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Conductometry of Solutions of Very Weak Electrolytes and Dibasic Acid Solutions

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Abstract—The method for phoreograms processing using the least squares method, taking into account the water conductivity and carbon dioxide content was developed. Thus we reduced the threshold concentration of test solutions to 10^{-6} M. The method was used in processing the results of measurements of conductivity of aqueous solutions of a number of phenols and dibasic organic acids.

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Since the XIX century and until recently the conductometry was used traditionally to study aqueous electrolyte solutions [1]. This method is unique for the study of protolytic equilibria in binary systems, since it does not require the use of buffer solutions. As a consequence, the conductivity measurement is very sensitive to the amount of carbon dioxide and other impurities in water.

Usually, the deionized water used for the conductometry has a specific conductivity of 0.2 to 0.3 μS cm^{-1}. This value is defined mainly by the carbon dioxide at a concentration of 10^{-6} M absorbed from the air, and, to a lesser extent, by water autoprotolysis. The contribution of other impurities in the conductivity of deionized water is no more than 0.01 μS cm^{-1}. Experiments carried out in complete isolation from the atmosphere, especially preparation of solutions by weighing, are inconvenient for practical reasons.

Measuring the conductivity of solutions of weak electrolytes is generally carried out at a concentration of the substance 10^{-4} M and higher. At lower concentrations, the conductivity of solutions to a large extent is due to the acid–base interaction with the participation of carbonic acid, whose concentration is not precisely known. This distorts the results of measurements [2].

Thus, the concentration range 10^{-7} to 10^{-5} M, which is informative in determining the dissociation constants of very weak (p*K* 6–8) electrolyte and constants of the second and higher levels of dissociation of polybasic acids is unavailable for research on the above reasons. The only known exception is [3], where the authors succeeded to identify specific molar conductivity for a number of electrolytes at concentrations to 10^{-8} M by a thorough cleaning solutions from the traces of carbon dioxide.

The aim of this work is to extend the limits of the conductometry method by changing the experimental data processing and accounting for the content of carbon dioxide in solution in order to enhance the accuracy and convenience of the experiment. A necessary condition for the applicability of our method is to maintain a *constant* (quasi-equilibrium) content of CO_2 in the solution for the entire conductometric series, achieved by isolation of solutions from the air and dilution with freshly purified water. This condition is really fulfilled, as follows from the results of the blank experiments without substance (see Experimental). The presence of carbonic acid is accounted for in the material balance equation, and the data processing makes it possible (along with other unknown quantities) to estimate the average concentration of carbon dioxide X within the experimental series.

It was shown earlier [4] that the Arrhenius equation which relates the degree of ionization of the electrolyte α with a specific molar conductivity of its solution Λ and specific molar conductivity Λ_0 at the infinite dilution limit [Eq. (1)] does not hold for weak electrolytes.

$$\alpha = \frac{\Lambda}{\Lambda_0}. \qquad (1)$$

Given that at the infinite dilution limit the weak electrolytes does not entirely dissociate, the Arrhenius equation was transformed to Eq. (2).

$$\frac{\alpha}{\alpha_0} = \frac{\Lambda}{\Lambda_0}, \qquad (2)$$

where α_0 is the degree of dissociation of the compound at this limit. Obviously, the value of the specific molar conductivity Λ_0 at the infinite dilution depends not only on the values of the limiting conductivity (Λ_+ and $\Lambda_–$) of the ions in the electrolyte [Eq. (3)], but also on the ratio of the acid–base properties of the solvent.

$$\alpha_0(\Lambda_+ + \Lambda_–) = \Lambda_0 \qquad (3)$$

In binary aqueous solutions (in the absence of dissolved carbon dioxide) the value of α_0 depends on the dissociation constant K_a and a constant of the water autoprotolysis K_w [Eq. (4)].

$$\alpha_0 = \frac{K_a}{K_a + \sqrt{K_w}}. \qquad (4)$$

The presence of carbonic acid decreases the maximum degree of dissociation of acids and increases it for the bases. Apparently, these facts explain why the value of K_a, determined by different authors using conductometry frequently agrees only in the order of magnitude [5].

To eliminate the uncertainty associated with the interpretation of the values of the limiting specific molar conductivity Λ_0, in this paper we operate with the values of specific conductivity of solutions L obtained from the direct reading of the conductometer. For calculation of the material balance of protolytic equilibria in aqueous solutions we used the Brønsted and Lowry dissociation scheme (5).

$$\begin{gathered}
HA + H_2O \rightarrow H_3O^+ + A^-;\ K_a = [\alpha/(1-\alpha)][H_3O^+],\\
H_2CO_3 + H_2O \rightarrow HCO_3^- + H_3O^+;\ K_c = [\beta/(1-\beta)][H_3O^+],\\
2H_2O \rightarrow H_3O^+ + OH^-;\ K_w = [H_3O^+][OH^-], \qquad (5)
\end{gathered}$$

where α is the degree of dissociation of the studied acid, β is the degree of the first stage dissociation of carbonic acid, K_c is the constant of the latter. The solution of Eq. (5) with respect to two variables K_a and X, the studied acid dissociation constant and content of carbonic acid (mol l^{-1}), respectively, at a known concentration of the acid c [mol l^{-1}] is expressed by Eqs. (6).

