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NON-TRIVIAL BEHAVIOR OF THE ACID-BASE BALANCE OF PURE WATER NEAR THE TEMPERATURE OF ITS DYNAMIC PHASE TRANSITION

The acid-base balance (pH) of distilled water at temperatures (35.0; 40.0; 42.0; 45.0) °C depending on the time passed since the production of distillate is experimentally investigated. In the zero approximation, the time dependences of the acid-base balance of distilled water could be approximated by the exponential law. It is taken into account that the decrease in pH over time occurs, when water comes into contact with atmospheric air. As a result, carbon dioxide dissolves in water. In a vicinity of the Bulavin–Malomuzh temperature of 42 °C, the significant oscillations of the pH values of water during measurements are observed, which allows us to obtain only the average pH values. The time dependence of the change in the acid-base balance of distilled water at a temperature of 42 °C is approximated by a linear dependence. It is noted with some reservations that the temperature dependence of the coefficient of determination (R^2) on the exponential approximation of the time dependences of the change in the acid-base balance of distilled water may have a minimum close to the Bulavin–Malomuzh temperature.

Keywords: pure water, acid-base balance, carbon dioxide, dynamic phase transition.

1. Introduction

The acid-base balance (pH) is calculated as the negative decimal logarithm of the hydrogen ion concentration and, by definition, equals

$$\mathrm{pH} = -\lg\left[\mathrm{H}^+\right]. \quad (1)$$

It is assumed that the acid-base balance of extremely dilute neutral aqueous solutions is equal to 7.0. The addition of an acid leads to an increase in the concentration of hydrogen ions and a decrease in pH, whereas the addition of an alkali – to a decrease in the concentration of hydrogen ions and an increase in pH. It seems clear that the pH value is not an additive value of the concentration of acids or alkalis, as experimentally demonstrated in [1].

In [2, 3], the temperature dependence of the acid-base balance of pure water in the interval (25–50) °C was presented. It is shown that the acid-base balance of pure water decreases linearly from pH 7.0 at 25 °C to pH 6.65 at 50 °C. Definitely, theoretical calculations of the acid-base balance of pure distilled water show that its pH should be equal to 7.0 at 25 °C. However, in experimental measurements researchers manifest the value of the acid-base balance of pure water, which is much lower than pH 7.0 [4, 5]. Among the causes for the discrepancy between the theoretically calculated and experimentally measured values of the acid-base balance of pure distilled water, which can affect the pH of distilled water, is the

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presence of impurities, including salts, metals, and volatile organic compounds. Nevertheless, the dissolution of atmospheric carbon dioxide in water tends to be the crucial cause for a significant pH level decrease for distilled water. This problem has been studied only at certain temperatures (e.g., at 18, 25, and 38 °C in [6]). The mechanism and kinetics of changes in the acid-base balance of pure water and aqueous solutions due to the dissolution of carbon dioxide in water remain poorly understood.

The aim of this research is to study the behavior of the acid-base balance of pure water in a vicinity of a temperature of 42 °C. It Is shown in [7–13] that, at a temperature of 42 °C, the dynamic phase transition in pure water takes place – a significant change in the thermal motion of water molecules and a redistribution of hydrogen bonds occur. Since the first investigation of this phenomenon belongs to the authors of [7, 8], the temperature of 42 °C will be marked hereinafter as the Bulavin–Malomuzh temperature (T_{BM}). Because the dynamic phase transition affects the physical properties of pure water, it should also affect the value of the acid-base balance and the time dependence of the pH of pure water in a vicinity of T_{BM}.

2. Experimental Part

Experimental measurements of the acid-base balance were performed at temperatures (35.0; 40.0; 42.0; 45.0) °C ((308, 313, 315, 318) K). The thermostatic control was provided by the UTU-10 thermostat (Krakow, Poland) with the accuracy equal to ±0.1 K. Freshly made twice distilled water was used.

