

APPLICATION OF A CONDUCTOMETRIC METHOD TO RESEARCH THE PROTOLYTIC EQUILIBRIA IN ISOPROPYL ALCOHOL. SODIUM HYDROXIDE IS USED AS A TITRANT

The existing method to determine the dissociation constants of weak electrolytes using the direct conductometry and titration in aqueous solutions was successfully applied to the study in isopropyl alcohol medium. The sodium hydroxide was firstly applied as a titrant for the conductometric titration. Obtained values of dissociation constants of such electrolytes as: H_2CO_3 , $HClO_4$, $NaOH$, $NaClO_4$, $NaHCO_3$ in isopropyl alcohol allow to use them in potentiometric and spectrophotometric studies and ionic equilibria modeling in the presence of carbonic acid.

Key words:

Protolytic equilibria, isopropyl alcohol, sodium hydroxide, carbonic acid, conductometric titration.

Isopropyl alcohol (IPA) has been provoking interest of researchers as a perspective protic solvent for a long period of time. Like other alcohols, IPA has a scheme of prototropic equilibria that is similar to that of water. Due to the influence of the ionic association related to the low dielectric coefficient (permittivity) ($\epsilon=18.3$ [1]), most of the electrolytes, including salts are weak in IPA. Being a weak donor and a strong acceptor of H-bonds, IPA has a differentiating effect on acids, which results in the enlarged acidity scale with respect to the water. These properties allow to use IPA for titration of mixtures of weak organic acids [2, 3].

A number of publications is devoted to the study of the protolytic equilibria in IPA [2-6]. Usually, the potentiometric titration of the acid to be studied with tetraethyl- or tetrabutylammonium (Bu_4NOH) hydroxides was used to determine dissociation constants of weak acids. In a preliminary separate experiment, the dissociation constant for tetraalkylammonium salt of the acid was obtained using the

conductometry method. The obtained value of the salt constant was used to process potentiometric data in order to obtain the constant value of the acid.

We previously worked out the method of determining the dissociation constants for the weak electrolytes in the diluted (approx. 10^{-4} M) aqueous solutions, using the data of *direct conductometry* [7] and conductometric *titration* [8], considering the carbonic acid influence. In this present study, the above-mentioned method was used to analyze the strength of weak acids in IPA, taking into account the more complex pattern of protolytic equilibria.

It should be noted that Bu_4NOH is unstable in all solution except aqueous ones [9] and contains a significant amount of water (e. g. commercial base from Sigma-Aldrich CAS: 147741-30-8 contains 30 mol water per 1 mol reagent), i. e. the use of this reagent as a titrant may cause a change in the solvent composition during the titration process and a shifting of values of constants to be determined. In this regard, it was suggested to use easily available sodium hydroxide (NaOH) as the alkali. We failed to find any information on NaOH being either used as a titrant or its dissociation constant in IPA.

As far as we know, researchers did not give much attention to study the protolytic equilibria associated with the presence of the dissolved carbon dioxide in IPA: we failed to find any information on the dissociation constants of either carbonic acid or carbonates. Due to the contacts of solutions with the air, the carbonic acid represents a hard-to-eliminate impurity. Obviously, the air contact can be avoided by conducting measurements in a nitrogen atmosphere. However, it is inconvenient from a practical standpoint. In accordance with the goal of the research, it was necessary to develop a method accessible for a common usage. The carbonic acid reduces the degree of the dissociation of similar in strength and weaker acids, which may result in the distorted values of constants to be determined.

In view of foregoing, it was decided to carry out preliminary studies, using the conductometric titration method for determining the dissociation constants for sodium hydroxide, carbonic acid and sodium bicarbonate in dilute (approx 10^{-3} M) IPA

solutions. The obtained values of constants were supposed to be used to consider the effect of carbonic acid, while determining, through conductometric titration, the dissociation constants of weak acids and bases in IPA, as well as for spectrophotometric studies.

Method summary

To simplify the used mathematical models for the diluted solutions (up to 10^{-4} M) [7, 8], the ion mobilities was adopted to be limiting and additive, while the equilibria concentration constants were close to thermodynamic ones. Nothing but the equations of material and charge balance with the involvement of carbon acid and autoprotolysis of the solvent, within the framework of Bronsted-Lowry Theory, were used for mathematical modeling.

The titrant concentrations reached 10^{-3} M in experiments described below. However, given the significant decrease in the strength of all electrolytes under the transition from water to IPA, the ion concentration and ionic strength (I) of solutions are much lower and usually have the same order of 10^{-4} M. That is why, the above-mentioned assumptions can be considered as relevant: for a solution of the known composition, containing j ions, taking into account

$$\lambda_j \approx \lambda_j^0 \equiv \text{const}(I). \quad (1)$$

It is possible to calculate the theoretical conductivity Lt ($\mu\text{s}/\text{cm}$) as the sum of productions of individual ions mobilities by their concentrations:

$$Lt_i = 1000 \sum c_j \lambda_j, \quad (2)$$

where c_i (mol/l) and λ_i ($\text{cm} \cdot \text{cm}^2/\text{mmol}$) are concentrations and mobilities (ion conductivities) of the ions in the solution.