$$\begin{gathered}
\alpha c + \beta X + [OH^-] = K_a\frac{1-\alpha}{\alpha},\\
\beta = \left(\frac{(1-\alpha)K_a}{\alpha K_c} + 1\right)^{-1}, \qquad (6)\\
[OH^-] = \frac{\alpha K_w}{(1-\alpha)K_a}.
\end{gathered}$$

The value of the specific conductivity L (μS cm^{-1}) of the aqueous solution of studied acid with molarity c_i was determined using Eq. (7).

$$\begin{aligned}
L\{[\Lambda(H^+) + \Lambda(A^-)], K_a, X, c_i\} = 10^3\{\alpha c_i[\Lambda(H^+) + \Lambda(A^-)]\\
+ \beta X[\Lambda(H^+) + \Lambda\{H(CO_3)\}] + [OH^-][\Lambda(H^+)\\
+ \Lambda(OH^-)]\}, \qquad (7)
\end{aligned}$$

where $\Lambda(H^+)$, $\Lambda(HCO_3^-)$ and $\Lambda(OH^-)$ are known published values of the limiting ionic conductivity of the proton, hydrocarbonate, and hydroxyl, respectively, $\Lambda(A^-)$ is the unknown value of the limiting ionic conductivity of the investigated acid anion.

Values of pK_w (13.995), pK_c (6.352), $\Lambda(H^+)$ (350.1), $\Lambda(HCO_3^-)$ (44.5), and $\Lambda(OH^-)$ (198) were obtained from the literature sources [6].

Search for unknown values was performed by minimizing the sum of the squares of the relative deviations of the experimental L_i values from the calculated ones [Eq. (8)].

$$\begin{aligned}
&S\{[\Lambda(H^+) + \Lambda(A^-)], K_a, X\}\\
&= \sum_i^N \frac{\{L[\Lambda(H^+) + \Lambda(A^-)], K_a, X, c_i] - L_i\}^2}{L_i^2}, \qquad (8)
\end{aligned}$$

where N is the total number of experimental data. At a minimum S value three conditions must be fulfilled [Eq. (9)].

$$\begin{aligned}
&\frac{\partial S\{[\Lambda(H^+) + \Lambda(A^-)], K_a, X\}}{\partial(\Lambda_{H^+} + \Lambda_{A^-})} = \frac{\partial S\{[\Lambda(H^+) + \Lambda(A^-)], K_a,\}}{\partial K_a}\\
&= \frac{\partial S\{[\Lambda(H^+) + \Lambda(A^-)], K_a, X\}}{\partial X} = 0. \qquad (9)
\end{aligned}$$

The solution of the system of three equations was performed numerically using MATCAD 14 software package. Initially the first condition of system (9) was applied, which with accounting for expression (7) led to Eq. (10).

$$\sum_i^N \frac{L\{[\Lambda(H^+) + \Lambda(A^-)], K_a, X, c_i\} - L_i}{L_i^2}\alpha(K_a, X, c_i)c_i = 0. \qquad (10)$$

where $\alpha(K_a, X, C_i)$ was determined with the equations (6) as a function of two variables (K_a and X) using the methods of Muller or secants, Ridder, or Brent (function *root*). The solution of Eq. (10) gave the dependence of K_a on two variables, X and $[\Lambda(H^+) + \Lambda(A)]$. Thus the sum of the squares determined by Eq. (8) is dependent only on the two variables, X and $[\Lambda(H^+) + \Lambda(A)]$. The minimization procedure of the sum of squares we managed to fulfill using the conjugate gradient or Quasi-Newton methods. This resulted in the desired values of K_a, X, and $[\Lambda(H^+) + \Lambda(A)]$.

For dibasic acids we used a similar scheme of dissociation (11).

$$
\begin{gathered}
H_2A + H_2O \rightarrow H_3O^+ + HA^-;\ K_{a1} = [\alpha_1/(1 - \alpha_1 - \alpha_2)][H_3O^+],\\
HA^- + H_2O \rightarrow H_3O^+ + A^{2-};\ K_{a2} = (\alpha_2/\alpha_1)[H_3O^+],\\
H_2CO_3 + H_2O \rightarrow HCO_3^- + H_3O^+;\ K_c = [\beta/(1 - \beta)][H_3O^+],\\
2H_2O \rightarrow H_3O^+ + OH^-;\ K_w = [H_3O^+][OH^-]. \quad (11)
\end{gathered}
$$

where α_1 and K_{a1} are the values of the degree and the constant of dissociation of the acid in the first stage, α_2 and K_{a2}, the same in the second stage. The solution of the system (11) with respect to the three unknowns, K_{a1}, K_{a2}, and X is Eq. (12).

$$
\begin{gathered}
(\alpha_1 + 2\alpha_2)c + \beta X + \frac{\alpha_2 K_w}{\alpha_1 K_{a2}} = K_{a2}\frac{\alpha_1}{\alpha_2},\\
\beta = \left(\frac{\alpha_1 K_{a2}}{\alpha_2 K_c} + 1\right)^{-1}\\
\alpha_1 = \frac{\alpha_2 K_{a1}}{2K_{a2}}\left(\sqrt{1 + 4\frac{(1 - \alpha_2)K_{a2}}{\alpha_2 K_{a1}}} - 1\right). \quad (12)
\end{gathered}
$$