The acid-base balance was measured according to the current IUPAC recommendations [14] using an AZ Bench Top Water Quality Meter 86505 (AZ Instrument Corp., Taiwan) with a temperature-sensitive probe. The total relative error of pH measurement was determined to be 0.5% [15]. Before the measurements, the pH meter was calibrated with the use of reference buffer solutions with acid-base balance of 4.0 and 7.0.

3. Time Dependences of the Acid-Base Balance of Pure Water

We assume that the acid-base balance of pure distilled water is 7.0 at 25 °C. However, in experimental measurements, researchers indicate the pH of pure water, which is much less than 7.0 [4, 5]. Numerous studies identify the dissolution of the atmospheric carbon dioxide in water as the main cause for a decrease in the pH level of distilled water. Carbon dioxide is approximately 0.036% of the atmosphere, and the partial pressure of carbon dioxide in the atmospheric air is $\mathrm{p_{CO_2}} = 0.0003$ atm. The solubility of $\mathrm{CO_2}$ in water at the atmospheric pressure and a temperature of 25 °C is approximately 0.034 mol/l [16]. Nearly 0.1% of the dissolved carbon dioxide is converted to carbonic acid, which dissociates into hydrogen ion and bicarbonate:

$$\mathrm{CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-}. \qquad (2)$$

Next, the bicarbonate dissociates to the carbonate, releasing a second hydrogen ion:

$$\mathrm{HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}}. \qquad (3)$$

Thus, the interaction of distilled water with the atmospheric air leads to a decrease in pH, i.e. the concentration of hydrogen ions increases, and the pH decreases.

According to [17], the equilibrium value of the acid-base balance of water in contact with the atmospheric air is about pH 5.6. The evaluation of the values of the acid-base balance of distilled water with dissolved carbon dioxide leads to pH values of 5.64 at 20 °C [18] and pH 5.65 at 25 °C [16, 19]. Attempts to take into account as much as possible the factors that may affect the pH were performed in [4], which offers the value of pH 5.62 for carbon dioxide-saturated distilled water at a temperature of 20 °C and the normal atmospheric pressure.

In [17], it was shown that the solubility of carbon dioxide in water in contact with the atmospheric air does not obey Henry's law. According to Henry's law, at a constant temperature, the solubility (concentration) of a gas in a liquid is directly proportional to the pressure of this gas over the solution. One of the causes for a deviation from Henry's law is the reaction of the dissolved gas with a liquid. Indeed, for partial pressures of carbon dioxide less than $\mathrm{p_{CO_2}} = 0.0005$ atm, a deviation from Henry's law is due to the fact that a part of the dissolved gas turns into the form of bicarbonate ions due to reactions (2) and (3) [17].

In addition, under the atmospheric air conditions, the solubility of carbon dioxide decreases nonlinearly

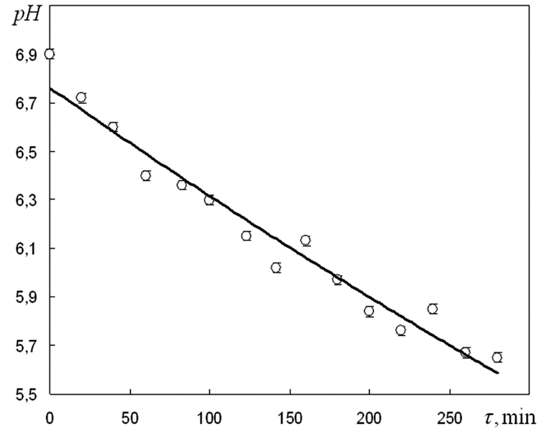

Fig. 1. Time dependence of the acid-base balance of twice distilled water at a temperature of 35.0 °C