Through conductometric titration and direct conductometry, series of experimental points (L_i, C_i) with specific conductivity L ($\mu\text{s}/\text{cm}$) in relationship to the concentration of the added titrant C (mol/l) were obtained. Concentrations of all the types of ions c_j were calculated through mathematical modeling that took into the account the ion

balances in the particular experiment, and the theoretical specific conductivity Lt_i was represented as a function with several variables: an array of ion mobilities $\{\lambda\}$, concentrations of the titrated substance (Y_i), titrant (C), medium concentration of carbonic acid (X), an array of constants of ionic equilibria $\{K\}$:

$$Lt_i = f(\{\lambda\}, C, X, Y, \{K\}). \quad (3)$$

A series of experimental data (L_i , C_i) were processed by non-linear regression method, with the goal of obtaining the minimal values of the sum of squared relative (4) or absolute (5) deviations Ξ of the experimental L_i and theoretical Lt_i values of specific conductivity:

$$\Xi = \sum_i \left(\frac{L_i - Lt_i}{L_i} \right)^2 = f(\{\lambda\}, X, Y, \{K\}), \quad (4)$$

$$\Xi = \sum_i (L_i - Lt_i)^2 = f(\{\lambda\}, X, Y, \{K\}). \quad (5)$$

By minimizing the Ξ functions, we managed to make an estimate of the unknown values of their arguments – the dissociation constants of the weak electrolytes, ion mobilities and concentrations of the components.

Specific features of applied mathematical models

Under the formulation of mathematical models to process the conductometry data, we took into account the effect of carbonic acid, inevitably forming as a result of the carbon dioxide absorption out of the air by electrolyte solutions during their preparation, storage and experiments. Due to the greater solubility of CO_2 compared to the water [10], the concentration of carbonic acid in IPA can reach 10^{-4} M, especially if no special measures have been provided to reduce it, e. g. blow-off with the air free from carbon dioxide. Being a weak acid, it can distort the results of determining $\text{p}K_{HA}$, especially those similar in strength. Since the carbonic acid is a hard-to-eliminate impurity, to consider its effect, we used the method, earlier elaborated under the research of aqueous solutions [7, 8], while studying the dilute solutions of electrolytes in IPA. In the mathematical model to process results of experiments, the presence of X

mol/l of carbonic acid was taken into account. The value of X was considered as an unknown and was found along with the other unknown parameters while processing the experimental data.

Karl Fischer titration of IPA samples used to study protholytic equilibria showed the presence of water of ca. 0.05% (weight), or 0.02 M, i. e. 1-2 times higher than concentrations of objects of the study. Therefore the increase of the water content through the neutralization of the acids with alkalies in the process of titration was not taken into the account.

If we consider IPA as a mixed solvent (the IPA-water mixture) and Alexandrov theory [11] is applied, the ionic product K_i of the binary solvent can be represented as the sums of activities of the lyonium ions multiplied by the sums of activities of lyate ions: $K_i = (a_{\text{H}_3\text{O}^+} + a_{\text{H}_2\text{O-iPr}^+})(a_{\text{OH}^-} + a_{\text{O-iPr}^-})$. We deal here with concentration constants and cannot determine the concentration of the individual lyonium and lyate ions. Therefore, we will designate the ionic product of IPA as $K_w = [\text{H}^+][\text{OH}^-]$, bearing in mind that $[\text{H}^+]$ is the sum of the concentrations of protons, solvated by water and IPA, while $[\text{OH}^-]$ is the sum of the concentrations of products of the deprotonation of water and IPA. In accordance with the literature data [12], we assumed that $pK_w = 20.74$, and is known (fixed) in all calculations.

Under the transition from water to IPA, the formation of the mathematical model is complicated by the necessity to consider the incomplete dissociation of salts. There appear additional unknown arguments of Ξ function: constants of dissociation of salts, for instance of sodium salt NaA of weak acid HA, shall it be titrated with sodium

hydroxide: $K_{\text{NaA}} = [\text{Na}^+] \frac{[\text{A}^-]}{[\text{NaA}]}$. To calculate the ionic concentration through

mathematical modeling, it is necessary to numerically solve system of equations with the help of the iteration method, which results in the calculations to be time-consuming. The constants of sodium salts for most acids in IPA have the values of ca.

10^{-4} M, while the constants for the analyzed acids $K_{HA} = \frac{[H^+][A^-]}{[HA]}$ are several orders of magnitude weaker. The ionic concentration and specific conductivity of these mixtures are extremely weakly depend on K_{HA} . As the result, the conductometric method application is restricted for the study of acids with $pK_{HA} > 9$, although it can be used in combination with the potentiometry.

Mathematical model for the titration of carbonic acid with sodium hydroxide

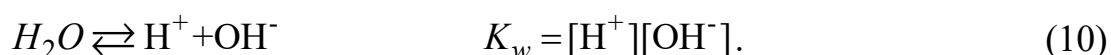
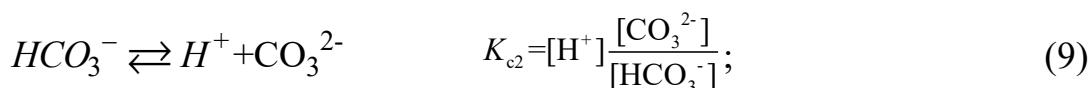
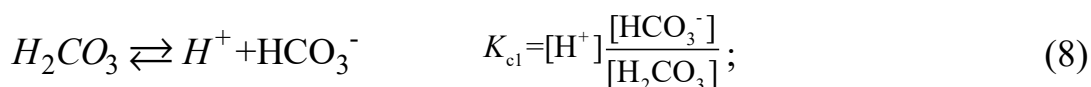
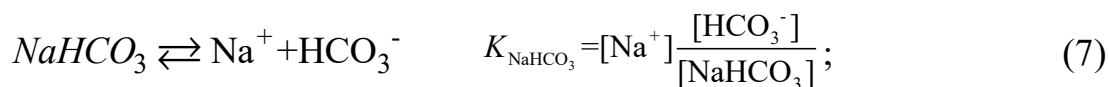
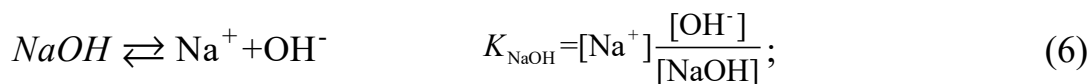
We've conducted several experiments in conductometric titration of H_2CO_3 , or the mixture of chloric and carbonic acids with sodium hydroxide.

