ON TREATMENT OF CONDUCTOMETRIC DATA

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A procedure for treatment of phoregrams, based on published experimental data, is developed. The resulting ionization constants and limiting molar conductivities of aqueous solutions of organic acids differ from published values.

Keywords: conductometry, interpretation of experimental data, ionization constant.

Conductometry is the oldest technique for research on electrolyte solutions, but it still holds importance [1, 2]. This technique is widely used for measuring the dissociation constants of weak acids and ionophores. A characteristic feature of this technique is that does not require the use of buffer solutions.

Certain disadvantages of conductometry stem from its advantages. This technique provides less reliable results for very weak electrolyte solutions and is hardly suitable for poorly soluble electrolytes.

Experimental data are interpreted in terms of models based, to a greater or lesser extent, on the Debye−Hückel−Onsager theory. As a result, the theoretical concentration dependences of conductance (phoregrams) for electrolyte solutions include the dielectric constants and viscosities of solvents, ion charges, as well as a series of unknown parameters [1].

Phoregrams are usually treated in two stages. The first involves determination of the limiting molar conductivity by extrapolation to infinite dilution. The Lee−Wheaton [3], Quint−Viallard [4], Fuoss–Kraus [5], and other equations [2], which are most commonly used in this case, make it possible to account, to a greater or lesser extent, for the contributions of the electrophoretic and relaxation effects into the theoretical concentration dependence of the conductivity of electrolyte solutions. Then, the known Λ_0 value is used to obtain the dependence of the ionization degree of the compound on its concentration in the solution, from which the protolytic equilibrium constant K_a is found. Therewith, as mentioned in the review [1], most of the equations give close Λ_0 values, whereas the calculated K_a values coincide at best within an order of magnitude. This is quite natural, since in force of the nature of the

theoretical dependences used for treatment of phoregrams, even minor variations in the molar conductivities strongly affect the protolytic equilibrium constants. As a result, the acidity constants determined by conductometry by different authors sometimes differ from each other more than an order of magnitude. Therewith, as will be shown below, even the same authors may obtain quite different K_a values.

In the present work we set ourselves the task to facilitate the procedure of treatment of phoregrams and simultaneously obtain data better fitting the experimental molar conductivities Λ of weak electrolyte solutions. In the simplest case, the dependence of the ionization degree α of a compound on its concentration C in the solution is described in terms of the Ostwald dilution law:

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

A linear dependence of the ionization degree of an electrolyte on the molar conductivity of its solution was established by Arrhenius

$$\alpha = \frac{\Lambda}{\Lambda_0}. \tag{2}$$

Substituting (1) into (2) we obtain an equation relating the conductivity of a solution to its concentration and two values to be determined, i.e. Λ_0 and K_a:

$$\Lambda = \frac{\Lambda_0 K_a}{2C} \left(\sqrt{1 + \frac{4C}{K_a}} - 1 \right). \tag{3}$$

It is easy to check that in the infinite dilution limit this equation turns to be an identity. If Ostwald dilution law for weak electrolytes holds fairly well at concentrations traditionally used in conductometry, it is questionable whether this will be true of Eq. (2). Its fulfillment at $C \to 0$ implies complete ionization of all compounds, which is valid only for strong electrolytes. Apparently, Eq. (2) is better to be rewritten in a different form:

$$\frac{\alpha}{\alpha_0} = \frac{\Lambda}{\Lambda_0}, \tag{4}$$

This equation converts into an identity at infinite dilution, if α_0 is the ionization degree in this limit. To find this value, we can make use of an equation from the monograph [6]

$$C = \frac{K_a(1-\alpha)}{\alpha^2} - \frac{K_s}{K_a(1-\alpha)},$$ (5)

where K_S is the solvent autoprotolysis constant.

From this it follows that at infinite dilution of the solution the ionization degree of the electrolyte tends to a limiting value:

$$\alpha_0 = \frac{K_a}{K_a + \sqrt{K_s}}.$$ (6)

In view of Eqs. (4) and (6), Eq. (3) can be slightly changed:

$$\Lambda = \Lambda_0 \frac{K_a + \sqrt{K_s}}{2C}\left(\sqrt{1 + \frac{4C}{K_a}} - 1\right).$$ (7)

Strictly speaking, Eq. (7) already does not convert into an identity at $C \to 0$. However, this is not a problem, since the treatment of Λ values is performed at concentrations higher than 10^{-6} M. This inconsistency can be avoided by substituting the α value calculated by Eq. (5) into Eq. (7). However, this is not necessary, because at the above concentrations Eqs. (1) and (5) are almost coincident. On the other hand, at any concentrations of aqueous solutions of acids with $pK_a > 5$, Eqs. (2) and (4) will differ considerably from each other. Therefore, Eq. (7) as more correct is more expedient to use in further calculations than Eq. (3). Naturally, if the solvent autopropotysis constant can be neglected, there is no longer difference between Eqs. (3) and (7).

