A Method for Conductivity Measurements in Quantitative Analysis of Two-Component Solutions of Electrolytes

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Abstract—A method for computer processing of the results of conductometric measurements for a mixture of solutions of two electrolytes that differ in specific electrical conductivity is developed. This method makes it possible to determine the concentration of certain components taking into account the measurements of specific electrical conductivity and temperature. The method is based on approximations of theoretical dependences of electrical conductivity of electrolytes on concentrations according to the Robinson—Stokes and Kohlrausch equations and reference data on the dependence of electrical conductivity on temperature. In the region of concentrations of $C \leq 0.02$ M and temperatures of 15—25°C, the dependences are well approximated by algebraic polynomials up to the third order. The system of approximation functions describes a 3D region $\chi = f(C_1, C_2, T)$ inside of which there is a point that corresponds to the result of the measurements. This method is verified by the system of NaCl—NaOH and is applicable for the solutions of any concentrations by way of dilution of a sample to the required level. Two algorithms of processing of experimental data are studied. A simplified algorithm is based on the independence of molar electrical conductivity of the concentrations of the diluted solutions. The result of the processing of the experimental data has an overestimated systematic error from 1 to 5% in the mixtures with a high content of alkali. A more precise algorithm is based on the approximation of functions of dilution by the Kohlrausch equation. The systematic error of the specified algorithm is less than 0.05% in the mixtures with the highest electrical conductivity, and it is commensurable with the sensitivity of the conductometric measuring method.

Keywords: approximation, electrical conductivity, mixed electrolyte, concentration, algorithmic error

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INTRODUCTION

The method of electrical conductivity is extensively used in chemical analysis owing to the possibility of unmistakable determination of the point of equivalence during the titration of acids, alkalis, and certain salts in the reactions of acid-base interaction, deposition, complex formation, etc. Using this method makes it possible to authentically define the solubility product of partially soluble compounds, dissociation constant, and so on. The conductometric method is highly sensitive (the lower level of the concentrations under study is 10^{-4}–10^{-5} M) and accurate; hence, potentially it is rather promising.

The conductometric method can be easily used for direct analytic purposes using simple calibration curves. However, this is possible only in the case of simple single-component electrolytes. In addition, the application of the conductometric method for analytical aims becomes more complicated because of a fairly substantial temperature dependence of the electrical conductivity (1–2% per degree). Therefore, precise measurements of the electrical conductivity require temperature stabilization. The conventional chemical analysis, which imposes no severe requirements on temperature, in general turns out to be simpler and more preferable.

For the determinations not requiring especially high precision, the conductometric method of control over the concentrations is at present extensively used owing to simple and reliable instrumentation and, which is most important, owing to the possibility of automation of a continuous control [1]. This control is used in the food industry for the check of liquid media, for the detergent test of wastewater, for determination of concentrations of synthetic fertilizers in irrigation systems, for the quality evaluation of potable water, and for determination of concentration of salts in mineral, river, and seawater, in physiological salt solutions, in water after rinsing the sediments, etc. For these purposes, industry produces high frequency

(frequencies of the order of megahertz) titrators used to measure the electrical conductivity of the solutions by a contactless method.

For complex multicomponent solutions, the application of the conductometric method is restricted to some special cases, e.g., for the estimation of the degree of removal of ionic impurities from water. This method can be useful for the analytical control over the process of regeneration of ionites in the systems for ionite purification, where the initial compositions of the solutions are known.

STATEMENT OF THE PROBLEM

Earlier [2], we proposed the method of conductometric analysis of mixtures that was tested by example of the system sulfuric acid−nickel sulfate with arbitrary concentrations of components and constant temperature of 20°C. This method was based on a calibration function of dilution—the dependences of electrical conductivity on the concentration of the solution during a slow dilution of the sample. A certain arbitrary amount N of experimental functions of dilution with different ratio of the components were approximated using polynomials of degrees $M = 3-5$:

$$\chi = k_1 + k_2 c + k_3 c^2 + \dots k_M c^{M-1}. \quad (1)$$

The system of calibration functions in matrix form appears as follows:

$$\begin{bmatrix} k_{11} \dots k_{m1} \dots k_{M1} \\ \dots\dots\dots\dots\dots \\ k_{1n} \dots k_{mn} \dots k_{Mn} \\ \dots\dots\dots\dots\dots \\ k_{1N} \dots k_{mN} \dots k_{MN} \end{bmatrix} \begin{bmatrix} 1 \\ \dots\dots \\ C^m \\ \dots\dots \\ C^{M-1} \end{bmatrix} = \begin{bmatrix} \chi_1 \\ \dots\dots \\ \chi_N \end{bmatrix}. \quad (2)$$