The mathematical modeling and data processing for a more simple case are detailed below:

H_2CO_3 – is a titrated substance, with its concentration being X (mol/l);

$NaOH$ – is a titrant, with its concentration being C (mol/l);

The expression of concentration equilibrium constants considered in the model (particles $NaCO_3^-$ and Na_2CO_3 in IPA will be considered as strong electrolytes):



Material balance in sodium and carbonic acid:

$$[Na^+] + [NaOH] + [NaHCO_3] = C, \quad (11)$$

$$[\text{H}_2\text{CO}_3] + [\text{NaHCO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = X \quad (12)$$

Equation for the electroneutrality of the solution:

$$[\text{H}^+] + [\text{Na}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad (13)$$

After substituting (6)-(10) in (11) and (12) and transforming, we obtain:

$$[\text{Na}^+] = \frac{C}{1 + \frac{[\text{OH}^-]}{K_{\text{NaOH}}} + \frac{[\text{H}^+][\text{CO}_3^{2-}]}{K_{\text{NaHCO}_3} K_{c2}}} \quad (14)$$

$$[\text{CO}_3^{2-}] = \frac{K_{c1} K_{c2} X}{[\text{H}^+]^2 + \left(\frac{[\text{Na}^+]}{K_{\text{NaHCO}_3}} + 1 \right) K_{c1} [\text{H}^+] + K_{c1} K_{c2}} \quad (15)$$

Numerical solution for the set of equations (13)-(15) allows to calculate the equilibrium concentrations for all the charged particles through the values of the constants (6)-(10) and concentrations C and X:

$$\begin{aligned} [\text{H}^+] &= f_1(K_w, K_{c1}, K_{c2}, K_{\text{NaOH}}, K_{\text{NaHCO}_3}, C, X) \\ [\text{Na}^+] &= f_2(K_w, K_{c1}, K_{c2}, K_{\text{NaOH}}, K_{\text{NaHCO}_3}, C, X) \\ [\text{CO}_3^{2-}] &= f_3(K_w, K_{c1}, K_{c2}, K_{\text{NaOH}}, K_{\text{NaHCO}_3}, C, X) \end{aligned} \quad (16)$$

Lt is expressed either in terms of the ion mobility λ_i as:

$$\frac{Lt}{1000} = \lambda_{\text{H}^+} [\text{H}^+] + \lambda_{\text{Na}^+} [\text{Na}^+] + \lambda_{\text{OH}^-} \frac{K_w}{[\text{H}^+]} + (\lambda_{\text{HCO}_3^-} \frac{[\text{H}^+]}{K_{c2}} + 2\lambda_{\text{CO}_3^{2-}}) [\text{CO}_3^{2-}] \quad (17)$$

or through the sums of ion pairs mobility $\Lambda_w = \lambda_{\text{H}^+} + \lambda_{\text{OH}^-}$, $\Lambda_{\text{NaOH}} = \lambda_{\text{Na}^+} + \lambda_{\text{OH}^-}$,

$\Lambda_{c1} = \lambda_{\text{H}^+} + \lambda_{\text{HCO}_3^-}$, $\Lambda_{c2} = \lambda_{\text{H}^+} + \lambda_{\text{CO}_3^{2-}}$, taking into account Equation (13), as:

$$\frac{Lt}{1000} = (\Lambda_{\text{NaOH}} - \Lambda_w) [\text{Na}^+] + \Lambda_w \frac{K_w}{[\text{H}^+]} + (\Lambda_{c1} \frac{[\text{H}^+]}{K_{c2}} + 2\Lambda_{c2}) [\text{CO}_3^{2-}] \quad (18)$$

When processing the data with the help of the above-described model, Expressions (3)-(5) can be represented as functions:

$$Lt_i = f(\Lambda_w, \Lambda_{\text{NaOH}}, \Lambda_{c1}, \Lambda_{c2}, K_w, K_{c1}, K_{c2}, K_{\text{NaOH}}, K_{\text{NaHCO}_3}, C_i, X) \quad (3a)$$

$$\Xi = \sum_i \left(\frac{L_i - Lt_i}{L_i} \right)^2 = f(\Lambda_w, \Lambda_{\text{NaOH}}, \Lambda_{c1}, \Lambda_{c2}, K_w, K_{c1}, K_{c2}, K_{\text{NaOH}}, K_{\text{NaHCO}_3}, X) \quad (4a)$$

$$\Xi = \sum_i (L_i - Lt_i)^2 = f(\Lambda_w, \Lambda_{\text{NaOH}}, \Lambda_{c1}, \Lambda_{c2}, K_w, K_{c1}, K_{c2}, K_{\text{NaOH}}, K_{\text{NaHCO}_3}, X) \quad (5a)$$

In this case study, the minimization of the sum of squared deviations Ξ allows us to estimate the value of 9 unknown arguments (K_w was treated as determinate), including the equilibrium constants (6)-(9): K_{NaOH} , K_{NaHCO_3} , K_{c1} , K_{c2} .