The procedure of treatment of phoregrams by Eq. (7) is as follows. Let conductometric measurements gave N pairs of experimental values (Λ_i and C_i). The molar concentrations of solutions are determined with a sufficiently high accuracy. Obviously, the errors in the measured conductivities of solutions will be larger for instrumental reasons. Thus, it is desirable that the gap between an experimental Λ_i value and the Λ_i value calculated with the corresponding C_i value calculated by Eq. (7) is as small as possible

$$\Delta\Lambda_i = \Lambda_i - \Lambda_0 \frac{K_a + \sqrt{K_S}}{2C_i}\left(\sqrt{1 + \frac{4C_i}{K_a}} - 1\right) \tag{8}$$

for any *i*. In statistics this task is traditionally solved by minimization of the sum of squared $\Delta\Lambda_i$ over all *i* values. Obviously, this sum of squares

$$\Xi(\Lambda_0, K_a) = \sum_i^N \Delta\Lambda_i^2 \tag{9}$$

is explicitly dependent only on two variables (Λ_0 and K_a), provided the solvent autoprotolysis constant K_S is determined independently. Consequently, we have to find such Λ_0 and K_a values ay which the function $\Xi(\Lambda_0, K_a)$ calculated by Eq. (9) will have a global minimum. Let us assume that this minimum does exist. Then there are two conditions that must be met in this point:

$$\frac{\partial\Xi(\Lambda_0, K_a)}{\partial\Lambda_0} = \frac{\partial\Xi(\Lambda_0, K_a)}{\partial K_a} = 0. \tag{10}$$

Thus, the target Λ_0 and K_a values can be found by solving a system of two equations following from (10). In an explicit form, this system has the following form:

$$\sum_i^N \frac{\Delta\Lambda_i}{C_i}\left(\sqrt{1 + \frac{4C_i}{K_a}}\right) = 0 \tag{11}$$

$$\sum_i^N \frac{\Delta\Lambda_i}{\sqrt{K_a + 4C_i}} = 0. \tag{12}$$

Theoretically, the system of Eqs. (11) and (12) can have several solutions, since conditions (10) are valid not only for the global, but also for local minima, as well as saddle and other special points. However, in practice the target Λ_0 and K_a values determined by conductometry with a greater or lesser accuracy are already reported, and, therefore, numerical solution of the system of Eqs. (11) and (12) was not too hard. The results of our calculations with the experimental values published in [7−29] in comparison with the Λ_0 and K_a values found in the mentioned works are presented in Table 1. Table 1 also contains the dispersions of the calculated Λ_0 и K_a (denoted by $\sigma\Lambda_0$ and σK_a, respectively). Here and hereinafter, Λ_0 and K_a denote the values,

obtained by solving the system of Eqs. (11) and (12). By setting Eq. (8) equal to zero, we obtained N values of the limiting molar conductivity of solutions of the corresponding concentration C_i:

$$\Lambda_0(C_i) = \frac{2\Lambda_i C_i}{K_a + \sqrt{K_s}} \left(\sqrt{1 + \frac{4C_i}{K_a}} - 1 \right)^{-1}.$$ (13)

The dispersion of the resulting values was calculated by the following equation:

$$\sigma\Lambda_0 = \sqrt{\frac{\sum\limits_{i}^{N}(\Lambda_0 - \Lambda_0(C_i))^2}{N-2}}.$$ (14)

The dispersion of the ionization constants calculated by the system of Eqs. (11) and (12) was found in a similar way. Equation (8) was set equal to zero, and the calculated Λ_0 value was substituted in this equation. Thus we obtained N values of the K_a (C_i) constant, each corresponding to one C_i value. The resulting $K_a(C_i)$ series was treated by an expression analogous to (14), using a specific K_a value.

For consistency in calculations, the experimental values obtained at normal pressure and 298.15 K for aqueous solutions were used. The water autoprotolysis constant K_S under these conditions was taken to be equal to $1.008 \cdot 10^{-14}$ mol^2/l^2. The upper concentration limit was set at 0.1 M, based on the reasoning of Izmailov in his monograph [30]. At this concentration the activity coefficients of organic acid ions in aqueous solutions are close to 1, which is necessary for fulfillment of the Ostwald law, Eq. (1). In the overwhelming majority of works [7−9, 11, 14−25, 27−29], measurements were performed just in such conditions. Exclusions are the works of Saxton and Darken [10] (23 of 40 measurements for formic acid and 16 of 37 measurements for butyric acid), Boncina et al. [12] (2 of 17 measurements for cyclohexylsulfamic), MacInnes and Shedlovsky [13] (4 of 18 measurements for acetic acid), and Mehl and Schmidt [26] (2 of 8 measurements for glutamic acid), where the measurements were performed at the concentrations 0.1 M and higher, and these values were omitted from the calculations. In the case of dibasic acids, the second dissociation step was neglected. In the tables and figures, the following units of measure were used: $S \cdot sm^2/mol$ for Λ and M for K_a

Discussion

The Λ_0 and K_a constants calculated in the original works almost all fail to fit in the ranges of the mean values of these constants plus dispersions, calculated in the present work. An exception are the values calculated with data in [14] for acetic, cyanoacetic, and 3,5-dinitrobenzoic acids, with data in [15] for *o*-phenylbenzoic acid, with data in [23] for *p*-bromophenylacetic acid, and with data in [25] for L-glutamic acid.