The estimated value of the specific conductivity of the dibasic acid solution was determined by Eq. (13).

$$
\begin{aligned}
L(c_i) = 10^3\ \{&\alpha_1 c_i[\Lambda(H^+) + \Lambda(HA^-)] + 2\alpha_2 c_i[\Lambda(H^+) + \Lambda(A^{2-})]\\
&+ \beta X[\Lambda(H^+) + \Lambda(HCO_3)] + \frac{\alpha_2 K_w}{\alpha_1 K_{a2}}[\Lambda(H^+) + \Lambda(OH^-)]\}. \quad (13)
\end{aligned}
$$

The difference between the calculated and experimental values of specific conductivity of the solution with a molar concentration C_i depends on five unknown quantities: the two constants (K_{a1} and K_{a2}), the content of carbon dioxide X, and the limiting ionic conductivity of single- and double-charged anions of the studied acid $[\Lambda(HA^-)$ and $\Lambda(A^{2-})]$ [Eq. (14)].

$$
\Delta L[K_{a1}, K_{a2}, [\Lambda(H^+) + \Lambda(HA^-)], [\Lambda(H^+) + \Lambda(A^{2-})], X, c_i] = L_i - L(c_i). \quad (14)
$$

As a consequence, the sum of the squares of all the relative deviations of calculated values of specific conductivity from experimental data depends on the same five unknowns: K_{a1}, K_{a2}, X, $\Lambda(HA^-)$, and $\Lambda(A^{2-})$ [Eq. (15)].

$$
S = \sum_{i=1}^{N}\frac{\Delta L[K_{a1}, K_{a2}, (\Lambda_{H^+} + \Lambda_{HA^-}), (\Lambda_{H^+} + \Lambda_{A^{2-}}), X, c_i]^2}{L_i^2}. \quad (15)
$$

If there is a global minimum of this sum, five conditions are fulfilled [Eq. (16)].

$$
\begin{gathered}
\frac{\partial S}{\partial(\Lambda_{H^+} + \Lambda_{HA^-})} = \frac{\partial S}{\partial(\Lambda_{H^+} + \Lambda_{A^{2-}})} = \frac{\partial S}{\partial K_{a1}}\\
= \frac{\partial S}{\partial K_{a2}} = \frac{\partial S}{\partial X} = 0. \quad (16)
\end{gathered}
$$

The first of these conditions is Eq. (17).

$$
\sum_{i}^{N}\frac{\Delta L[K_{a1}, K_{a2}, (\Lambda_{H^+} + \Lambda_{HA^-}), (\Lambda_{H^+} + \Lambda_{A^{2-}}), X, c_i]}{L_i^2}\alpha_1(K_{a1}, K_{a2}, X, c_i)c_i = 0, \quad (17)
$$

where $\alpha_1(K_{a1}, K_{a2}, X, C_i)$ was determined from Eqs. (12) as a function of three variables (K_{a1}, K_{a2}, and X) using the methods of Muller or secants, Ridder, or Brent. The numerical solution of Eq. (17) gave the dependence of K_{a1} on the four variables, K_{a2}, $[\Lambda(H^+) + \Lambda(HA^-)]$, $[\Lambda(H^+) + \Lambda(A^{2-})]$, and X. The second condition in Eq. (16) is Eq. (18), where $\alpha(K_{a1}, K_{a2}, X, C_i)$ was determined from equations (12) as a function of three variables (K_{a1}, K_{a2} and X) using the methods of Muller or secants, Ridder, or Brent. By the numerical

$$
\sum_{i}^{N}\frac{\Delta L[K_{a1}, K_{a2}, (\Lambda_{H^+} + \Lambda_{HA^-}), (\Lambda_{H^+} + \Lambda_{A^{2-}}), X, c_i]}{L_i^2}\alpha_2(K_{a1}, K_{a2}, X, c_i)c_i = 0. \quad (18)
$$

solution of equation (18) the dependence of $[\Lambda(H^+) + \Lambda(HA^-)]$ on three variables, K_{a2}, $[\Lambda(H^+) + \Lambda(A^{2-})]$ and X was obtained.

We succeeded to minimize by the conjugate gradient method the sum of squares determined from Eq. (15), which is a dependence on three variables, K_{a2}, $[\Lambda(H^+) + \Lambda(A^{2-})]$, and X. Thus, we obtained the required five values, K_{a1}, K_{a2}, $[\Lambda(H^+) + \Lambda(HA^-)]$, $[\Lambda(H^+) + \Lambda(A^{2-})]$, and X.

As an initial approximation for the unknown quantities K_a, K_{a1}, K_{a2}, $\Lambda(A)$, $\Lambda(HA^-)$, and $\Lambda(A^{2-})$ we used the values published in the literature [6–8], the initial value of carbon dioxide concentration X was selected using the measurements of the conductivity of water L_s.