Mathematical model for the titration of acid HA in the presence of carbonic acid

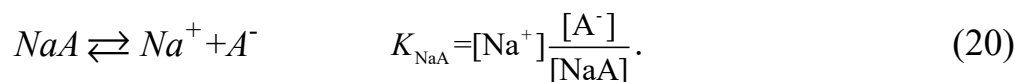
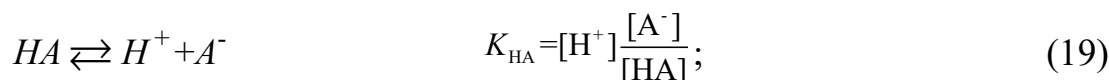
We will further provide the model for the titration of a weak acid HA, e. g. chloric acid, by sodium hydroxide in the presence of carbon acid:

HA – is a titrated acid, its concentration being Y (mol/l);

H_2CO_3 – is a hard-to-eliminate impurity with its concentration being X (mol/l);

$NaOH$ – is a titrant with its concentration being C (mol/l);

Equilibria (6)-(10) should be supplemented by incomplete dissociation of HA acid and its salt:



The equation of sodium material balance (11) acquires an additional component:

$$[Na^+] + [NaOH] + [NaA] + [NaHCO_3] = C. \quad (21)$$

The equation of acid HA material balance is added:

$$[HA] + [NaA] + [A^-] = Y. \quad (22)$$

The material balance on H_2CO_3 (12) remains the same. The equation for electroneutrality of the solution:

$$[H^+] + [Na^+] = [OH^-] + [A^-] + [HCO_3^-] + 2[CO_3^{2-}]. \quad (23)$$

After substituting (6)-(10), (19), (20) in (21), (22) and (12) and transforming, we obtain:

$$[Na^+] = \frac{C}{1 + \frac{[OH^-]}{K_{NaOH}} + \frac{[A^-]}{K_{NaA}} + \frac{[H^+][CO_3^{2-}]}{K_{NaHCO_3} K_{c2}}}, \quad (24)$$

$$[A^-] = \frac{Y}{\frac{[H^+]}{K_{HA}} + \frac{[Na^+]}{K_{NaA}} + 1}, \quad (25)$$

$$[CO_3^{2-}] = \frac{K_{c1}K_{c2}X}{[H^+]^2 + \left(\frac{[Na^+]}{K_{NaHCO_3}} + 1\right)K_{c1}[H^+] + K_{c1}K_{c2}}. \quad (15a)$$

Numerical solution for the set of equations (23)-(25) and (15) renders the equilibrium concentrations for all the charged particles per values of the constants (6)-(10) (19), (20) and concentrations C, X, Y:

$$\begin{aligned} [H^+] &= f_1(K_w, K_{c1}, K_{c2}, K_{HA}, K_{NaA}, K_{NaOH}, K_{NaHCO_3}, C, X) \\ [Na^+] &= f_2(K_w, K_{c1}, K_{c2}, K_{HA}, K_{NaA}, K_{NaOH}, K_{NaHCO_3}, C, X) \\ [A^-] &= f_3(K_w, K_{c1}, K_{c2}, K_{HA}, K_{NaA}, K_{NaOH}, K_{NaHCO_3}, C, X) \\ [CO_3^{2-}] &= f_4(K_w, K_{c1}, K_{c2}, K_{HA}, K_{NaA}, K_{NaOH}, K_{NaHCO_3}, C, X) \end{aligned} \quad (26)$$

Lt is expressed either in terms of the ion mobility λ_i as

$$\frac{Lt}{1000} = \lambda_{H^+}[H^+] + \lambda_{Na^+}[Na^+] + \lambda_{OH^-} \frac{K_w}{[H^+]} + \lambda_{A^-}[A^-] + (\lambda_{HCO_3^-} \frac{[H^+]}{K_{c2}} + 2\lambda_{CO_3^{2-}})[CO_3^{2-}]. \quad (27)$$

or through the sums of ion pairs mobility $\Lambda_w = \lambda_{H^+} + \lambda_{OH^-}$, $\Lambda_{NaOH} = \lambda_{Na^+} + \lambda_{OH^-}$, $\Lambda_{HA} = \lambda_{H^+} + \lambda_{A^-}$, $\Lambda_{c1} = \lambda_{H^+} + \lambda_{HCO_3^-}$, $\Lambda_{c2} = \lambda_{H^+} + \lambda_{CO_3^{2-}}$, taking into account Equation (23), as

$$\frac{Lt}{1000} = (\Lambda_{NaOH} - \Lambda_w)[Na^+] + \Lambda_w \frac{K_w}{[H^+]} + \Lambda_{HA}[A^-] + (\Lambda_{c1} \frac{[H^+]}{K_{c2}} + 2\Lambda_{c2})[CO_3^{2-}]. \quad (28)$$

Expressions (3)-(5) can be represented as functions:

$$Lt_i = f(\Lambda_w, \Lambda_{NaOH}, \Lambda_{HA}, \Lambda_{c1}, \Lambda_{c2}, K_w, K_{c1}, K_{c2}, K_{HA}, K_{NaOH}, K_{NaHCO_3}, C_i, X, Y), \quad (3b)$$

$$\Xi = \sum_i \left(\frac{L_i - Lt_i}{L_i}\right)^2 = f(\Lambda_w, \Lambda_{NaOH}, \Lambda_{HA}, \Lambda_{c1}, \Lambda_{c2}, K_w, K_{c1}, K_{c2}, K_{HA}, K_{NaOH}, K_{NaHCO_3}, X, Y), \quad (4b)$$

$$\Xi = \sum_i (L_i - Lt_i)^2 = f(\Lambda_w, \Lambda_{NaOH}, \Lambda_{HA}, \Lambda_{c1}, \Lambda_{c2}, K_w, K_{c1}, K_{c2}, K_{HA}, K_{NaOH}, K_{NaHCO_3}, X, Y). \quad (5b)$$

In this case the minimization of the sum of squared deviations Ξ allows us to estimate the value of 12 indeterminate arguments (K_w was treated as determinate), including the equilibrium constants (6)-(9), (19), (20): K_{NaOH} , K_{NaHCO_3} , K_{c1} , K_{c2} , K_{HA} , K_{NaA} .