In every column m of matrix $[k_{mn}]$, coefficients k_{mn} are continuous functions of a composition parameter, i.e., a mass fraction of one component of the mixture, $\alpha_1 = C_1/(C_1 + C_2)$. Therefore, in each column $m = 1, \dots, M$, a secondary approximation of coefficients $k_n = f(m = \text{const}, n)$ by polynomial (1) of degree K was performed. As a result, we obtained the matrix of coefficients $[d_{km}]$, which determined the values of coefficients k_{mn}:

$$\begin{bmatrix} d_{11} \dots d_{k1} \dots d_{K1} \\ \dots\dots\dots\dots\dots \\ d_{1m} \dots d_{km} \dots d_{Km} \\ \dots\dots\dots\dots\dots \\ d_{1M} \dots d_{kM} \dots d_{KM} \end{bmatrix} \begin{bmatrix} 1 \\ \dots\dots \\ \alpha^k \\ \dots\dots \\ \alpha^{K-1} \end{bmatrix} = \begin{bmatrix} k_1 \\ \dots\dots \\ k_M \end{bmatrix}. \quad (3)$$

The system of equations of dilution functions (1) with coefficients that were determined by matrices $[k_{mn}]$ and $[d_{km}]$ describes curved surface $\chi = f(C_1, C_2)$, to which all dilution functions belong, including the

experimental functions for the samples of arbitrary composition. The solution of the analytical problem, i.e., determination of concentrations of the mixture components, consists in plotting of a single experimental function of the sample dilution and a further search using the least-squares method for such a calculation function of dilution which would coincide with that of the experimental function at the points of measurements.

The method of the dilution functions showed a good result for solutions of H_2SO_4 + $NiSO_4$ with a total concentration of up to 0.5 M. The mean-square deviation in electrical conductivity was up to 2.3% at $M, K = 4$ and 0.7% at $M, K = 5$.

The method of dilution functions, however, can be used only at such a temperature which makes it possible to obtain the experimental functions of dilution. Transition to another temperature requires recurrence of all calibration operations, which considerably complicates the solution of the analytical problems. Moreover, in the processes of calibration and plotting of the dilution functions, certain measurement errors are inevitable which can be attributed to the accuracy of a measuring instrument.

Nevertheless, the application of approximation techniques of the concentration functions of electrical conductivity for analytical purposes can be efficient with the use of some other algorithm, which would make it possible to avoid or significantly diminish the two aforementioned restrictions.

THE ALGORITHM OF APPROXIMATION OF REFERENCE CONCENTRATION FUNCTIONS

This study describes a similar method of reference functions which excludes the indicated restrictions and which is more convenient in use. The algorithm of this method is based on two principles.

Firstly, for the approximation, we use reliable equations of concentration functions based on the known theoretical papers of Fuoss, Onsager, Robinson, and Stokes and confirmed with precision measurements, whose results are presented in the reference literature [3−5]. Reliable initial information makes the results of further general mathematical operations accurate and standardizing. Moreover, using this method makes the calibrating operations superfluous; i.e., this method is universal and it contains no random measurement errors in the algorithm of data processing itself.

Secondly, the algorithm provides for the use of diluted solutions in the range of concentrations up to 0.02 M. Under these conditions, the dilution functions and a number of other dependences are close to linear, and nonlinearities with a high precision are approximated by polynomials of degree 2 and 3. The restriction of the region of working concentrations