The Λ_0 values calculated with data in [9, 22, 23, 27-29] proved to be lower than 349.85 S·cm^2/mol (which corresponds to the limiting molar conductivity of proton), which is unacceptable. Here either our procedure is unsuitable for compounds studied in those works or the measurements were performed in different conditions.

Table 1.

The overestimated Λ_0 values obtained for glutaric, succinic, pimelic, and suberic acids by the experimental data in [21] can be explained by the sensitivity of the procedure to double-charged ions. Apparently, our procedure can provide correct constants for dibasic acids only at concentrations higher than 10^{-3} M, where there are very little double-charged ions. Probably, the proposed procedure can be adapted for calculation of constants for dibasic acids by changing Eqs. (1) and (4) to include the second dissociation constants and limiting conductivities of double-charged ions. In this case, a system of four nonlinear equations will have to be solved.

The essential divergence from published data of the Λ_0 and K_a values obtained by treatment of data from [27] can be explained by the fact that the phoregrams contained as little as 4−6 measurements performed in two different cells and with different constants. Such data are unadvisable to combine in a single dataset, but it is even less correct to treat phoregrams by 2−3 points. The overestimated Λ_0 values obtained on treatment of data in [25] and [26] для for glutamic acid in are probably explained by the basic properties of this acid, which was not accounted for by the procedure.

The concentrations dependences $K_a(C_i)$ и Λ_0 (Ci) for bezoic and phenylacetic acid solutions are shown in Fig. 1. The $K_a(C_i)$ and Λ_0 (C_i) plots are quite similar up to the coincident slopes. In most cases, like in Fig. 1a, preliminary analysis revealed a lack of explicit concentration dependence of the K_a values. However, more careful statistical analysis is required to state that the calculated K_a and Λ_0 values are invariant. If the distribution of $\Delta\Lambda_i$ with respect to zero was close to a normal distribution, we could state that the K_a and Λ_0 values in Eq. (7) are true values. However, even with 27 pairs of Λ_i and C_i values, and this is the maximum number of data in the published works in hand, we still have insufficient evidence for a proper analysis.

Fig. 1.

Nevertheless, analysis of the concentration dependences of the deviations of calculation from experiment ($\Delta\Lambda_i$) revealed some interesting facts. Sometimes (Fig. 2a) the $\Delta\Lambda_i$ values for one−two measurements strongly (several times) differed from all other values. Exclusion of such outliers from the calculation did not improve considerably the newly calculated K_a and Λ_0 values, implying experimental errors in the input data for the outlying values.

Fig. 2.

Some authors included into a single dataset the results of series of experiments performed under two different conditions. Such a combination of the results obtained at different concentrations and at crossed values is clearly illustrated in Fig. 2b.

Noteworthy is the fact that the dispersions in the calculated Λ_0 values (in relative units) is smaller by an order of magnitude compared with the respective dispersions in K_a. Therefore, even though the calculated K_a values generally do not show an explicit concentration dependence within one experimental series, the question of whether they correspond to thermodynamic constants is the subject of discussion.

Comparison of Approximation Results

The most important result of a theory is its fit to experimental results. The authors of [11, 12, 16-18, 24, 25, 28, 29] reported the standard dispersions of calculated Λ values with respect to experimental values. In terms of the present work, the corresponding values were calculated by the formula:

$$\sigma\Lambda = \sqrt{\frac{\Xi(\Lambda_0, K_a)}{N-2}}. \qquad (15)$$

Papadopoulos and Avranas [17] gave the dispersions of calculated Λ values in relative units. In the present work these values were calculated by the formula:

$$\sigma\Lambda = 100\%\sqrt{\frac{1}{N-2}\cdot\sum_{i}^{N}\left(\frac{\Delta\Lambda_i}{\Lambda_i}\right)^2}. \qquad (16)$$

Table 2.

The results of comparison are shown in Table 2. The units of measure of $\sigma\Lambda$ are $S\cdot sm^2/mol$, except for the values specified in percent. The dash means that $\sigma\Lambda$ is not reported explicitly.

This is only 4 of 17 cases that the dispersions calculated in original works are lower than those obtained in the present work. This is the work of Boncina et al. [11] on formic acid, which is the only work where molal rather than molar concentrations were used. Furthermore, in [17] the results of calculations for three of the four treated phoregrams better fitted the experimental data, as judged from a comparison of relative dispersions.

However, in [17] the authors give a formula for absolute dispersion, while the calculation results refer to relative dispersions without any explanations and formulas. Possibly, relative dispersions are not quite correct to compare in this case. In any case, the least-squares relative calculation error within 0.08% points to a good fit of the calculated values to experiment.