Potentiometric Data Processing

In separate experiments on the titration of carbonic acid, conductometric and potentiometric data were recorded synchronously. The specific conductivity L_i and the potential difference of a pair of electrodes E_i were obtained for each concentration of the added titrant C_i . A recording glass electrode was used together with a double-chamber silver-chloride reference electrode. The electrolyte diffusion out of the inner chamber of the reference electrode into the test solution and the associated increase of the specific conductivity cannot be completely eliminated. That is why, such experiments cannot be considered as sufficiently “pure” ones.

When processing the potentiometric data, it was assumed that the theoretical difference Et of potentials is linearly dependent on the logarithm of the proton concentration (Nernst equation with unknown coefficients):

$$Et_i = E_0 + B \log([H^+]) \quad . \quad (29)$$

No buffer calibration of the electrode pair was performed. When processing the data, coefficients E_0 and B were considered as the unknown ones. In view of (16), we can put down:

$$Et_i = f(E_0, B, K_w, K_{c1}, K_{c2}, K_{NaOH}, K_{NaHCO_3}, C_i, X) \quad . \quad (30)$$

For the co-processing of conductometric and potentiometric data, the sum of squares of absolute deviations can be expressed as

$$\begin{aligned} \Xi &= \omega_L \sum_i (L_i - Lt_i)^2 + \omega_E \sum_i (E_i - Et_i)^2 = \\ &= f(E_0, B, \Lambda_w, \Lambda_{NaOH}, \Lambda_{c1}, \Lambda_{c2}, K_w, K_{c1}, K_{c2}, K_{NaOH}, K_{NaHCO_3}, X) \end{aligned} \quad (31)$$

where $\omega=1 \text{ cm}/\mu\text{s}$, and $\omega=1 \text{ mV}^{-1}$ are statistical weights, matching the dimension of the terms.

Estimated Inaccuracy of the Dissociation Constants Values

The following approach was used for estimating the inaccuracy of the obtained constants values. Let us assume that Ξ_{\min} is the minimal value of function of n arguments $\Xi(x_1, x_2, \dots, x_n)$; scatter of values of argument x_j , e. g. constant K_{c1} is to be estimated. Therefore, we minimized the sum of squared deviations for the remaining

n-1 arguments $\Xi'(x_1, \dots, x_j = \text{const.}..x_n)$ for a number of fixed values x_j (for instance, $0.05K_{cl}$, $0.2K_{cl}$, $0.5K_{cl}$, $2K_{cl}$, $5K_{cl}$, $20K_{cl}$). Such changes of argument x_j , which satisfy the inequality $\Xi'(x_1, \dots, x_j = \text{const.}..x_n) \geq \sqrt{e}\Xi_{\min}$, i.e. resulting in an increase of the value Ξ' by 1.65 times after the minimization of the remaining arguments, were taken as the upper or lower limits of the probable values range. The approach to the estimation of the inaccuracy of the parameters is empirical and lacks a convincing analytical background. However, it allows to compare and evaluate the sensitivity of a minimum value of the function Ξ to a change of its arguments.

Results and discussion

The experiments conducted in the course of the preliminary studies and the results of the experimental data processing are shown in Table 1. Concentrations of titrated substances and concentration ranges for the titrant are quoted therein. Standard deviation σ was calculated as $\sqrt{\frac{\Xi}{N-1}}$; if Ξ is expressed in absolute deviations (5a), the value in the table is marked with (abs); if Ξ is expressed through relative deviations (5a); the value is unmarked. Dissociation constant values are given together with the upper and lower limits of the “dispersion area” of value.

The results show that NaOH in IPA is a weaker (approx. 100 times) base in comparison with Bu_4NOH ($\text{p}K_{\text{Bu}_4\text{NOH}}$ 2.58 [5]). Sodium salts are also weaker electrolytes than tetrabutylammonium salts, with their values of $\text{p}K$ in IPA being in the range of 2.5...2.9 under the published data [5]. The values of $\text{p}K_{\text{NaOH}}$ (4.6, 4.7, 4.6, 4.8) obtained in four independent experiments are in accordance with each other. $\text{p}K_{\text{NaOH}}$ 4.7 can be recommended for subsequent calculations.

The hydrocarbonate constant K_{NaHCO_3} is more reliably determined through conductometric titration, with the interval of the possible values range being less than 0.4 logarithmic units. The deviance Ξ is highly dependent on the value of this constant; while the titration conductogram has a distinctive “break” at the equivalence point (the conversion of all alkali into hydrocarbonate). This fact allows to titrate

carbonic acid in IPA (in contrast to water) with a reasonable accuracy, even using the simple graphic processing of the conductogram. The high sensitivity of the method is also manifested for the dissociation constants of perchloric acid and sodium perchlorate.