(a)   (b)
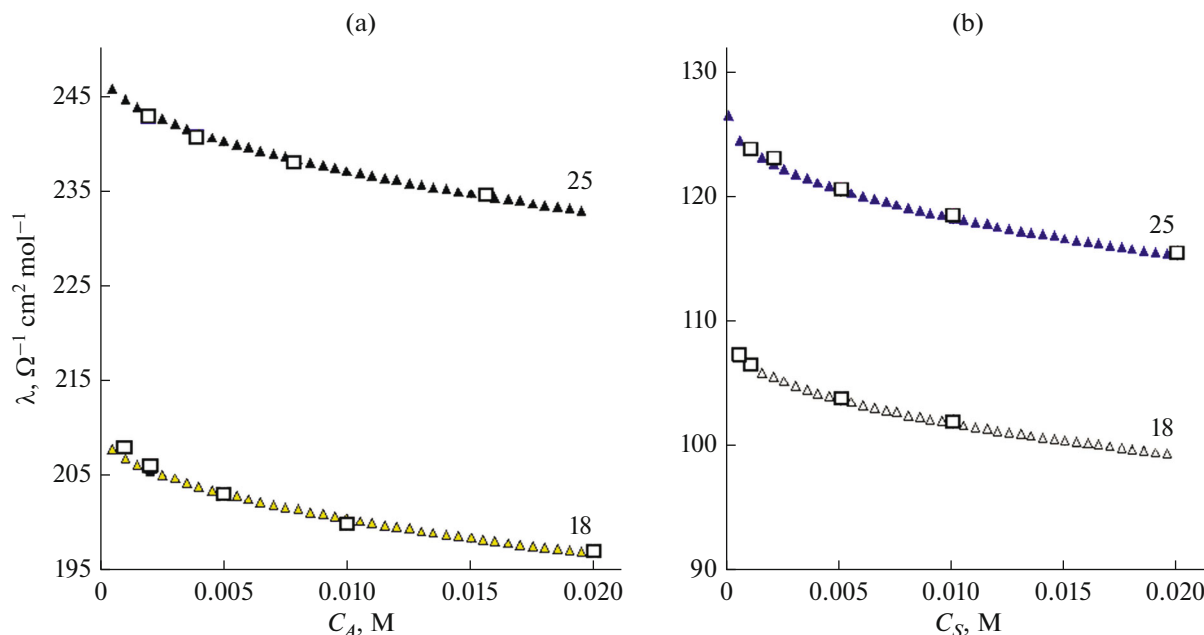
Fig. 1. Concentration dependences of molar electrical conductivity of (a) NaOH and (b) NaCl solutions at 18 and 25°C calculated using the Robinson−Stokes equation. Square points are experimental data [3−5].

presents no difficulties, since the sample can be diluted to the optimal level.

Unlike the method of the empirical dilution functions, in the proposed method of the reference functions, the algorithm additionally requires approximation of temperature dependences of electrical conductivity in accordance with the reference data. Hence, the solution region is a 3D region, in which the solution is only the point $\chi = f(C_S, C_A, T)$, but not a curved surface.

The basic dependences of the molar electric conductivity of single-component solutions both on the concentrations of NaOH (C_A) and NaCl (C_S) and at temperatures 18 and 25°C [3] are shown in Fig. 1. In the region of concentrations up to 0.02 M, they are approximated by polynomials of degree 3:

$$\lambda = k_3 C^3 + k_2 C^2 + k_1 C + k_0 \qquad (4)$$

with coefficients (see Table 1), where $d\lambda/dT$ is the temperature slope and R^2 is the coefficient of correlation of the approximation function.

The obtained table of coefficients is the ultimate result of a number of preliminary calculation operations. The concentration dependence of the molar electrical conductivity of the solutions was calculated using the Robinson−Stokes equation [3]:

$$\lambda = \lambda^0 - \frac{(B_1 \lambda^0 - B_2)\sqrt{C}}{1 + Ba\sqrt{C}}, \qquad (5)$$
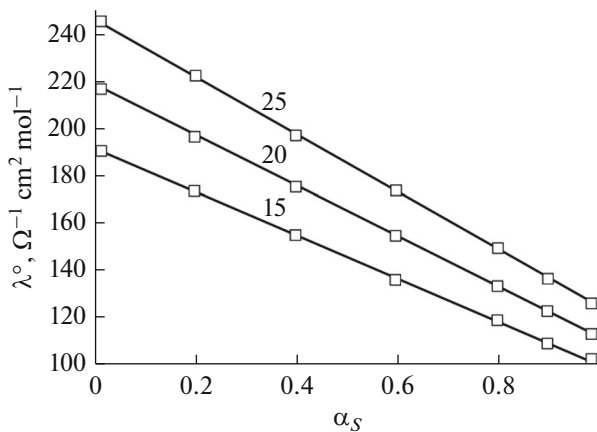
where λ^0 is the maximum electrical conductivity, Ω^{-1} cm^2 mol^{-1}, B_1 and B_2 are the coefficients of relaxation and electrophoretic terms in the theory of electrical conductivity of Fuoss−Onsager, a is the ion radius, and $Ba \sim 1$. All enumerated parameters except for product Ba, depend on temperature. The tempera-