The results of calculations based on experimental data of conductivity of aqueous solutions of phenols, succinic, oxalic, maleic, phthalic, and benzoic acids, triethylamine, and acetic acid derivatives are listed in the table. The table also lists the values of the standard deviations of the calculated values of conductivity of test solutions in relative units [Eq. (19)].

$$\sigma = \sqrt{[S/(N-1)]}. \qquad (19)$$

With the used calculation procedure of the constants, probably, the value of the first moment of ΔL_i, the deviations of calculated values from experimental data is no less but more significant.

$$\Delta L = \frac{1}{N}\sum_i^N \Delta L_i\,. \qquad (20)$$

According to the statistical concepts [9], in the limit $N\to\infty$ the value of this moment should approach zero. That is, if at the increase in the number of measurements N the first moment does not tend to reduce the value of its module, then this indicates the inadequacy of the theoretical model and the infringement of the invariance of the calculated constants. In the case under consideration, this means that the calculated constants would depend on the concentration, hence they are not thermodynamic ones, and the values of the limiting ionic conductivity are not constants.

The values of the dissociation constants and limiting molar conductivities of ions of weak electrolytes and dicarboxylic acids derived from the original processing of conductograms at low concentrations are in good agreement with literature experimental data, obtained by other methods [6–8]. The rather rough results for phenols may arise from instrumental errors: due to the low conductivity of their solutions, we were forced to use values outside the linear region of the conductivity cell. Distortion of the results may be due to side reactions (e.g., nitro–aci-nitro tautomerism of nitrophenols) and to the insufficient purity of the used substances.

In the analysis of experimental data we selected the concentration ranges where the concentration dependence of the dissociation constants and molar conductivities of ions would be insignificant. The criterion for the selection of the interval of concentrations we used the dispersion of the relative deviations of the calculated conductivity values of the solution from the experimental values (σ). In many cases it was possible to obtain the values of σ at or below the instrumental error ($\sim 10^{-3}$), indicating the adequacy of the proposed model.

Obviously, in the studied range of concentrations it is not necessary to take into account the ionic strength of the solution, as well as operate with the values of activities instead of concentrations of electrolytes. This is confirmed by the low values of the first moment of error of indirect conductivity measurements: ΔL, the deviations of the calculated values from the data of the experiment, are at the level $\Delta L \sim 10^{-3}\sigma$. Thus, within the selected concentration the contribution of interionic interaction to the thermodynamics of the processes of protolytic interactions is negligible. Hence, the obtained values of dissociation constants can be regarded as thermodynamic ones, and the values of the ionic conductivity as limiting.

With increasing concentration of electrolyte solutions above the selected ones, the treatment of results in the framework of the suggested method detected the appearance of the concentration dependence. This is natural, since with increasing concentration manifestations of ion–ion interactions in electrolyte solutions, additional equilibria with ion associates, dimers of the acid neutral forms, the influence of the heat of reaction are possible, which has not been taken into account in the basic chemical schemes (5) and (11) of the proposed method.

Perhaps the most appealing aspect of practical significance of the elaborated method is that it has allowed us to obtain the data on the conductivity of weak electrolytes in the previously inaccessible concentration range of 10^{-6} to 10^{-4} M because of the masking

The results and literature data of conductomeric measurements

Compound, K_a^{lit} M $[\Lambda(H^+)+\Lambda(A^-)$, S cm^2 mol$^{-1}]^{lit}$	c, M (L_s,[a] μS cm^{-1})	N	$\Lambda(H^+)+\Lambda(A^-)$, S cm^2 mol^{-1}	Λ_0,[b] S cm^2 mol^{-1}	K_a, M	$\sigma\times10^3$	$\Delta L\times10^6$, μS cm^{-1}
4-Nitrophenol 7.079×10^{-8} [6]	1.3×10^{-5}–1.7×10^{-3} (0.1765)	8	247.3±0.087%	71.8	1.795×10^{-7}±0.18%	0.817	0.540
3-Nitrophenol 4.365×10^{-9} [6]	9.7×10^{-6}–0.015 (0.1943)	9	367±3.1%	4.0	5.4×10^{-9}±5.9%	20.08	255.5
2-Nitrophenol 5.998×10^{-8} [6]	1.8×10^{-6}–7.5×10^{-3} (0.2297)	13	383±4.7%	35.3	5.8×10^{-8}±9.1%	13.60	49.15
Phenol, 1.02×10^{-10} [6]	6.7×10^{-4}–0.020 (0.1574)	6	373±4.2%	0.14	1.40×10^{-10} ±8.1%	28.08	688.8
Succinic acid, 5.67×10^{-5} (386.26) [8] 2.31×10^{-6} (406.84) [8]	1.3×10^{-6}–3.8×10^{-4} (0.1617)	9	373.78±0.078% 398.8±0.20%	48.9 346.3	6.778×10^{-5}±0.81% 2.653×10^{-6}±0.45%	0.459	0.187
Oxalic acid 5.18×10^{-2} (390.89) [8] 5.30×10^{-5} (424.75) [8]	5.6×10^{-6}–4.3×10^{-3} (0.4459)	11	397.6±0.49% 431.8±1.05%	7.7 423.4	4.7×10^{-2}±53% 5.70×10^{-5}±2.2%	1.281	1.502
Maleic acid 1.14×10^{-2} (385.95) [8] 5.95×10^{-7} (413.53) [8]	1.3×10^{-6}–5.6×10^{-4} (0.1966)	10	391.70±0.026% 431±3.77%	195.19 216	1.003×10^{-2}±9.9% 4.93×10^{-7}±6.9%	0.251	0.057
Phthalic acid 1.123×10^{-3} (380.9) [8] 3.906×10^{-6} (405.91) [8]	1.8×10^{-6}–3.6×10^{-4} (0.1988)	9	379.44±0.026% 399.7±0.22%	39.2 358.4	1.162×10^{-3}±2.6% 4.302×10^{-6}±0.44%	0.166	0.032
Acetic acid 1.750×10^{-5} (390.77) [8]	1.6×10^{-6}–1.0×10^{-4} (0.1880)	7	391.18±0.020%	381.23	1.793×10^{-5}±0.16%	0.197	0.069
Chloracetic acid 1.359×10^{-3} (392.28) [8]	1.5×10^{-5}–2.0×10^{-3} (0.3391)	8	388.4±0.12%	388.2	1.494×10^{-3}±1.8%	1.163	1.184
Pivalic acid 9.33×10^{-6} (381.6) [7]	4.5×10^{-6}–6.1×10^{-3} (0.2492)	11	372.75±0.086%	350.52	9.86×10^{-6}±0.22%	0.853	0.732
Propionic acid 1.343×10^{-5} (386.11) [8]	4.7×10^{-6}–1.2×10^{-3} (0.1981)	9	382.2±0.15%	369.2	1.407×10^{-5}±0.43%	1.511	2.117
Benzoic acid 6.258×10^{-5} (383.11) [8]	1.4×10^{-6}–9.3×10^{-4} (0.1469)	10	384.1±0.12%	381.97	6.439×10^{-5}±1.17%	1.229	1.272
Triethylamine 1.778×10^{-11} (34.3[c]) [7]	5.1×10^{-6}–3.2×10^{-5} (0.2315)	19	29.9±0.87%[c]	228.0[d]	1.56×10^{-11}±15%[e]	1.305	1.602