The least sensitivity of the method is observed under the determination of the 1st constant of carbonic acid K_{c1} ; in a majority of experiments, substitution of pK_{c1} values from a wide range of 8 to 13 doesn't lead to a notable increase of the function Ξ in relation to Ξ_{\min} . It can be assumed that carbonic acid (at the first stage) in IPA should be weaker than acetic (pK 11.3[3, 13]) and benzoic acids (pK 11.75[5]) and stronger than 3-nitrophenol (pK 13.92[5]), as it is observed in water. The difference of pK values in water for carbonic and acetic acids is $6.35[14]-4.76[15]=1.59$. Taking into account coefficient value 1.0 of the resolution of acid strength for acetic acid derivatives in IPA with respect to water [3, 13] we get $pK_{c1} = 11.3+1.59*1.0=12.9$, with possible shift down due to better CO_2 solubility in IPA[10]. Various experiments showed pK_{c1} values from 12.1 up to 12.9, that satisfy the above-mentioned condition.

Co-processing of potentiometry and conductometry data showed a significant increase in the sensitivity of the combined function Ξ to the first carbonic acid function; the obtained value of pK_{c1} 12.4, has a relatively small "dispersion area," from 11.4 to 13.8. This result should probably be considered as the best.

The second carbonic acid constant is determined through conductometric titration with a reasonable accuracy. The value of pK_{c2} 17.3 can be adopted upon the results of the data processing of two experiments.

Considering the sums of ion pairs mobility we obtained better accuracy for A_{NaOH} , A_{HClO_4} and less accuracy for A_{c1} , A_{c2} .

Conclusion

Sodium hydroxide can be applied as a titrant for research of ionic equilibria in IPA by conductometric titration, instead of commonly used Bu_4NOH . Reported

dissociation constants are connected with presence of traces of carbonic acid in solvent and should be valuable in future research. Developed mathematic model can be used for processing experimental data of weak acids and bases titration in the presence of carbonic acid. The obtained results allow to reduce the number of the unknown values in processing conductometric titration data for determining the constants of weak acids and bases in IPA, with using NaOH и HClO₄ as titrants. We subsequently used the fixed values of carbon acid constants (pK_{c1} 12.4 pK_{c2} 17.3), while the medium concentration of carbonic acid X was considered as the unknown value for each experiment. Other parameters were fixed in a narrow range of values e. g.

$$pK_{NaOH}=4.6\pm 0.5, pK_{NaHCO_3}=4.4\pm 0.1, \Lambda_{NaOH}=35\pm 8.$$

The experimental procedure.

The purification of substances and solvent

IPA of “chemically pure (CP)” grading, being additionally purified with the help of ion-exchange resins used to deionize the water, was used to prepare solutions: several grams of cation exchange resin (KU-2-8 chs) and anion exchange resin (AV-17-8 chs), flushed several times with IPA to remove excess water, were added to 1 l of alcohol and had been stirred for 12 hours. The conductivity of the purified IPA was in the range of 0.001..0.003 $\mu\text{s}/\text{cm}$. The water content in the solvent didn't exceed 0.06% to the mass, it was determined by Karl Fischer titration using the Expert-007 (Ekros, St. Petersburg) device.

For the removal of carbon dioxide from the water and for obtaining de-ionized water, Vodoley-M (NPP Khimelektronika, Moscow) was used, as described in [7, 8].

Sodium hydroxide and perchloric acid of “chemically pure (CP)” grade were used without additional purification.

Weighing and density measurement

Gravimetric method was used for preparing the solutions. Small (up to 80 g) quantities of the substances and solutions were weighed on the SARTOGOSM MV-210-A analytical scale balance (sensitivity 0.01 mg). AND GX-1000 balance (with its

sensitivity being 1 mg) was used to weight large (up to 1100 g) objects.

To measure the density of the solutions, the automatic ultrasonic density meter DA-500 (Kyoto, Japan) was used, with the absolute accuracy being ± 0.0001 kg/l. Density measurements were used to re-calculate the mass concentrations (mol/kg) into the volume ones (mol/l).

Instrument and setup

InoLab Cond 740 (WTW GmbH) conductivity apparatus together with LR 325/001 dip-type cell was used to measure the specific conductivity of the solutions. The cell has two electrodes and built-in temperature sensor, with electrodes in a form of coaxial stainless-steel cylinders. The cell constant is $0.0100 \text{ cm}^{-1} \pm 2 \%$. ATP-02 (ZAO Akvilon, St. Petersburg) autotitrator was used to secure an accurate titrant dosage. UTU ZN-68 (Poland) ultra-thermostat was used to maintain the measurement temperature within the range of $25.00 \pm 0.05^\circ\text{C}$.

The experimental setup is described in detail in [7]. The conductometry cell 1 (Fig. 1) was tightly inserted into the large neck 3 of the 250 ml polypropylene mixing tank 2, equipped with two additional necks 4 (5 mm in dia.) and the anchor of the mounted magnetic stir bar 5. The necks 4 could be plugged hermetically. The smaller necks 4 were used for introducing the solutions of the titrated substance and the titrant, and, if necessary, to inlet and outlet the air free from carbon dioxide. Thus the solutions of the tested substances were isolated from the atmospheric air before and throughout the titration, and the concentration of the carbonic acid throughout the experiment could be taken for a constant.

Operation sequence

To reliably remove all traces of electrolytes after each experiment, the mixing tank and the cell were cleansed 4-5 times with de-ionized water, and then inserted into the deionizer circuit [7], to be washed until the conductivity of the circulating water reached the range of $0.06..0.07 \mu\text{s/cm}$ (25°C). After cleansing and water discharge, the cell was extracted from the mixing tank, and both were dried in the hot air flow.