Choosing a 0.1 % standard dispersion of the calculated Λ values with respect to experimental ones as a reliability criterion for the calculated Λ_0 and K_a constants values, we can mention 10 of all the considered acids, which meet this criterion (Table 3).

Table 3.

An undeniable advantage of the application of Eq. (7) for treatment of phoregrams is its mathematical simplicity and the fact that it operates by as little as three constants: limiting molar conductivity of an electrolyte solution Λ_0, protolytic equilibrium constant K_a, and solvent autoprotolysis constant K_S. Nevertheless, it is worth noting that Eq. (7) more correctly describes the results of conductometric measurements in the vast majority of the considered cases. To solve the problem of evidently overestimated Λ_0 values (above 400 S·sm²/mol) for monobasic acids in the proposed model, we have to take into account the presence of carbonic acid whose equilibrium concentration in aqueous solutions reaches 10^{-5} M [6]. To solve the problem of evidently underestimated Λ_0 values (below 350 S·sm²/mol), it is desirable either to perform measurements at low concentrations or to treat experimental data presented, instead of the molar conductivities, as the conductivity of solutions ($\Lambda \cdot C$), which are direct readings of a conductometer.

In whole, smaller dispersion values can be obtained for weaker electrolytes and for less concentrated solutions. This fact suggests that the proposed procedure will allow conductometry to be applied for solutions of very weak acids and bases.

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Table 1. *Number of treated phoregram points N and calculated and published Λ_0 and K_a values for certain organic acids.*