[a] L_s is the average conductivity of the water within the experimental series, calculated basing on an average concentration of CO_2 X. [b] $\Lambda_0 = [\Lambda(H^+) + \Lambda(A^-)]\alpha_0$, where α_0 is the degree of dissociation of the electrolyte at infinite dilution, adjusted to the average concentration of CO_2 X. [c] $\Lambda(BH^+)$. [d] $\Lambda_0 = [\Lambda(BH^+) + \Lambda(OH^-)]\alpha_0$. [e] K_{BH+}.

effect of CO_2. In this concentrations range the influence of the second ionization constant of the same order of magnitude (pK_{a2} ~ 6) on the conductivity of the solution reached the maximum (Fig. 2), which made it possible to determine both constants for the studied dibasic acids from the data of one conductometric series.

This method may be useful for the quantitative determination of acids and bases in the concentrations of the order of 10^{-5} M, therewith, the presence of linear regions on the conductogram required in traditional methods of conductometric titration is unnecessary [14].

It is also possible to use the method to account for the influence of other hard to remove impurities (e.g., the influence of traces of water on the protolytic equilibrium in non-aqueous solutions) when the impurity contribution to the specific conductivity of the solution can be explicitly or implicitly expressed through the appropriate constants.

EXPERIMENTAL

Potassium chloride, succinic acid, and oxalic acid (dihydrate) of chemically pure grade, phenol, *o*- and *p*-nitrophenols, benzoic acid, maleic acid, and phthalic acid of analytically pure grade, trimethylacetic and chloroacetic acid of pure grade were used without further purification. *m*-Nitrophenol of pure grade was purified by crystallization from water and ethanol and by sublimation in a vacuum. Propionic acid and triethylamine of pure grade were purified by distillation at atmospheric pressure. Acetic acid of chemically pure grade was purified by freezeing at 14–15°C, the conductivity of the purified acid L did not exceed 0.014 μS cm^{-1} at 25°C.

Water purification. Pure water for the conductivity measurements was obtained from bidistilled water with a Vodoley deionizer (Khimelektronika, Moscow). The instrument first purifies water in the inner loop (for 15 min), then in the external circuit (within 60–90 min), and the water under the excess pressure is circulated through a removable plastic bottle. To the bottle an output polymeric tube with a clamp is mounted. This modification made it possible to produce up to 750 ml of water at a convenient moment of time (during the whole cleaning cycle in the external circuit of the water deionizer).

The water was considered clean enough for the preparation of solutions when its resistivity (according to the built-in sensor) exceeded 16 MΩ cm (specific conductivity L was no more than 0.063 μS cm^{-1} at 25°C). After taking a large (250 ml) amount of water the deionizer was refueled with the double-distilled water and then the cycle of water treatment started again. Usually, to preparation of a new portion of water required 20 min, which corresponds to a measurement time of one experimental point by dilution method (see below).

Air purification. The air was cleaned of acid (carbonic acid) and basic (ammonia) impurities. The atmospheric air by the compressor R-200 equipped with the possibility of flow control (pressure up to 0.05 atm, gas flow rate 300 ml min^{-1}) passed successively through a washing bottle with concentrated sulfuric acid, column (diameter 30 mm, height 250 mm) with solid sodium hydroxide (pellet diameter 1 to 1.5 mm), washing bottle with a saturated solution of sodium hydroxide and water, check valve and a filter of porous glass.