Table 1.

		k_3	k_2	k_1	k_0	R^2
NaOH	25	-2×10^6	70356	−1436.3	246.02	0.9986
	18	-1×10^6	50814	−1126.3	207.74	0.9995
$d\lambda_A/dT$		−14285	2797.7	−44.286	5.4686	1
NaCl	25	-2×10^6	76383	−1281.1	125.24	0.9913
	18	-2×10^6	64504	−1081.9	107.78	0.9913
$d\lambda_S/dT$		0	1697	−28457	2.4943	1
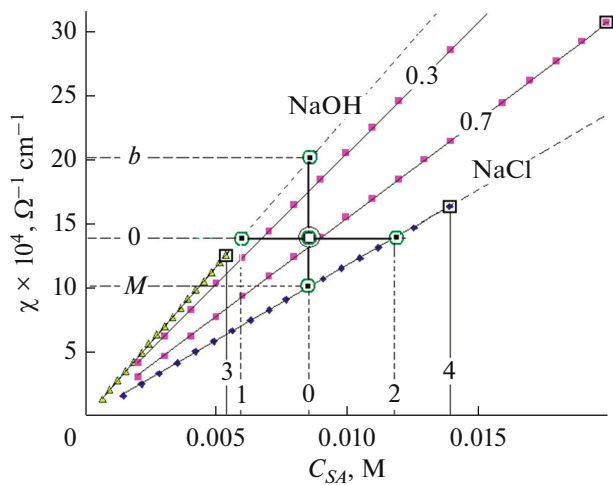
Fig. 2. Dilution functions $\chi(C_{SA})$ calculated according to approximation results for $T = 25°C$ and $C_{SA} = 0.02$ M. Numbers on graphs are the values of parameter α_S. Square points denote coordinates of states of NaCl and NaOH solutions forming a mixture (concentrations are denoted by lines 3 and 4) and mixtures. Lines b and M show boundaries of regions of values of specific electrical conductivity in which λ changes with the change in mixture composition with a constant total concentration C_{SA}.

Fig. 3. Approximated dependence of maximum molar electrical conductivity of binary mixture on parameter of composition α_S. Numbers on graph denote temperature, °C.

ture dependences were approximated according to the reference data [3]:

$$\lambda_A^0 = 4.6135T + 130.51, \qquad (6)$$

$$\lambda_S^0 = 2.3602T + 66.591, \qquad (7)$$

$$B_1 = 2 \times 10^{-6}T^2 + 3 \times 10^{-4}T + 0.2211, \qquad (8)$$

$$B_2 = 0.0076T^2 + 1.0432T + 29.819. \qquad (9)$$

For NaCl solutions, the reference experimental data correspond exactly to the calculation in accor-

dance with Eq. (5) at $Ba = 1$. However, for NaOH, the calculations using the Robinson−Stokes equation give somewhat overestimated λ values compared to the reference data [3]. In (5), parameter Ba was introduced as an empirical value, which allowed us to expand the effect of the Onsager limiting law ($Ba \rightarrow 0$) in many electrolytes up to concentrations of ∼0.05−0.1 M. For NaOH solutions, we used the value of $Ba = 0.5$ selected so that the compatibility of the calculation functions with the experimental data was maximal. Note that, in [6] during the calculations of conductivity for the natural water components in (5) in the region of concentrations up to 1 M and temperatures of 0−45°C, for NaCl, we used the value of the empirical parameter of $Ba = 1.7$; for NaOH, it was 0.2; and for HCl, it was 0.01. The calculation and experimental data accepted here as basic are listed in Fig. 1.