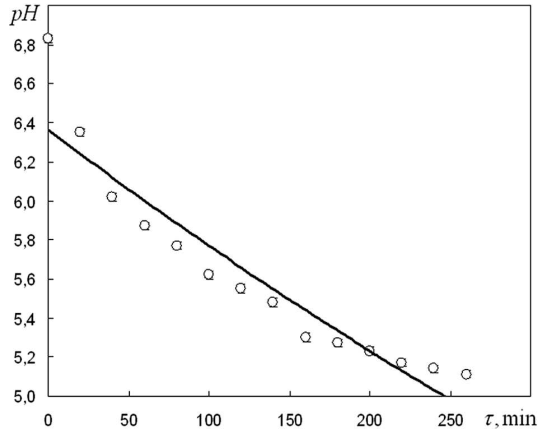

Fig. 2. Time dependence of the acid-base balance of twice distilled water at a the temperature of 40.0 °C

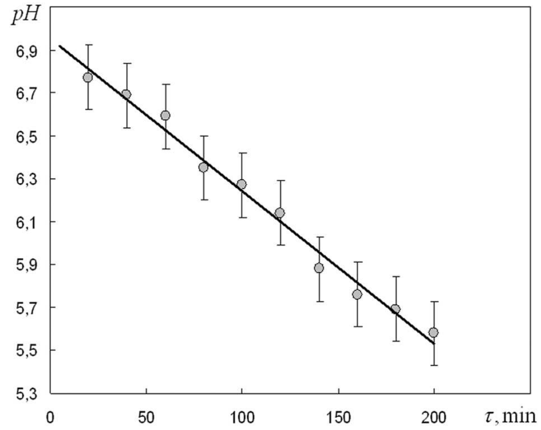

Fig. 3. Time dependence of the acid-base balance of twice distilled water at a temperature of 42.0 °C

from 0.30 cm^3/l at 25 °C to 0.20 cm^3/l at 50 °C [17]. It is easy to see that there are 3300 molecules of water per one CO_2 molecule in pure water at a temperature of 25 °C, whilst it is 5000 molecules of water per one CO_2 molecule in pure water at a temperature of 50 °C. This suggests that the acid-base balance of pure water in contact with the atmospheric air should decrease with the temperature growth.

In [20, 21], the solubility of oxygen in aqueous solutions of ethyl alcohol has a peculiarity at temperatures $T < 50$ °C and low concentrations of ethanol $x_{\mathrm{EtOH}} < 0.2$: oxygen solubility is nonmonotonic. However, at the temperature $T = 50$ °C, the solubility isotherm decreases monotonically to concentrations $x_{\mathrm{EtOH}} < 0.2$. At lower ethanol concentrations, the solubility of oxygen remains almost constant and is equal to the solubility in pure water. It remains unclear whether such behavior is inherent in the solubility of carbon dioxide in water.

The results of studies of the acid-base balance of twice distilled water at the temperatures (35.0; 40.0; 42.0; 45.0) °C depending on the age of the solution are given in Figs. 1–4. It is shown that the time dependence of the logarithm of the acid-base balance of twice distilled water at the temperatures (35.0; 40.0; 45.0) °C is approximated well by a linear dependence.

In the zero approximation, the time dependences of the acid-base balance of distilled water are approximated by exponential dependences:

$$\mathrm{pH}(t) = A \exp\left(-\frac{t}{\tau}\right), \tag{4}$$

where A is the pH value of pure water at the initial time moment, t is the time that has passed since the preparation of the distillate, τ is the relaxation time of the acid-base balance of pure water. The results of calculations are presented in Table.

It is worth mentioning that the coefficient A in Eq. (4) corresponds to the initial value of the acid-base balance in pure water at the listed temperatures. The coefficient A decreases linearly from pH 7.0 at 25 °C to pH 6.65 at 50 °C [2, 3].

Figure 5 presents the temperature dependence of the coefficient of determination R^2 in the exponential approximation of the time dependences of changes in the acid-base balance of distilled water. In Fig. 3, the time dependence of a change in the acid-base balance of distilled water is approximated by a linear relation. Therefore, the calculation of the coefficient R^2

is not correct at the temperature $T_{\mathrm{BM}} = 42$ °C. With some reservations due to the limited experimental data, we mention that the dependence in Fig. 5 may have a minimum close to the Bulavin–Malomuzh temperature 42 °C.

