region allows the minimum point to be determined by different methods.

The determinant of the Fisher information matrix is close to zero ($5.5 \cdot 10^{-8}$), and the normalized index is 0.988 (Fig. 1).

Thus, our results indicate the existence of practical non-identification of parameters, which is quite close to structural non-identification (Table 1). In addition, the coefficient of equation (18), as can be seen from the equation of the trend line (Fig. 2) is 1.64, which practically coincides with the value of ratio $\frac{\lambda_0}{\sqrt{K_a}}$.

The value of coefficient of determination (R^2) of the linear dependence, which is shown in Fig. 2, indicates that the experimental data are well described by equation (18).

As can be seen from Fig. 3, the dependence of equivalent electrical conductivity on $1/C^{0.5}$ for the entire interval of acetic acid concentrations, the linear dependence is more characteristic of the region of maximum acetic acid concentrations (Fig. 2).

Our results indicate that with increasing acetic acid concentration, the conditions for fulfilling the ratio $\sqrt{1+4K_a c} >> 1$ improve and equation (15) is transformed into equation (18). Such an analysis confirms the proposed model of the electrical conductivity of dilute solutions of weak electrolytes.

In addition to analysis of the Fisher information matrix and the normalized indicator, the dependence of objective function ($F(a,b) \cong F(K_a, \lambda_0)$) was constructed, which has the form of a ravine and also indicates the presence of practical non-identification of parameters (Fig. 4).

As can be seen from Fig. 5, the shape of the confidence ellipse is elongated and flattened, close to degenerate ("thin sausage"), which indicates the existence of an almost indefinite direction in the parameter space. This means that the experimental data do not make it possible to reliably estimate parameters separately but only their combination, which is a manifestation of the practical non-identification of the model parameters.

The use of the Fisher information matrix, the normalized index, and the form of the confidence ellipse make it possible to detect the existence of practical non-identification of parameters for the conductometric model of ionic association of weak electrolytes.

Determining reliable parameters for the mathematical model of electrical conductivity of electrolyte solutions contributes to the further advancement of the theory of solutions.

The results of our study will be useful to researchers in determining the optimal intervals of concentrations of electrolyte solutions during conductometric studies.

The limitations inherent in the model (neglect of electrostatic interactions between ions) in this study could be eliminated in further research by using modern models of the electrical conductivity of dilute electrolyte solutions [12].

The development of our study by applying modern equations of electrical conductivity of dilute electrolyte solutions may encounter difficulties on this path, which are associated with the presence of different mathematical models of electrical conductivity of dilute electrolyte solutions. The practical application of our results should take into account the differences in different models of the electrical conductivity of dilute electrolyte solutions [12–15].

7. Conclusions

1. The constructed Fisher information matrix for the mathematical model of electrical conductivity of electrolyte solutions makes it possible to determine the identifiability of the association constant and the limiting equivalent electrical conductivity. Determining the determinant of the matrix has made it possible to estimate the parameters necessary for further study of model predictions.

2. The results of our study on the nonlinear regression, which describes the equivalent electrical conductivity of diluted solutions, under the condition that the random error in determining experimental data obeys the Gaussian distribution, allowed us to obtain characteristics of the identifiability of parameters for the conductometric model. Analysis of the mathematical model of electrical conductivity of electrolyte solutions confirmed the possibility of emergence of non-identifiability of parameters for the mathematical model of electrical conductivity of weak electrolyte solutions, which makes it possible to solve the general problem of reliable estimation of model parameters from experimental data. The importance of reliable estimation of model parameters (λ_0 and K_a) is due to the fact that they are reference values.

3. The program, developed in the VBA language in the MS Excel environment for determining the reliability of parameter estimation, provided the possibility of simultaneous calculation of parameters for the mathematical model of electrical conductivity (λ_0 = 388.3 ± 11.5 S*cm^2/mol, K_a = 55,844.8 ± 3,910 L/mol) and the determinant of the Fisher information matrix ($5.5 \cdot 10^{-8}$) and the normalized index (0.988).

4. Calculation of the determinant of the Fisher information matrix and the normalized index showed that parameters for the electrical conductivity model correlate with each other, which leads to their practical non-identification, despite the formal certainty of the model. Dependences of the error function and the confidence ellipse clearly confirm the non-identification of parameters for the conductometric model. Thus, to confirm the reliability of values for conductometric parameters during the processing of experimental data on weak electrolytes in dilute solutions, an analysis of the Fisher information matrix is required. To reduce or eliminate the existence of practical non-identification of parameters for the conductometric model, it is necessary to conduct an experiment (if possible) in the region of small values of electrolyte concentrations, if condition $\sqrt{1+4K_a c} >> 1$. is not met. If it is impossible to change the conditions for conducting conductometric studies on dilute electrolyte solutions, it is necessary to use other methods for determining one of the parameters for a conductometric equation. For example, determining the λ_0 value of acetic acid by measurements of transfer numbers.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study, as well as the results reported in this paper.

Funding

The study was conducted without financial support.

Data availability

All data are available, either in numerical or graphical form, in the main text of the manuscript.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

Authors' contributions

Vitaly Chumak: Conceptualization, Software, Writing – original draft; **Maria Maksymiuk:** Methodology, Writing – review & editing; **Andrey Кopanytsia:** Formal analysis, Investigation.

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