The calculated functions of specific electrical conductivity of NaOH and NaCl solution mixtures (the dilution lines) are shown in Fig. 2. The region of the total concentration $C_{SA} < 0.02$ M with an error of ∼1% can be accepted as linear. The slopes of dilution lines $d\chi/dC_{SA}$ depend on temperature and the ratio of components in the mixture, which is denoted by the value of $\alpha_S = C_S/C_{SA}$, where $C_{SA} = (C_S + C_A)$. For mixture $\alpha_S = 0.9$ at the point $C_{SA} = 0.2$ at 15°C, the relative deviation of the value of χ in a linear approximation is 0.011; however, in a quadratic approximation, it is 0.0018. For the mixtures with $\alpha_S \rightarrow 0$ and $T = 25°C$, i.e., in mixtures with the highest electrical conductivity, the deviation is less and is 0.005−0.007 in a linear form of $d\chi/dC_{SA}$.

The linearity of the dilution functions extrapolated to zero of the coordinate system allows us to calculate using a single point (χ, C_{SA}) the very sought function $\chi = f(C_{SA})$ and the molar electrical conductivity $\lambda = \chi/C_{SA}$. The value of λ depends only on temperature and composition of the solution, which is denoted by parameter α_S. An almost linear form of functions $\chi = f(C_{SA}, \alpha_S)$ results from the fact that, upon the total dilution to $C_{SA} \rightarrow 0$, the change in the molar electrical conductivity of the mixture is on the order of 1% for the concentration $C_{SA} = 0.02$ M (the working region of the method), whereas during the transition from $\alpha_S = 0$ to $\alpha_S = 1$ the value of λ becomes almost 2 times less (Fig. 3). The described peculiarities of the system of dilution functions $\chi(C_{SA}, \alpha_S)$ for the diluted binary mixture does not permit using a single point $\chi(C_{SA}, \alpha_S = const)$ to determine both parameters: C_{SA} and α_S. Figure 1 shows that one and the same value of χ corresponds to a wide region of compositions. Note that in method [2] this analytical problem was solved, to be exact, owing to a significant nonlinearity of the functions of dilution $\chi(C_{SA}, \alpha_S)$ in the region of high concentrations.

SIMPLIFIED SOLUTION AT A KNOWN TOTAL CONCENTRATION OF THE MIXTURE

The determination of the mixture composition at the known value of C_{SA} is performed using successive calculations in accordance with the approximation dependences. At first, we find the effective value of the molar electrical conductivity of the mixture using the experimental data as the slope of the linear dilution function $\lambda_{exp} = \chi_{exp}/C_S$. The value of α_S is determined from the following equation:

$$\alpha_S = k_2\lambda_{exp}^2 + k_1\lambda_{exp} + k_0. \tag{10}$$

Figure 3 shows the dependence $\alpha_S = f(T, \lambda_{exp})$ under the condition of maximal dilution $C_{SA} \to 0$ in the reciprocal form $\lambda_{exp} = f(T, \alpha_S)$. The coefficients of Eq. (10) depend on the composition of the mixture and temperature. They were defined in the following order. First, for a number of temperatures in the range of 15–20°C, the values of the slopes of the dilution functions $\lambda(\alpha_S, T) = \chi/C_{SA}$ were modeled using the initial linear approximations of the reference data. Then, for certain temperatures, we found the approximation functions $\alpha_S = f(\lambda_{exp})_{t\,=\,const}$ in the general form of a polynomial of the second degree (10) with coefficients (see Table 2).

In order to use Eq. (10) at any random temperature, the columns of coefficients k_2, k_1, and k_0 were approximated for the second time with respect to temperature using the following polynomial of second degree:

$$k_m^N = g_2^{(N)}T^2 + g_1^{(N)}T + g_0^{(N)}, \; N, m = 2, ..., 4, \tag{11}$$

with coefficients $g_m^{(N)}$, where $m = 2$–4:

	g_2	g_1	g_0
$N = 2$	−0.2354	12.884	−187.54
$N = 3$	0.0374	−2.0403	23.281
$N = 4$	−0.0018	0.1099	0.0001

From this final selection of coefficients $g_m^{(N)}$ using Eq. (11), we calculated coefficients k_2, k_1, and k_0 in Eq. (10), from which we also found the value of α_S. Now let us estimate the value of the error of the calculation algorithm. It is easy to do this by comparison of the coordinates of separate preset points on the plane C_S–C_A (Fig. 4) with the calculated coordinates according to the described algorithm. The sources of the error are the error of the linear approximation of the dilution functions $\chi(C_{SA})$ and the calculation operations, which used the secondary approximation functions. The preset initial concentrations and primary approximation functions $\chi(C_{SA})$ will be "exact" in such approaches.