Acid	Ref.	N	Λ_0	K_a	Calculated in the present work			
					Λ_0	$\sigma\Lambda_0$	K_a	σK_a
Benzoic	[7]	27	382,10	$6,312\cdot10^{-5}$	374,41	0,51	$6,739\cdot10^{-5}$	$0,020\cdot10^{-5}$
	[8]	10	381,72	$6,3314\cdot10^{-5}$	371,72	0,20	$6,8287\cdot10^{-5}$	$0,0094\cdot10^{-5}$
	[9]	16	383,13	$6,297\cdot10^{-5}$	349	11	$8,32\cdot10^{-5}$	$0,60\cdot10^{-5}$
Formic	[10]	17	404,50	$1,825\cdot10^{-4}$	369,1	2,1	$2,370\cdot10^{-4}$	$0,028\cdot10^{-4}$
	[11]	11	404,08	$1,46\cdot10^{-4}$	394,3	4,9	$1,588\cdot10^{-4}$	$0,045\cdot10^{-5}$
Cyclohexyl-sulfamic	[12]	15	$378,31-380,15^{a}$	$1,55\cdot10^{-2}-1,67\cdot10^{-2\ a}$	372,64	0,83	$1,913\cdot10^{-2}$	$0,085\cdot10^{-2}$
Acetic	[13]	14	390,59	$1,753\cdot10^{-5}$	384,53	1,99	$1,816\cdot10^{-5}$	$0,019\cdot10^{-5}$
	[14]	6	387,55	$1,765\cdot10^{-5}$	387,90	0,22	$1,8266\cdot10^{-5}$	$0,0021\cdot10^{-5}$
Cyanoacetic	[10]	21	391,71	$3,360\cdot10^{-3}$	383,3	1,6	$3,867\cdot10^{-3}$	$0,076\cdot10^{-3}$
	[14]	8	380,54	$3,501\cdot10^{-3}$	383,7	3,5	$3,876\cdot10^{-3}$	$0,095\cdot10^{-3}$
o-Nitrobenzoic	[14]	6	373,1	$5,995\cdot10^{-3}$	375,3	1,8	$6,74\cdot10^{-3}$	$0,12\cdot10^{-3}$
	[15]		378,5	$6,71\cdot10^{-3}$	379,20	0,15	$6,529\cdot10^{-3}$	$0,017\cdot10^{-3}$
o-Chlorobenzoic	[14]	5	377,2	$1,215\cdot10^{-3}$	379,31	0,26	$1,2961\cdot10^{-3}$	$0,0025\cdot10^{-3}$
3,5-Dinitro-benzoic	[14]	4	375,3	$1,505\cdot10^{-3}$	377,9	3,3	$1,541\cdot10^{-3}$	$0,043\cdot10^{-3}$
o-Mehtylbenzoic	[15]	5	381,2	$1,23\cdot10^{-4}$	376,9	1,9	$1,306\cdot10^{-4}$	$0,015\cdot10^{-4}$
o-Phenylbenzoic	[15]	5	373,2	$3,47\cdot10^{-4}$	373,1	1,4	$3,472\cdot10^{-4}$	$0,054\cdot10^{-4}$
o-Methoxy-benzoic	[15]	6	380,0	$8,06\cdot10^{-5}$	383,64	0,98	$8,050\cdot10^{-5}$	$0,046\cdot10^{-5}$
o-Phenoxy-benzoic	[15]	5	373,0	$2,97\cdot10^{-4}$	371,07	0,53	$3,078\cdot10^{-4}$	$0,016\cdot10^{-4}$
m-Phenoxy-benzoic	[15]	5	373,3	$1,12\cdot10^{-4}$	389,2	1,1	$9,885\cdot10^{-5}$	$0,087\cdot10^{-5}$
p- Phenoxy-benzoic	[15]	5	374,5	$3,00\cdot10^{-5}$	371,7	1,8	$3,061\cdot10^{-5}$	$0,042\cdot10^{-5}$
o-Nitrophenyl-acetic	[15]	6	378,6	$9,90\cdot10^{-5}$	389,22	0,83	$9,566\cdot10^{-5}$	$0,046\cdot10^{-5}$
o-Chlorocinnamic	[15]	6	377,8	$5,83\cdot10^{-5}$	366,6	1,6	$6,575\cdot10^{-5}$	$0,093\cdot10^{-5}$
n- Chlorocinna-mic	[15]	4	378,1	$3,86\cdot10^{-5}$	353,3	1,9	$4,764\cdot10^{-5}$	$0,084\cdot10^{-5}$
DL-Pyroglutamic	[16]	6	383,75	$4,83\cdot10^{-4}$	358,5	1,2	$6,298\cdot10^{-4}$	$0,064\cdot10^{-4}$
Salicylic	[17]	8	380,20	$1,020\cdot10^{-3}$	378,19	0,16	$1,0517\cdot10^{-3}$	$0,0031\cdot10^{-3}$
2,4-Dihydroxy-benzoic	[17]	7	374,80	$4,83\cdot10^{-4}$	371,69	0,29	$5,068\cdot10^{-4}$	$0,016\cdot10^{-4}$
2,5-Dihydroxy-benzoic	[17]	7	381,36	$1,086\cdot10^{-3}$	378,88	0,29	$1,1314\cdot10^{-3}$	$0,0057\cdot10^{-3}$
2,6-Dihydroxy-benzoic	[17]	7	385,44	$5,10\cdot10^{-2}$	383,16	0,12	$4,025\cdot10^{-2}$	$0,083\cdot10^{-2}$
Glutaric	[18]	7	378,45	$4,53\cdot10^{-5}$	446,2	4,1	$3,371\cdot10^{-5}$	$0,066\cdot10^{-5}$
	[19][6]	5	-	-	398,08	0,77	$4,201\cdot10^{-5}$	$0,016\cdot10^{-5}$
	[20][6]	7	-	-	385,98	0,99	$4,482\cdot10^{-5}$	$0,024\cdot10^{-5}$
	[21]	14	378,0	$4,535\cdot10^{-5}$	481,3	2,0	$2,856\cdot10^{-5}$	$0,027\cdot10^{-5}$
Malonic	[21][в]	8	383,5	$1,397\cdot10^{-3}$	393,2	2,4	$1,415\cdot10^{-3}$	$0,030\cdot10^{-3}$
		8			387,2	1,3	$1,462\cdot10^{-3}$	$0,018\cdot10^{-3}$
		6			389,2	1,4	$1,472\cdot10^{-3}$	$0,015\cdot10^{-3}$
Succinic	[21][в]	8	379,5	$6,626\cdot10^{-5}$	399,1	3,5	$6,08\cdot10^{-5}$	$0,11\cdot10^{-5}$
		7			406,2	2,9	$5,929\cdot10^{-5}$	$0,090\cdot10^{-5}$
		6			426,3	2,2	$5,318\cdot10^{-5}$	$0,059\cdot10^{-5}$
Adipic	[21][в]	8	376,6	$3,715\cdot10^{-5}$	520,8	2,2	$1,954\cdot10^{-5}$	$0,018\cdot10^{-5}$
		7			511,2	1,8	$2,030\cdot10^{-5}$	$0,015\cdot10^{-5}$
Pimelic	[21]	12	374,6	$3,097\cdot10^{-5}$	562,5	1,6	$1,3805\cdot10^{-5}$	$0,0080\cdot10^{-5}$
Suberic	[21]	12	373,1	$2,994\cdot10^{-5}$	443,6	3,0	$1,898\cdot10^{-5}$	$0,057\cdot10^{-5}$