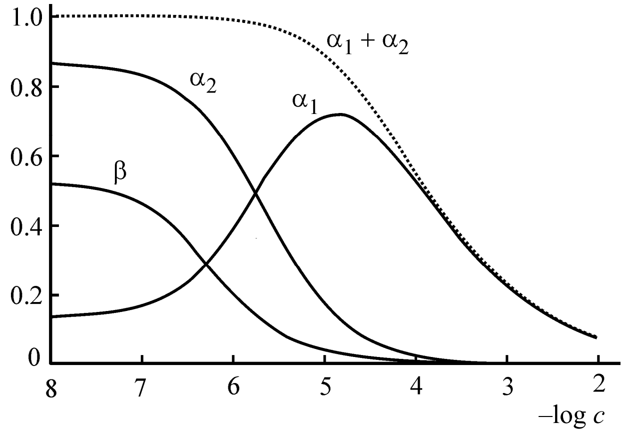

Fig. 1. Dependence of the first (α_1) and a second (α_2) degree of ionization of succinic acid and ionization degree (β) of the carbonic acid on concentration of succinic acid. The concentration of carbon dioxide in solution of 7.12× 10^{-7} M.

For the preparation and processing of dilute aqueous solutions we used flasks and bottles of polypropylene and polyethylene (VITLAB GmbH) with tight screwed lids. For passing solutions and supply air were used fluoroplastic tubes (internal diameter 3 mm), connected in the right places through conical adapters of polypropylene. Glassware (PYREX) we used only for preparation of stock solutions (concentration above 0.01 M), the effects of leaching glass were insignificant. The storage duration of the solutions did not exceed 24 h.

The solutions were prepared by weighing. Small (up to 80 g) sample materials and solutions were weighed on an analytical balance SARTOGOSM MV-210-A (sensitivity 0.01 mg). For weighing large (up to 1100 g) objects we used an AND GX-1000 balance (sensitivity of 1 mg.) No correction of the weight to the vacuum was performed.

EXPERIMENTAL

In this procedure a series of conductometric measuring began with the most concentrated (stock) solution. Half of the solution was used to wash the cell and to perform a measurement, and then discarded. To

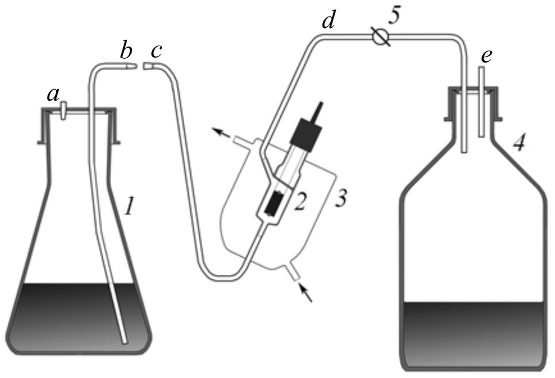

Fig. 2. Installation for measuring conductivity of solutions by dilution method. (*1*) Mixer, (*2*) cell, (*3*) jadet for temperature control of the cell, (*4*) a collecttor of the solutions used, (*5*) valve. To the remaining notations, see the text. The arrows show the movement of water from the thermostat.

the other half about an equal volume of water was added, then the procedure of measuring conductivity was repeated. Thus the concentration of the following solution was approximately two times lower than that of the previous one.

The concentration was calculated after weighing solutions before and after dilution. Because of the necessity to weigh, it was impossible to exclude completely the contact of the solution with atomspheric air. However, the dilution with fresh deionized water when diluted in half compensated the increase in carbon dioxide concentration due to the diffusion of CO_2 in the solution during the measurement. At a constant cycle time of measurement (20 min) and uniformity of operations, the concentration of carbon dioxide is approximately constant for each experimental point in the series. Thus, in the blank experiments without a substance the values of L were in the range 0.15 to 0.19 μS cm^{-1} (25°C) after the second measurement, which is consistent with the quasi-equilibrium concentration of H_2CO_3 10^{-6} M.

The relative error of concentration at the twofold dilution also remained almost constant for the entire series and did not exceed 0.1%.

. The measurements of solutions conductivity were carried out with a KL-C-1 conductivity meter (Sibpromprobor-Analit, Barnaul) equipped with a flow-type cell B. The cell is three-electrode, the electrodes are made of smooth platinum, the cell constant 0.07639 cm^{-1} (according to factory specification). To maintain the temperature in the cell within 25.0±0.1°C we used a LT-316b thermostat (LOIP, Saint-Peters-burg). The relative error of solution conductivity measurements in these conditions was ~0.1%.

To measure the density of the solutions we used an automatic ultrasonic densitometer DA-500 (Kyoto, Japan), the absolute error of ±0.0001 kg l^{-1}. The measured density values were used to convert mass concentration (mol kg^{-1}) in the volume concentration (M).