Cleaned and dried, the mixing tank 2 (Fig. 1) was weighed, filled with purified

IPA and weighed again. With the weight of the empty mixing tank being known, the weight of the solvent was determined (usually 170-180 g). After that, the conductometric cell 1 was inserted into the big neck 3 of the mixing tank 2, the small necks 4 were plugged, and the solution was thermostated for 20-40 min, stirred constantly; conductivity of the solvent was controlled at 25°C, the value normally reaching 0.001..0.003 $\mu\text{s}/\text{cm}$.

If needed, carbonic acid was blown off out of the solvent: a fluoroplastic tube was inserted into the neck 4 of the mixing tank 2, with its end positioned halfway down the column of fluid or lower, and the purified air was bubbled for 15-20 min, with the air being re-introduced into the purification system through the second neck.

For the conductometry titration experiments, a sample weigh of the mother solution (with its concentration being approx. 0.01..0.04 M) of the titrated substance inserted through a neck 4 of the mixing tank using a polypropylene injector. , in order to achieve, taking into the account the weight of the solvent, the required (approx. 10^{-4} M) concentration Y in the mixing tank. Under the titration of carbonic acid, 1 ml of gasiform CO_2 , obtained before the experiment by the thermal decomposition of sodium bicarbonate and collected in a small gas-meter above the water, was injected under the liquid layer. After the introduction of the weighed solution, the conductometer readings were expected to stabilize for several minutes.

The solution of the titrant was prepared in a separate container, isolated from the ambient air, and then charged into the dispenser of the autotitrator. The dispenser was calibrated before the conductometric analysis and upon its completion, weighing ~ 10 ml of solution squeezed out of the dispenser until the stability of the mass/volume ratio within the range of 0.0005 g/ml. The titrator dispenser was thermostated simultaneously with the conductivity cell.

Shall stable values of the solution conductivity of the titrated substance (or a solvent in the experiments of the direct conductometry) being achieved, a capillary tube, connected to the dispenser, was introduced into the small neck of the mixing tank. Further, the titrator control was launched. This program secured the addition of a

titrant solution in small portions (about 0.1 ml), equilibrating for 1..2 minutes to stabilize the readings of the conductometer and recording of the values of the specific conductivity depending on the added volume of the titrant solution. The concentration of titrant at each point was calculated from the added volume, with reference to the known weight of all the components. 50 to 150 experimental points were obtained in one experiment over 1-3 hours, while stirring in a mixing tank and under the active thermostat. After the experiment was completed, the density of the solution in the mixing tank was measured (density value was used to calculate the concentrations of the titrant). After that, the mixing tank and the cell were cleansed as described above.

For potentiometry measurements, a separate mixing tank was used, similar to the one described above, but with the additional inlets for the electrodes. The glass electrode ES 10308 (Aquilon) and the two-chamber silver chloride reference electrode OP-0820P (Radelkis) were inserted tightly into inlets of the mixing tank, and thus both the conductivity and the voltage differential could be registered simultaneously. The registration time for one experimental point was 10 minutes. The saturated solution of KCl in IPA and a pure solvent with a small amount of ion-exchange resins (used for the additional purification of IPA, see above) were introduced in the inner and outer chambers of the reference electrode, respectively.

References

1. *Reichardt C.* Solvents and Solvent Effects in Organic Chemistry. Weinheim: WILEY-VCH Verlag GmbH, 2003. 609 p.
2. *Bosch E., Rafols C., Roses M.* Ionic Equilibria in Neutral Amphiprotic Solvents: Structural Effects on Dissociation Constants of Several Substituted Phenols and Mercaptopyrimidines in Isopropyl Alcohol // *Talanta*. 1989. Vol. 36. N. 12. P. 1227-1231. doi 10.1016/0039-9140(89)80054-2
3. *Chantooni M.K., Kolthoff I.M.* Resolution of Acid Strength in *tert*-Buthyl Alcohol and Isopropyl Alcohol of Substitued Benzoic acids, Phenols, and Aliphatic Carboxylic Acids // *Anal. Chem.* 1979. Vol. 51. N. 1. P. 133-140. doi 10.1021/ac50037a039
4. *Chantooni M.K., Kolthoff I.M.* Proton Solvation in the Lower Aliphatic Alcohols with Emphasis on Isopropyl and *tert*-Buthyl Alcohols // *J. Phys. Chem.* 1978. V. 82. N. 9. P. 994-1000. doi 10.1021/j100498a006
5. *Bosch E., Rafols C., Roses M.* Variation of acidity constants and pH values of some organic acids in water-2-propanol mixtures with solvent composition. Effect of preferential solvation // *Anal. Chim. Acta*. 1995. Vol. 302. P. 109-119. doi 10.1016/0003-2670(94)00435-O
6. *Bosch E., Rodes C., Roses M.* Dissociation Constants of Some Anti-Inflammatory Agents (α -Phenylpropionic Acids) in Isopropyl and *tert*-Butyl Alcohol media // *Electroanalysis*. 1991. Vol. 3. P. 365-370. doi10.1002/elan.1140030420
7. *Selitrenikov A.V., Zevatskii Yu.E.* Study of acid-base properties of weak electrolytes by conductometric titration // *Russ. J. of Gen. Chem.* 2015. Vol. 85. P. 7–13. doi 10.1134/S1070363215010028
8. *Zevatskii Yu.E., Selitrenikov A.V.* Conductometry of solutions of very weak electrolytes and dibasic acid solutions // *Russ. J. of Gen. Chem.* 2013. Vol. 83. P. 884–892. doi10.1134/S1070363213050022
9. *Marple L.W., Fritz J.S.* Potentiometric Studies of the Titration of Weak Acids with Tetrabutylammonium Hydroxide // *Anal. Chem.* 1962. Vol. 34. N. 7. P. 796-800. doi 10.1021/ac60187a025