Compound	Ref	N						
Phenylacetic	[22]ᵛ	7	380,7	4,884·10⁻⁵	353,70	0,14	5,9579·10⁻⁵	0,0050·10⁻⁵
		8			361,45	0,64	5,675·10⁻⁵	0,022·10⁻⁵
		7			303	21	9,1·10⁻⁵	1,5·10⁻⁵
	[23]	16	380,3	4,88·10⁻⁵	356,2	2,9	5,673·10⁻⁵	0,099·10⁻⁵
Diphenylacetic	[23]	20	375,0	1,15·10⁻⁴	365,5	1,9	1,264·10⁻⁴	0,022·10⁻⁴
p-Chlorophenyl-acetic	[23]	13	383,0	6,45·10⁻⁵	341,4	5,4	8,65·10⁻⁵	0,32·10⁻⁵
p-Bromophenyl-acetic	[23]	13	382,6	6,49·10⁻⁵	381,0	2,6	6,68·10⁻⁵	0,11·10⁻⁵
p-Iodophenyl-acetic	[23]	14	382,8	6,64·10⁻⁵	372,4	1,6	7,214·10⁻⁵	0,081·10⁻⁵
p-Nitrophenylacetic	[23]	14	377,8	1,41·10⁻⁴	364,3	3,2	1,580·10⁻⁴	0,032·10⁻⁴
DL-Aspartic	[24]	6	381,13	1,11·10⁻⁴	390	14	1,064·10⁻⁴	0,083·10⁻⁴
L-Glutamic	[25]	7	379,43	4,01·10⁻⁵	379	20	4,07·10⁻⁵	0,43·10⁻⁵
DL-Glutamic	[25]	6	-	-	416	16	3,16·10⁻⁵	0,25·10⁻⁵
Glutamic	[26]	6	-	-	455	11	2,59·10⁻⁵	0,13·10⁻⁵
Butyric	[27]	5	384,8	1,53·10⁻⁵	480,2	1,8	9,421·10⁻⁶	0,072·10⁻⁶
	[10]	21	381,69	1,518·10⁻⁵	346,4	5,0	1,898·10⁻⁵	0,057·10⁻⁵
Valeric	[27]	6	383,1	1,41·10⁻⁵	307,0	1,0	2,216·10⁻⁵	0,015·10⁻⁵
Caproic	[27]	5	380,5	1,35·10⁻⁵	231,3	1,5	3,722·10⁻⁵	0,051·10⁻⁵
Heptanoic	[27]	5	378,9	1,31·10⁻⁵	366,1	1,0	1,3755·10⁻⁵	0,0080·10⁻⁵
Octanoic	[27]	5	378,5	1,29·10⁻⁵	332,0	1,2	1,695·10⁻⁵	0,013·10⁻⁵
Nonanoic	[27]	5	376,8	1,12·10⁻⁵	415,8	4,4	8,80·10⁻⁶	0,20·10⁻⁶
Isobutyric	[27]	5	383,9	1,41·10⁻⁵	370,5	2,2	1,499·10⁻⁵	0,019·10⁻⁵
Isovaleric	[27]	5	382,4	1,71·10⁻⁵	659,9	2,8	5,384·10⁻⁶	0,048·10⁻⁶
Diethylacetic	[27]	6	380,1	1,82·10⁻⁵	308,3	1,9	2,783·10⁻⁵	0,036·10⁻⁵
Trimethylacetic	[27]	4	381,6	9,09·10⁻⁶	359,5	1,3	1,0040·10⁻⁵	0,0076·10⁻⁵
Quinic	[28]	15	374,6	2,708·10⁻⁴	334,3	1,5	3,739·10⁻⁴	0,039·10⁻⁴
Ascorbic	[29]	11	378,09	5,04·10⁻⁵	318,7	3,7	7,73·10⁻⁵	0,26·10⁻⁵

ᵃ – Depending of the procedure of interpretation of experimental data;

ᵇ – experimental data from this reference are published in [18];

ᵛ – depending on the cell design and the water conductivity.

Table 2. *Number of treated points N in phoregrams and calculated least-squares dispersions by published procedures and by the procedure developed in the present work.*

Acid	Ref.	N	σΛ in the reference	Calculated in the present work	
				σΛ	σΛ, %
Benzoic	[7]	27	-	0,0910	0,14
	[8]	10	-	0,0702	0,054
	[9]	16	-	1,76	3,1
Formic	[10]	17	-	0,142	0,55
	[11]	11	0,87	0,941	1,2
Cyclohexylsulfamic	[12]	15	4,11[а]; 8,61[б]	0,682[б]	0,22[б]
Acetic	[13]	14	-	0,0940	0,51
	[14]	6	-	0,00624	0,057
Cyanoacetic	[10]	21	-	0,846	0,43
	[14]	8	-	1,06	0,89
o-Nitrobenzoic	[14]	6	-	0,903	0,48
	[15]	6	-	0,123	0,040
o-Chlorobenzoic	[14]	5	-	0,108	0,069
3,5-Dinitrobenzoic	[14]	4	-	1,77	0,87
o-Mehtylbenzoic	[15]	5	-	0,405	0,51
o-Phenylbenzoic	[15]	5	-	0,931	0,37
o-Methoxybenzoic	[15]	6	-	0,177	0,25
o-Phenoxybenzoic	[15]	5	-	0,318	0,14
m-Phenoxybenzoic	[15]	5	-	0,576	0,28
p- Phenoxybenzoic	[15]	5	-	0,775	0,49
o-Nitrophenylacetic	[15]	6	-	0,169	0,21
o-Chlorocinnamic	[15]	6	-	0,880	0,43
n- Chlorocinnamic	[15]	4	-	1,06	0,53
DL-Pyroglutamic	[16]	6	2,70	0,554	0,35
Salicylic	[17]	8	0,02 %	0,125	0,043
2,4-Dihydroxybenzoic	[17]	7	0,01 %	0,179	0,078
2,5-Dihydroxybenzoic	[17]	7	0,03 %	0,224	0,077
2,6-Dihydroxybenzoic	[17]	7	0,06 %	0,121	0,032
Glutaric	[18]	7	1,34	0,432	0,90
	[19][в]	5	0,65	0,0514	0,19
	[20][в]	7	0,60	0,0652	0,26
	[21]	14	1,06	0,407	0,42
Malonic	[21][г]	8	-	1,09	0,59
		8	-	0,669	0,32
		6	-	0,623	0,35
Succinic	[21][г]	8	-	0,375	0,88
		7	-	0,297	0,71
		6	-	0,242	0,52
Adipic	[21][г]	8	-	0,243	0,43
		7	-	0,102	0,34