Conductivity measurements were made using a setup (Fig. 1) consisting of a mixer *1*, cell *2*, a collector of used solutions *4*, conductivity meter, thermostat and air purification systems (see above). Mixer *1* is a 500 ml Erlenmeyer flask with a lid. The lid has an inlet *a* for air supply and tube *b* used for the transport of the solution, reaching the flask bottom. Cell *2* is inclined relative to the vertical, so that air bubbles do not stay in its upper part. The cell is in a jacket *3* for temperature control, coolant (water) comes in the jacket through the bottom fitting and returns to the thermostat through the upper fitting. For the solution transport, to the cell are attached two tubes, *c* (bottom) and *d* (top), the latter can be switched off with a stopcock *5*. Collector of solutions *4* is a 500 ml plugged flask. The plug has a tube *e* for transport solutions and *f* to connect with the atmosphere or air source.

Prior to a series of measurements, mixer *1* was washed with de-ionized water, dried to constant weight and purged with purified air for 20–30 min. Then to the mixer through tube *b* was passed ~500 ml of the stock solution (prepared in a separate flask). In other cases, the stock solution was prepared directly in the mixer: a weighed sample of solid substance was quickly put into the mixer removing the lid, the liquid sample was injected through inlet *a*, the water was poured through the pipe *b* from deionizer, the mixer was shaken to dissolve the sample. Then inlet *a* end was closed by the end of tube *b*, the mixer filled with the stock solution was weighed, the mass of the solution was determined taking into account the weight of the dry mixer.

Next was the washing of the cell and the actual measurement. The tubes *b* and *c* were connected, 20–40 ml of solution was passed to collector *4* through cell *2* (purified air was supplied through connector *a*, valve *5* open). The mixer was detached from the cell, the solution was removed from the cell through pipe *c*, feeding air into the tube *d* of the collector. Mixer was connected to the cell again, and solution was passed through the cell while in the mixer remained a half (~250 ml) of its original amount of liquid. Valve *5* was closed and the mixer with the rest of the solution was disconnected and weighed. After 10–12 min (long enough for leveling the temperature of the solution in the cell) the conductivity meter readings were recorded. The part of the solution remained after the cell washing was used to measure the density (when the solution density after the previous dilution differed from that of water: 0.9971 kg l^{-1} at 25°C).

During the incubation of the given solution, the next solution was prepared: to a mixer was added ~ 250 ml of water through the tube *b*, mixture was stirred by shaking, the mixer with fresh solution was weighed and solution concentration was calculated. The procedure was repeated for all solutions of a conductometric series. At the end of a series the cell was washed with water to a constant L (less than 0.1 µS cm^{-1} at 25°C), filled with water and stored for the next experiment.

It is known that the conductometric cell constant depends on the resistance of the electrolyte solution in it, which leads to a distortion of data. In the region of high resistivity due to various factors lower values of conductivity of solutions are usually obtained. At low resistance and the use of smooth electrode the instrument readings are usually too high due to the effects of polarization [10, pp. 60–75]. Hence, it is desirable to determine experimentally the range of the region of linearity for each cell, where the cell constant can be considered unchanging, and the measured values of conductivity reliable.

To solve this problem, the cell was calibrated using potassium chloride as a standard substance. We used the calibration concentration dependence of the specific molar conductivity of potassium chloride Λ_{KCl} [11]. According to the calibration experiments we revealed the linear region for the cell used in this method within the range of conductivity L 0.7–1000 µS cm^{-1}, and obtained satisfactory results: σ (Λ_{KCl}) < 0.8 S cm^2 mol^{-1}. At further dilution of potassium chloride solutions we obtained underestimated values of conductivity, possibly due to the effects of stray capacitance of thermostatic water [12], or partial adsorption of ions at interfaces [13]. Therefore, at the subsequent processing of the phoreograms of substances the experimental points corresponding to L < 0.7 µS cm^{-1} were rejected if possible.

Experimental data. Below are the phoreograms as experimental points µM (L, µS cm^{-1}). In bold are shown the data used for the calculations.

4-Nitrophenol: 100100 (33.75), 51110 (24.18), 25750 (17.1), 12920 (12.04), 6513 (8.509), 3286 (6.015), **1669 (4.27), 828.2 (3), 412.8 (2.117), 203.8 (1.49), 102.3 (1.06), 52.03 (0.764), 26.36 (0.558), 13.16 (0.413).**

3-Nitrophenol: **14580 (3.352), 6108 (2.158), 2227 (1.305), 1012 (0.8833), 402.9 (0.5691), 149.1 (0.3875), 55.55 (0.29), 24.4 (0.2484), 9.703 (0.2165),** 4.364 (0.2113), 2.29 (0.2024), 1.076 (0.203).

2-Nitrophenol: **7438 (8.04), 3649 (5.624), 1837 (3.985), 913.7 (2.815), 442.9 (1.965), 226.2 (1.419), 112.7 (1.015), 56.49 (0.7353), 28.3 (0.544), 14.39 (0.4182), 7.279 (0.3402), 3.577 (0.2927), 1.821 (0.2737),** 0.883 (0.233).

Phenol: **20280 (0.636), 11180 (0.5188), 5563 (0.383), 2777 (0.3021), 1373 (0.2306), 675.7 (0.2043),** 329.3 (0.204), 157.8 (0.189), 78.08 (0.1702), 39.15 (0.1818), 19.35 (0.1581).