The coefficient of determination R^2 is a statistical value that shows how the obtained experimental data confirm the proposed model. The true coefficient of determination of the model of the dependence of the random variable y on the factors x is determined as follows:

$$R^2 = 1 - \frac{\sigma^2}{\sigma_y^2}, \tag{5}$$

where σ^2 is the variance of the model error (conditional variance on factors x), σ_y^2 is the variance of the random variable y [22]. In our study, the coefficient of determination R^2 numerically shows what part of the time variation of the acid-base balance is explained by model (4):

$$R^2 = 1 - \frac{\sum\limits_{i=1}^{n} (y_i^{\exp} - y_i^{\mathrm{calc}})^2}{\sum\limits_{i=1}^{n} (y_i^{\exp} - \bar{y})^2}, \tag{6}$$

$$\bar{y} = \frac{1}{n} \sum_{i=1}^{n} y_i^{\exp}, \tag{7}$$

where $y_i^{\exp}$ is the experimental value of the acid-base balance, y_i^{calc} is the value of the acid-base balance calculated by formula (4).

During the acid-base balance measurements of twice distilled water at a temperature of 42.0 °C, the device readings were unstable: there was a constant fluctuation of pH ±(0.15–0.20) units around certain average values. They are presented in Fig. 3 with corresponding errors. The last peculiarity of the acid-base balance of distilled water reveals itself only in the narrow temperature interval (41÷43) °C.

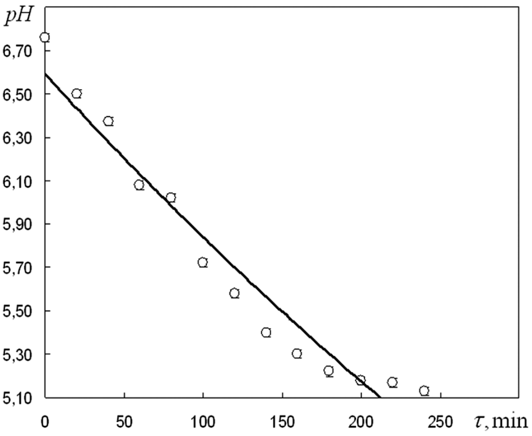

Fig. 4. Time dependence of the acid-base balance of twice distilled water at a temperature of 45.0 °C

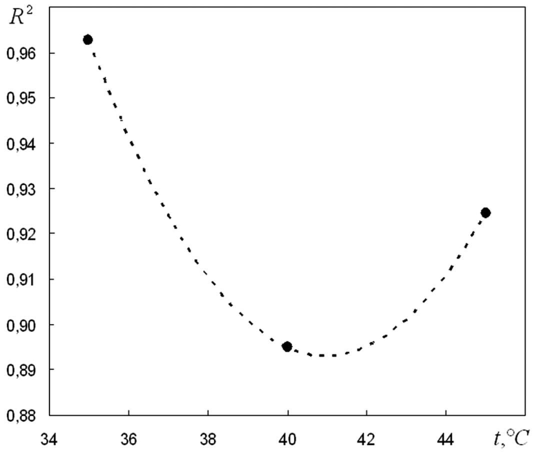

Fig. 5. Temperature dependence of the coefficient of determination R^2 by the exponential approximation of the time dependences of the acid-base balance change for distilled water. The dashed line demonstrates a probable temperature dependence of the coefficient of determination R^2 in the exponential approximation of the time dependences of a change in the acid-base balance of distilled water

Calculation of constant values from Eq. (4)

T, °C	A	τ, min
35.0	6.912	1465
40.0	6.834	1021
45.0	6.758	982

4. Peculiarities of the Acid-Base Balance of Distilled Water near the Temperature 42.0 °C

In [7, 8, 11, 13, 23], it was shown that, in water near the temperature 42.0 °C, there is a significant change in the thermal motion of molecules: the oscillating motion of a crystal-like type turns into a continuous thermal drift of the argon-like type. Works [7, 8, 11, 13, 23] imply that such change occurs in a relatively narrow temperature interval, which allows us to interpret it as a dynamic phase transition in the system. Conclusions about the presence of a dynamic phase transition in pure water are made on the base of the analysis of the temperature dependences of, especially, 1) the residence time of water molecules [11]; 2) kinematic viscosity of water [24]; 3) the entropy on the liquid-vapor coexistence curve for water [7]; 4) the dipole relaxation time for water molecules [25].