Pimelic	[21]	12	-	0,103	0,28
Suberic	[21]	12	-	0,379	0,67
Phenylacetic	[22][г]	7	-	0,0181	0,038
		8	-	0,113	0,18
		7	-	3,59	6,4
	[23]	16	-	0,347	0,80
Diphenylacetic	[23]	20	-	1,08	0,53
p-Chlorophenylacetic	[23]	13	-	1,10	1,5
p-Bromophenylacetic	[23]	13	-	0,649	0,68
p-Iodophenylacetic	[23]	14	-	0,574	0,44
p-Nitrophenylacetic	[23]	14	-	0,834	0,87
DL-Aspartic	[24]	6	2,74	2,55	3,9
L-Glutamic	[25]	7	2,22	2,12	5,8
DL-Glutamic	[25]	6	2,28	1,70	4,2
Glutamic	[26][д]	6	3,43	1,21	2,6
Butyric	[27]	5	-	0,0750	0,37
	[10]	21	-	0,194	1,5
Valeric	[27]	6	-	0,0602	0,33
Caproic	[27]	5	-	0,135	0,65
Heptanoic	[27]	5	-	0,0639	0,28
Octanoic	[27]	5	-	0,151	0,35
Nonanoic	[27]	5	-	0,501	1,1
Isobutyric	[27]	5	-	0,0982	0,60
Isovaleric	[27]	5	-	0,0683	0,42
Diethylacetic	[27]	6	-	0,198	0,61
Trimethylacetic	[27]	4	-	0,0746	0,36
Quinic	[28]	15	0,6	0,323	0,46
Ascorbic	[29]	11	1,28	1,10	1,5

[а] – Dimerization included;

[б] – dimerization not included;

[в] – experimental data from this reference are published in [18];

[г] – depending on the cell design and the water conductivity;

[д] – calculation with the experimental data from [26] was performed in [25].

Table 3. *The most reliable Λ_0 and K_a values calculated with published experimental data by the proposed procedure.*

| Acid	Reference	Λ_0	K_a
Benzoic	[8]	$371,72 \pm 0,20$	$(6,8287 \pm 0,0094) \cdot 10^{-5}$
Acetic	[14]	$387,90 \pm 0,22$	$(1,8266 \pm 0,0021) \cdot 10^{-5}$
o-Clorobenzoic	[14]	$379,31 \pm 0,26$	$(1,2961 \pm 0,0025) \cdot 10^{-3}$
o-Nitrobenzoic	[15]	$379,20 \pm 0,15$	$(6,529 \pm 0,017) \cdot 10^{-3}$
Salicylic	[17]	$378,19 \pm 0,16$	$(1,0517 \pm 0,0031) \cdot 10^{-3}$
2,4-Dihydroxybenzoic	[17]	$371,69 \pm 0,29$	$(5,068 \pm 0,016) \cdot 10^{-4}$
2,5-Dihydroxybenzoic	[17]	$378,88 \pm 0,29$	$(1,1314 \pm 0,0057) \cdot 10^{-3}$
2,6-Dihydroxybenzoic	[17]	$383,16 \pm 0,12$	$(4,025 \pm 0,083) \cdot 10^{-2}$
Phenylacetic	[22]	$353,70 \pm 0,14$	$(5,9579 \pm 0,0050) \cdot 10^{-5}$
Heptanoic	[27]	$366,1 \pm 1,0$	$(1,3755 \pm 0,0080) \cdot 10^{-5}$