Succinic acid: 11700 (322.8), 5797 (223.8), 2919 (155.8), 1496 (108.4), 742.1 (73.29), **374.8 (49.33), 183.8 (31.99), 90.7 (20.3), 46.1 (12.76), 23.46 (7.806), 11.62 (4.577), 5.852 (2.69), 2.761 (1.491), 1.378 (0.8699),** 0.7075 (0.5269), 0.3541 (0.3567), 0.1766 (0.2546), 0.08561 (0.205).

Oxalic Acid: 8984 (1885), **4260 (1592), 2117 (831.9), 1071 (440), 537.2 (233.5), 280.3 (130.7), 143.1 (72.97), 75.63 (42.58), 39.16 (24.52), 21.29 (14.65), 11.03 (8.267), 5.694 (4.56),** 2.716 (2.304), 1.34 (1.217), 0.6714 (0.6967), 0.3418 (0.4446), 0.1783 (0.3222).

Maleic acid: 8531 (1885), 4303 (1311), 2121 (714.4), 1061 (380.7), **563.1 (209.6), 287.2 (109.7), 145.2 (56.31), 74.36 (29.16), 38.69 (15.32), 20.19 (8.122), 10.59 (4.374), 5.433 (2.352), 2.677 (1.268), 1.34 (0.7383),** 0.6849 (0.4957).

Phthalic Acid: 8844 (1036), 4358 (670.7), 2345 (447.4), 1234 (286.7), 661.4 (180.2), **360.3 (111.3), 193.6 (65.84), 97.14 (35.87), 49.64 (19.65), 25.96 (11.04), 13.88 (6.403), 7.111 (3.639), 3.568 (2.056), 1.863 (1.214),** 1.1 (0.8278), 0.5936 (0.5628).

Acetic acid: 31510 (293.3), 13800 (192.7), 6084 (126.9), 2644 (82.32), 1148 (52.99), 514.8 (34.34), 222.3 (21.48), **99.2 (13.36), 50.33 (8.761), 25.78**

(5.612), 13.25 (3.483), 6.531 (2.015), 3.276 (1.15), 1.664 (0.672), 0.8475 (0.415), 0.4263 (0.291), 0.214 (0.2333), 0.1091 (0.1912), 0.05541 (0.1771), 0.02733 (0.1598).

Chloroacetic acid: 7170 (1023), 3728 (673.3), **1928 (428.9), 987.3 (262.3), 509.7 (155.4), 254.4 (85.82), 128.4 (46.13), 65.55 (24.45), 32.48 (12.37), 15.44 (5.963),** 7.686 (2.999), 3.964 (1.574), 2.005 (0.8375), 1.016 (0.4821), 0.4911 (0.2985), 0.2576 (0.225), 0.1288 (0.2075).

Pivalic acid: 11940 (125.8), **6064 (89.4), 3025 (62.64), 1489 (43.37), 739.1 (30.03), 373.2 (20.83), 186.7 (14.24), 94.37 (9.681), 45.11 (6.246), 21.19 (3.871), 9.846 (2.301), 4.598 (1.326),** 2.182 (0.7614), 1.003 (0.4435).

Propionic acid: 36860 (273.7), 18450 (193.1), 9237 (136.1), 4658 (95.72), 2347 (67.06), **1194 (47.04), 602.5 (32.63), 280.3 (21.45), 144.6 (14.73), 71.81 (9.743), 36.53 (6.384), 18.22 (4.01), 9.239 (2.456), 4.718 (1.46),** 2.371 (0.84), 1.138 (0.473), 0.536 (0.286).

Benzoic acid: 8000 (263.9), 3907 (181.1), 1883 (122.4), **922.6 (82.2), 470.6 (55.67), 242.8 (37.22), 123.7 (24.06), 64.02 (15.2), 31.4 (8.869), 15.08 (4.848), 6.94 (2.448), 3.045 (1.151), 1.438 (0.596),** 0.6831 (0.339).

Triethylamine: 0 (0.201), 0.2873 (0.162), 0.6064 (0.13), 0.9256 (0.124), 1.213 (0.144), 1.564 (0.195), 1.883 (0.258), 2.234 (0.328), 2.553 (0.394), 3.191 (0.534), 3.829 (0.676), 4.498 (0.821), **5.104 (0.961), 5.774 (1.106), 6.411 (1.246), 6.985 (1.377), 7.622 (1.52), 8.291 (1.669), 8.929 (1.81), 9.566 (1.951), 10.14 (2.08), 11.57 (2.39), 12.81 (2.67), 14.15 (2.96), 15.45 (3.24), 16.73 (3.52), 19.97 (4.22), 22.96 (4.86), 26.38 (5.59), 29.14 (6.17), 32.44 (6.85),** 35.48 (7.48), 39.06 (8.21), 42.29 (8.86), 48.92 (10.18), 55.11 (11.39), 61.22 (12.56), 68.01 (13.86), 74.14 (14.995), 80.48 (16.16), 86.65 (17.275), 92.88 (18.39), 99.06 (19.48).

The data for triethylamine were obtained using different experimental technique, a description of which is beyond the scope of this article. The data were processed taking into account the dissociation of the conjugate acid of triethylamine, and the dissociation of carbonic acid in two steps. The pK_{c2} value (10.329) and $\Lambda(CO_3^{2-})$ (69.3) were taken from the literature [6].

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