For the analysis, we selected a model solution with a maximum total concentration of 0.02 M and the

Table 2.

	k_2	k_1	k_0
25°C	−12.633	−4.2635	1.6483
22°C	−17.752	−3.6640	1.5902
20°C	−24.293	−2.4474	1.4897
18°C	−31.848	−1.2469	1.4038
15°C	−47.229	1.0620	1.2598

states located on diagonals and two rings with radii $R = 0.0025$ M and $R = 0.0075$ M. The concentrations on the rings meet the requirement $(C_S)^2 + (C_A)^2 = R^2$ (Fig. 4).

The relative error was calculated as the mean deviation with respect to both coordinates of the calculated point, related to the maximum value of the total concentration C_{SA}. The analysis showed that the error of the described algorithm is fairly large. It does not depend on temperature and its value is 1–5% (Fig. 4). The algorithm underestimates the experimental value of the electrical conductivity with an increase in alkaline content in the mixture. The errors for each point are constants, and they can be calculated. This makes it possible using a separate additional operation to compensate for the error of each measurement. However, the necessity of the additional elimination of an error makes this simple algorithm inconvenient for the work. A more precise solution can be obtained at once, provided that the secondary procedures of approximation are eliminated, and we need to construct only one finite function

$$\alpha_S = d_2\chi^2 + d_1\chi + d_0. \tag{12}$$

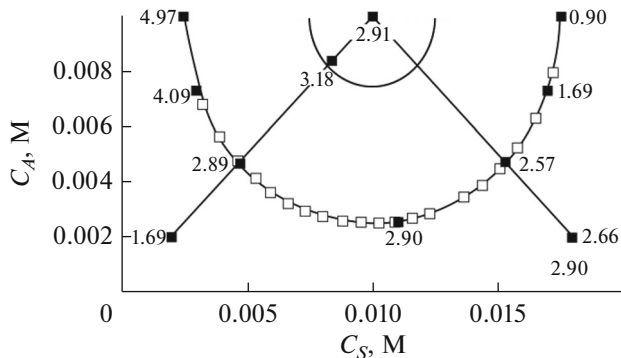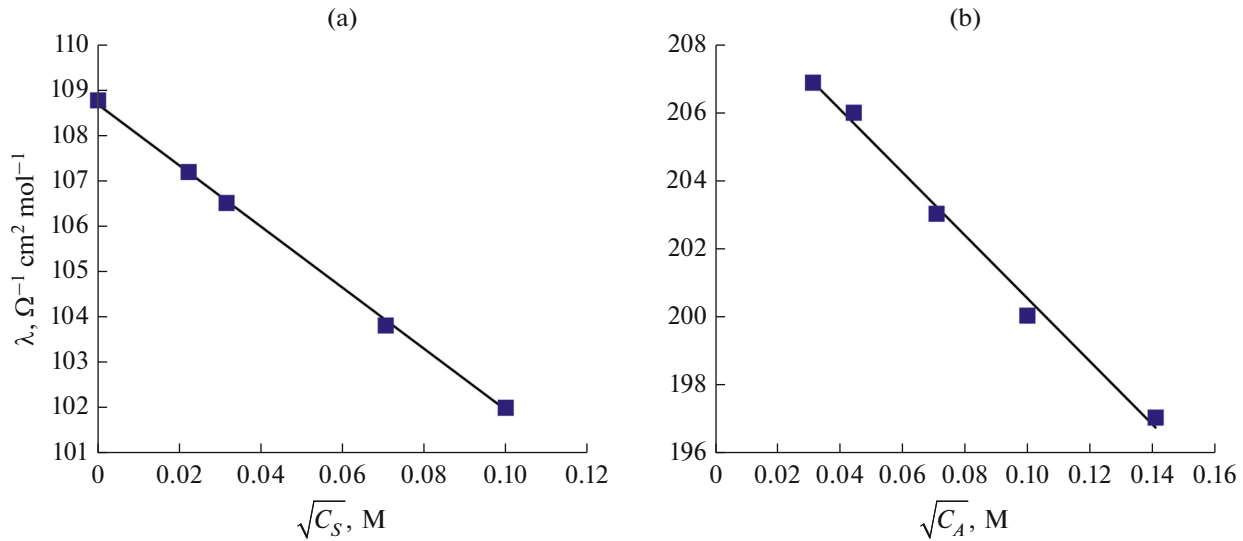The solution in this case consists of three coefficients of Eq. (12), and using the latter, we can further

Fig. 4. Distribution of errors of simplified algorithm of approximation on coordinate plane C_S–C_A, % (numbers on lines) for $T = 20$°C.