Fig. 1. Concentration dependences of the calculated (x) K_a and (○) Λ_0 values for aqueous solutions of (a) benzoic acid (treatment of the experimental data from [7], no explicit concentration dependence) and (b) cyanoacetic acid (treatment of the experimental data from [10], explicit concentration dependence.
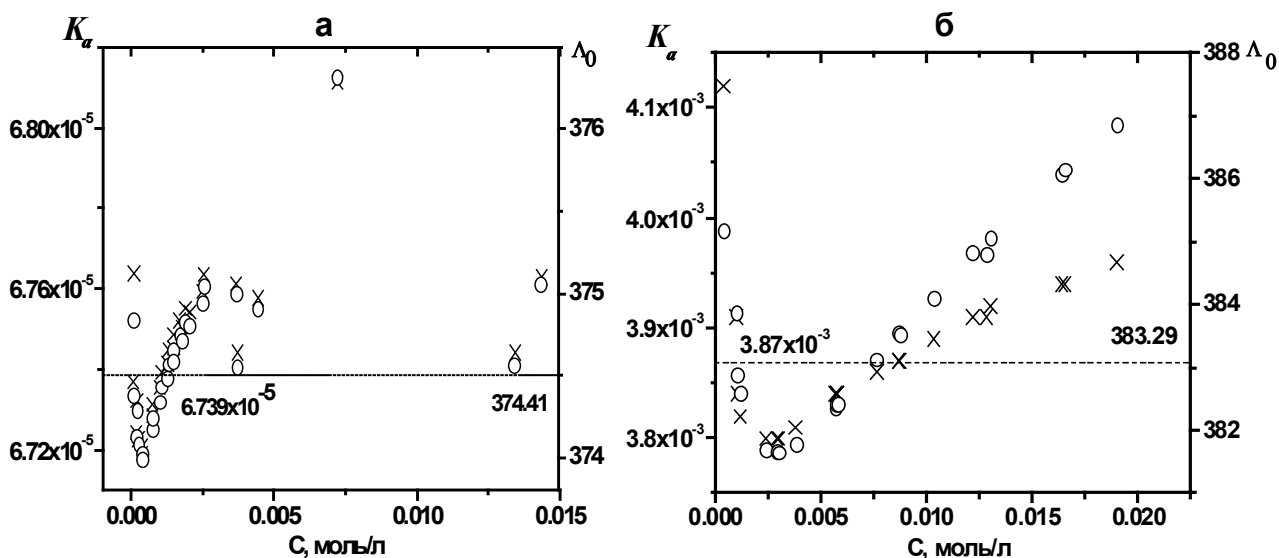
Рис.1. Концентрационные зависимости расчетных значений K_a (x) и Λ_0 (○) для водных растворов: **а)** бензойной кислоты при обработке экспериментальных значений из работы [7], без явной зависимости от концентрации; **б)** циануксусной кислоты при обработке экспериментальных значений из работы [10], с явной зависимостью от концентрации.

Fig. 2. Concentration dependences of the deviations of experiment from calculation (ΔΛ) for aqueous solutions of (a) phenylacetic acid (treatment of the experimental data from [22], including the outlying point) and (b) benzoic acid (treatment of the experimental data from [9], including data for two different experimental conditions).
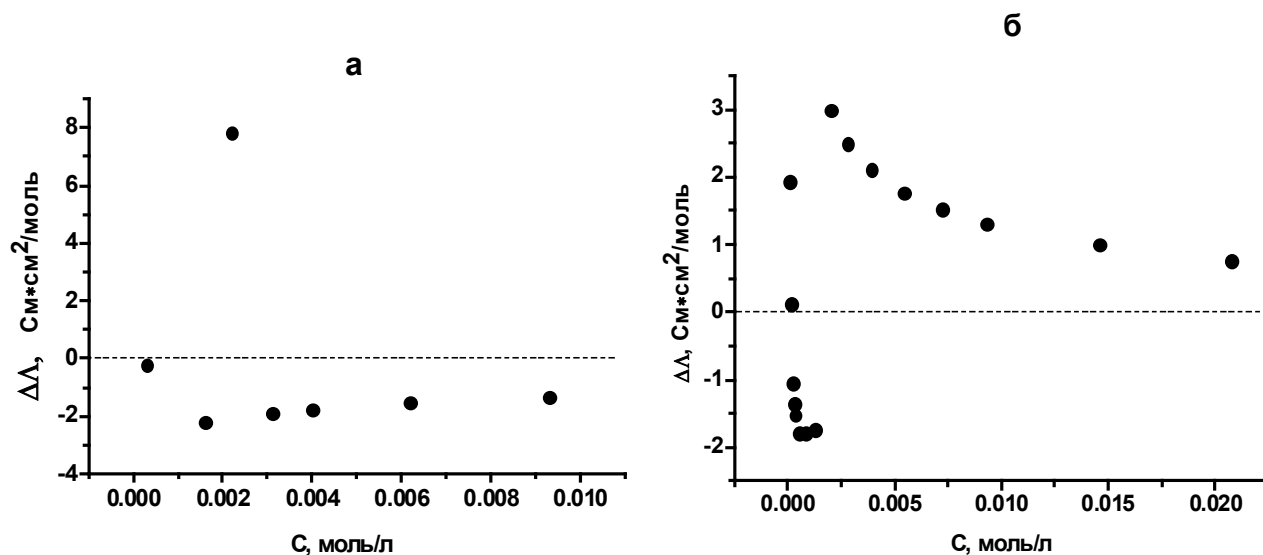
Рис. 2. Концентрационные зависимости отклонений между экспериментально определенной величиной молярной электропроводности и его расчетным значением ΔΛ для водных растворов: **а)** фенилуксусной кислоты при обработке экспериментальных значений из работы [22], с выпадающей точкой; **б)** бензойной кислоты при обработке экспериментальных значений из работы [9], с объединением результатов эксперимента при двух условиях.