This transition corresponds to a significant change in both the translational and rotational modes of molecular motions, which are closely related to changes in the properties of the network of hydrogen bonds. Nearby, a network of hydrogen bonds is transformed into a collection of small short-lived molecular associates.

Note that the most important elements in the structure of hexagonal ice are rings of six water molecules formed by hydrogen bonds. During the transition to liquid water, the density of such rings changes by leaps and bounds and continues to decrease with a further increase in the temperature [25]. However, in the supercooled region, their density increases with the degree of supercooling. We can assume that, at temperatures above 42.0 °C, hexagonal rings do not occur in water at all.

5. Conclusions

Thus, the acid-base balance of twice distilled water at temperatures of $(35.0; 40.0; 42.0; 45.0)$ °C depending on the time passed since the production of distillate has been experimentally investigated. The sensitivity of the acid-base balance of pure water to the temperature of its dynamic phase transition is shown: at the Bulavin–Malomuzh temperature 42.0 °C, there are significant oscillations of the acid-base balance of pure water during measurements, which allowed us to obtain only average pH values.

In the zero approximation, the time dependences of the acid-base balance of distilled water could be approximated by the exponential law. It is taken into account that a decrease in pH over the time occurs, when water comes into contact with the atmospheric air. As a result, carbon dioxide dissolves in water. The time dependence of the change in the acid-base balance of distilled water at a temperature of 42.0 °C is approximated by a linear dependence. It is noted with some reservations that the temperature dependence of the coefficient of determination R^2 in the exponential approximation of the time dependences of the change in the acid-base balance of distilled water may have a minimum close to the Bulavin–Malomuzh temperature. Therefore, the R^2 coefficient should be considered as one of an identifier of the dynamic phase transition in water.

The next step will be to study the acid-base balance of saline, i.e. 0.9 wt.% aqueous sodium chloride solution. After all, to correctly interpret the causes for changes in the pH of saline, one needs to understand the effect of atmospheric carbon dioxide on the acid-base balance of pure water.

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НЕТРИВІАЛЬНА ПОВЕДІНКА ПОКАЗНИКА КИСЛОТНО-ЛУЖНОГО БАЛАНСУ ВОДИ ПОБЛИЗУ ТЕМПЕРАТУРИ ЇЇ ДИНАМІЧНОГО ФАЗОВОГО ПЕРЕХОДУ

Експериментально досліджено показник кислотно-лужного балансу (pH) двічі дистильованої води за температур (35,0; 40,0; 42,0; 45,0) °C залежно від часу, який пройшов із моменту виготовлення бідистиляту. У нульовому наближенні залежності показника кислотно-лужного балансу дистильованої води від часу можуть бути апроксимовані експоненційним законом. Враховано, що зменшення pH із часом відбувається при контакті води з атмосферним повітрям, унаслідок чого у воді розчиняється вуглекислий газ. За температури Булавіна–Маломужа 42 °C спостережено значні осциляції значень показника кислотно-лужного балансу води протягом вимірювань, що дозволяє отримати тільки усереднені значення pH. Залежність зміни показника кислотно-лужного балансу дистильованої води від часу за температури 42 °C апроксимується лінійною залежністю. Із певними застереженнями відзначено, що температурна залежність коефіцієнта детермінації R^2 за експоненційної апроксимації часових залежностей зміни показника кислотно-лужного балансу дистильованої води може мати мінімум, близький до температури Булавіна–Маломужа.

Ключові слова: вода, показник кислотно-лужного балансу, вуглекислий газ, динамічний фазовий перехід.