(a)

(b)

Fig. 5. Approximation using the Kohlrausch equation of concentration dependence of molar electrical conductivity of (a) NaCl and (b) NaOH solutions at $T = 18°C$.

calculate the ratio between the components. In this variant, the maximum relative error is up to 1%.

Note that the solution in the form of (12) realizes the problem inverse to the construction of the dilution functions (Fig. 1). The solution is based on using the same primary functions $\lambda = f(C, T)$ and $d\lambda/dT$ that are approximated according to the reference data. This inverse solution gives precise initial data of the direct problem. The absolute error of the calculation corresponds to the error of primary approximation functions. It results from the error of linear representation of the dilution functions $\lambda = f(C_S)$—the less the total concentration of the mixed solution, the less the error.

FULL SOLUTION

The full solution, i.e., determination of the concentrations of two components, can be obtained only on the basis of two measurements. One measurement of the specific electrical conductivity is performed for a sample diluted with water. And the other is for a sample diluted with a solution of one of the components, e.g., NaCl, with a known concentration C_S^R. The equations of the dilution functions for both variants have the form

$$\chi_{SA}^R = \lambda_A C_{SA}^R (1 - \alpha^R) + \lambda_S^R C_{SA}^R \alpha^R, \quad (13)$$

$$\chi_{SA}^W = \lambda_A C_{SA}^W (1 - \alpha^W) + \lambda_S^W C_{SA}^W \alpha^W, \quad (14)$$

where the upper indices W and R correspond to the type of diluent (water or NaCl solution), and the lower indices correspond to separate components or to their mixture, $C_{SA}^W = C_S^W + C_A$, $C_{SA}^R = C_S^W + C_S^R + C_A$.

Equations (13) and (14) can be rewritten in a more convenient form:

$$\chi_{SA}^R = C_{SA}^R \left[\lambda_A \left(1 - \alpha^R \right) + \lambda_S^R \alpha^R \right],$$
$$\chi_{SA}^W = C_{SA}^W \left[\lambda_A \left(1 - \alpha^W \right) + \lambda_S^W \alpha^W \right]. \quad (15)$$

In Eqs. (15), we can take into consideration the nonlinearity of the dilution functions, which is related to the dependence of the molar electrical conductivity on the concentration. This dependence is more convenient to approximate using a simple Kohlrausch equation (Fig. 5):

$$\lambda = \lambda^0 - k\sqrt{C}. \quad (16)$$

Using it, we can represent Eqs. (15) in the form

$$\chi_{SA}^R = \lambda_A C_A + (C_S^W + C_S^R)\lambda_S^R,$$
$$\lambda_S^R = \left[\lambda_S^0 - k_S \sqrt{C_S^W + C_S^R} \right];$$
$$\chi_{SA}^W = \lambda_A C_A + \lambda_S^W C_S^W, \quad (17)$$
$$\lambda_A = \left[\lambda_A^0 - k_A \sqrt{C_A} \right].$$

Since concentration of NaOH C_A is the same upon dilution with water or NaCl solution, we can remove the first term from the two equations (17) and obtain one nonlinear algebraic equation with one unknown parameter, which is the NaCl concentration in the sample diluted with water, C_S^W:

$$(\chi_{SA}^R - \chi_{SA}^W) = (C_S^W + C_S^R)\left[\lambda_S^0 - k_S \sqrt{C_S^W + C_S^R} \right]$$
$$- C_S^W \left[\lambda_S^0 - k_S \sqrt{C_S^W} \right], \quad (18)$$

where λ_S^0 the maximum molar electrical conductivity of NaCl solution, which depends on temperature; and k_S is a constant, which depends on temperature. Both parameters were calculated by approximation of the data using the Kohlrausch equation obtained according to the Robinson–Stokes equation. The correlation coefficients of the approximation functions for solutions of NaCl and NaOH are $R^2 = 0.998$ and 0.992, respectively. The solution is easy to obtain by a numerical method with respect to the difference of the specific conductivities of the two samples. One has to find such a concentration of NaCl in the sample diluted with water at which the difference $\chi_{SA}^R - \chi_{SA}^W$ calculated using (18) is equal to that of the measured one.