10. *Tokunaga J.* Solubilities of Oxygen, Nitrogen, and Carbon Dioxide in Aqueous Alcohol Solutions // *J. Chem Eng. Data.* 1975. Vol. 20. N. 1. P. 41-46. doi10.1021/je60064a025
11. Alexandrov V. V. *Acidity of the Non-Aqueous Solutions.* Kharkiv: Vysshaya Shkols, 1981, 152 p.
12. *Roses M., Rafols C., Bosch E.* Autoprotolysis in Aqueous Organic Solvent Mixtures // *Anal. Chem.* 1993. Vol. 65. N. 17. P. 2294-2299. doi 10.1021/ac00065a021
13. *Bosch E., Roses M.* Ionic Equilibria in Neutral Amphiprotic Solvents: Resolution of Acid Strength in tert-Buthyl Alcohol. // *Talanta.* 1989. Vol. 36. N. 6. P. 627-632. doi 10.1016/0039-9140(89)80253-X
14. *Harned H.S. Bonner F.T.* The First Ionization of Carbonic Acid in Aqueous Solutions of Sodium Chloride. // *J. Am. Chem Soc.* 1945. Vol. 67. N.6 P. 1026-1031. doi 10.1021/ja01222a037
15. *Lange's Handbook of Chemistry* / Edited by J.A. Dean. McGraw-Hill Professional, 15th Edition (October 30, 1998), 1424 pp.

Table 1. Examples of experimental data processing.

Titrated substance (concentration Y, mol/l)	Titrant (end concentration C, mol/l)	σ	Calculated parameters and “dispersion area” of values
Conductometric titration			
HClO ₄ (1.01×10 ⁻⁵) H ₂ CO ₃ (1.91×10 ⁻⁴)	NaOH (9.7×10 ⁻⁴)	1.71×10 ⁻³ (abs) 1.71×10 ⁻³ (abs)	pK_{c1} 12.1 ^{+1.8} _{-4.2} , pK_{NaOH} 4.6 ^{+0.3} _{-0.3} , pK_{c2} 17.3 ^{+1.0} _{-0.6} A_{NaOH} 31 ⁺⁷ ₋₁₂ *, A_{c1} 29 ⁺⁷ ₋₂ *, A_{c2} 16 ⁺²¹ ₋₃ *
H ₂ CO ₃ (1.62×10 ⁻⁴)	NaOH (9.3×10 ⁻⁴)	1.86×10 ⁻³ (abs) 1.86×10 ⁻³ (abs) 1.87×10 ⁻³ (abs)	pK_{c1} 12.5 ^{+1.5} _{-5.0} pK_{NaOH} 4.7 ^{+0.5} _{-0.3} pK_{NaHCO3} 4.46 ^{+0.06} _{-0.07}
HClO ₄ (4.79×10 ⁻⁴) H ₂ CO ₃ (1.99×10 ⁻⁴)	NaOH(1.48×10 ⁻³)	3.25×10 ⁻⁴ 3.26×10 ⁻⁴ 3.40×10 ⁻⁴	pK_{c1} 12.9 ^{+2.1} _{-5.5} pK_{c2} 17.3 ^{+0.2} _{-0.2} A_{NaOH} 39 ⁺¹ ₋₃ *, A_{HClO4} 35.5 ⁺³ _{-0.5} *, A_{c1} 24 ⁺¹² ₋₂ *, A_{c2} 74 ⁺⁴ ₋₇₂ *
HClO ₄ (4.71×10 ⁻⁴) H ₂ CO ₃ (~10 ⁻⁵)	NaOH (1.55·10 ⁻³)	2.65×10 ⁻⁴ 2.66×10 ⁻⁴ 2.65×10 ⁻⁴ 2.66×10 ⁻⁴	pK_{NaClO4} 3.47 ^{+0.3} _{-0.07} pK_{HClO4} 3.01 ^{+0.3} _{-0.03} pK_{NaOH} 4.6 ^{+0.2} _{-0.1} A_{NaOH} 33 ⁺³ ₋₃ *, A_{HClO4} 38 ⁺³ ₋₁ *
H ₂ CO ₃ (2.24×10 ⁻⁴)	NaOH (6.55·10 ⁻⁴)	2.89×10 ⁻³ (abs) 2.91×10 ⁻³ (abs) 2.91×10 ⁻³ (abs) 2.91×10 ⁻³ (abs) 3.05×10 ⁻³ (abs)	pK_{c1} 12.6 ^{+1.5} _{-4.9} pK_{NaOH} 4.8 ^{+0.3} _{-0.3} pK_{NaHCO3} 4.42 ^{+0.15} _{-0.1} A_{NaOH} 39 ⁺¹ ₋₃ * A_{c1} 50 ⁺¹⁰ ₋₁₅ *, A_{c2} 45 ⁺¹⁰ ₋₂₅ *
H ₂ CO ₃ (2.18×10 ⁻⁴)	NaOH (1.20×10 ⁻³)	1.94×10 ⁻³ (abs)	pK_{c1} 12.8 ^{+1.5} _{-5.0}
Conductometric and potentiometric titration, co-processing			
H ₂ CO ₃ (2.18×10 ⁻⁴)	NaOH (1.20·10 ⁻³)	1.03×10 ⁻³ (abs)	pK_{c1} 12.4 ^{+1.4} _{-1.0}

(*) (values of ion mobility sums calculated assuming fixed $pK_{c1}=12.4$, $pK_{c2}=17.3$).

Illustrations

Figure 1. The cell and the mixing tank.