Further on, we can calculate successively the share of the specific electrical conductivity of NaCl and NaOH in the sample diluted with water:

$$\chi_S^W = C_S^W \left[\lambda_S^0 - k_S \sqrt{C_S^W} \right], \quad \chi_A = \chi_{SA}^W - \chi_S^W. \quad (19)$$

The unknown value of NaOH concentration can be found from the solution of the following nonlinear equation:

$$\chi_A = C_A \left[\lambda_F^0 - k_F \sqrt{C_A} \right], \quad (20)$$

and after that, all the remaining parameters of the sample C_{SA}, α_S, and α_A are calculated.

The solution obtained owing to consideration of the nonlinearity of the dilution functions $\chi = f(C)$ contains a smaller error of the algorithm than that in the previous variant. The calculations for 20°C and the mixture with a total concentration of 0.01 M give values of the algorithmic error of the order of 0.01% for the boundary compositions, which are close to pure solutions of separate components, $0.9 < \alpha_S < 0.1$. With commensurable concentrations of both components, the error in determination of the total concentration decreases by an order of magnitude. The deviation of the values α_S defined from these preset ones is maximal at the excess of alkali (at $\alpha_S = 0.1$, $\Delta\alpha \sim 0.003$), and it decreases by an order of magnitude at $\alpha_S > 0.9$.

VERIFIED SOLUTION OF THE PROBLEM WITH A KNOWN TOTAL CONCENTRATION

To analyze the dynamics of the change in the mixture composition at a known and constant value of total concentration C_{SA}^W, we can obtain a more accurate solution than using Eq. (12). For this purpose, we use the aforementioned algorithm, which takes into account the nonlinearity of the dilution functions by way of their approximation using the Kohlrausch equation. In this version, we can solve only one nonlinear equation with the unknown parameter α_S:

$$\begin{aligned} \chi_{SA}^W &= C_{SA}^W \alpha_S \left[\lambda_S^0 - k_S \sqrt{C_{SA}^W \alpha_S} \right] \\ &+ C_{SA}^W (1 - \alpha_S) \left[\lambda_A^0 - k_A \sqrt{C_{SA}^W (1 - \alpha_S)} \right]. \end{aligned} \quad (21)$$

The error in determining parameter α_S is the same as in the solution of the full problem.

CONCLUSIONS

The specific electrical conductivities of salts, acids, and alkalis differ greatly owing to the anomalous mechanism of H^+ and OH^- ion transfer in aqueous solutions. This makes it possible to use the method of electrical conductivity to determine concentrations in mixed solutions of simple salts with acids or alkalis. The method is developed for the mixed solutions of NaCl and NaOH. These solutions can form, e.g., in technological processes of electrolysis of sodium chloride or in the process of regeneration of ionite resin [7]. In the latter, the total concentration of the mixture remains constant and only the ratio between the components changes. Theoretical (calculated by the Robinson–Stokes equations) and reference experimental data were used for separate components in the range of concentrations up to 0.02 M and temperatures of 15–25°C. The dependences of molar electrical conductivity on concentrations and temperature were approximated. As approximation functions, we used polynomials of the first to third degrees and the Kohlrausch equation. The ultimate result of transformations of primary approximation functions was the dependence of the NaCl fraction in the mixed solution on its specific electrical conductivity at the preset values of total concentration and temperature, $\alpha_S = f(T, C_{SA})$. In accordance with this dependence and experimental value of the specific electrical conductivity, the composition of the mixed solution is determined. The simplified algorithms are based on the linear approximation of the dilution functions $\chi = f(C_{SA})$, i.e., independence of the molar electrical conductivity λ from concentration is assumed. They give an overestimated systematic error up to 5% for the compositions enriched in alkali. The error can be calculated; however, the additional operations for its elimination make the algorithm inconvenient for use. If we take into account the nonlinearity of the dilution functions and approximate them using the simple Kohlrausch equation, the absolute error of the algorithm will decrease to a level that is commensurable with the sensitivity of the conductometric method. Therefore, there is no reason to approximate the dilution functions using

algebraic equations of the second or higher degrees, more precise than the Kohlrausch equation.

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