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INFLUENCE OF ATMOSPHERIC CARBON DIOXIDE ON THE ACID-BASE BALANCE IN AQUEOUS SODIUM CHLORIDE SOLUTIONS

The influence of atmospheric carbon dioxide (CO₂) on the acid-base balance (pH) in dilute aqueous solutions of sodium chloride (NaCl) at the concentrations corresponding to 540, 675, 900, and 1620 water molecules per sodium or chlorine ion has been studied in a temperature interval of 294–323 K. The pH relaxation time in aqueous NaCl solutions with dissolved atmospheric CO₂ and the corresponding temperature and salt-concentration dependences are calculated. The similarity of the temperature behavior of the pH relaxation times in NaCl solutions with various salt concentrations is demonstrated. To clarify the nature and features of this phenomenon, the corresponding Debye radii are calculated, and it is shown that the electrostatic interaction does not play a decisive role in the examined solutions, thus not affecting appreciably the molecular processes. An attempt is made to construct a rigorous theoretical substantiation of the mechanisms driving the establishment of the pH equilibrium in pure water and in water contacting with atmospheric CO₂. The calculation results obtained using the derived formula correlate well with experimental results. Atmospheric CO₂ is proved to have a significant effect on the change of pH in water and aqueous NaCl solutions.

Key words: aqueous solution, sodium chloride, acid-base balance, carbon dioxide, relaxation time.

1. Introduction

This work is devoted to the study of the acid-base balance in dilute aqueous solutions of sodium chloride (NaCl), if atmospheric carbon dioxide (CO₂) is dissolved in them.

The acid-base balance (pH) in pure distilled water equals 7.0 at 25 °C. However, when reporting the results of experimental measurements, values much lower than pH 7.0 were indicated [1, 2]. The main reason for a substantial reduction of pH in pure water is

considered to be the dissolution of atmospheric CO₂ in it. According to work [3], the equilibrium value of the acid-base balance in water contacting with atmospheric air is equal to about pH 5.6. The evaluation of the acid-base balance in distilled water with dissolved CO₂ led to values of pH 5.64 at 20 °C [4] and pH 5.65 at 25 °C [5,6]. An attempt to account for all factors affecting pH was made in work [1], where the acid-base balance in distilled water saturated with CO₂ at a temperature of 20 °C and at the normal atmospheric pressure was proposed to be taken equal to pH 5.62. Experimentally, the problem was studied only at certain temperatures (see, for example, works

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[7, 8]). However, the peculiarities in the behavior of the acid-base balance in water and aqueous solutions stemming from the dissolution of CO_2 in water remain poorly studied.

The presence of NaCl in water decreases the pH of the solution [6, 9, 10]. First of all, the addition of salt leads to a rather appreciable reduction in the stability of water molecules because of the non-uniform field of ions. The reduction of the stability of CO_2 molecules in water in the presence of NaCl ions was discussed in work [9]. In works [11, 12], it was shown that, in aqueous NaCl solutions saturated with CO_2 , the acid-base balance decreases with the growth of the NaCl concentration, provided that the temperature and the partial pressure of CO_2 remain constant. In work [13], a decrease of pH was observed in aqueous NaCl solutions saturated with CO_2 , when the temperature grew, but the salt concentration remained constant. However, theoretical calculations in works [1, 6] predicted a slight reduction of pH in aqueous NaCl solutions saturated with CO_2 : by approximately 0.01 pH unit as compared with pure water. As a result, there arises a confusion, as if the addition of salt has almost no effect on the pH value. The contradiction between the experimental data and the results of theoretical calculations requires more thorough systematic research.

The mechanism governing the variation of the acid-base balance in water and aqueous solutions at the dissolution of CO_2 in water requires clear and rigorous theoretical justifications. Separate propositions of physical and chemical explanations for the influence of NaCl on the acid-base balance in water can be found in works [6, 9, 10, 14, 15]. It should be taken into account that pH is not an additive value of the H^+ and OH^- concentrations. If it had been so, then the pH of pure water with equal H^+ and OH^- concentrations would have been equal to zero at 25°C rather than to 7.0, which corresponds to an H^+ concentration of 10^{-7} .

It is worth highlighting problems that remain practically unexamined. First, this is the establishment of the equilibrium pH value in aqueous solutions in time. It is important that temporary fluctuations of the acid-base balance are one of the main problems dealing with the influence of pH on the human body. Since the local values of the temperature and the NaCl concentration in the human body perma-

nently vary, the temporal changes of pH are extremely important [16]. It is clear that homeostasis maintains pH values within a certain interval, because long-term changes of pH by 0.5 units are harmful to the body, but short-term and local pH changes take place steadily.

Second, this is the study of the temporal dynamics of the pH in aqueous NaCl solutions with various concentrations due to the dissolution of atmospheric CO_2 in them. Such a study is important, because similar processes take place in human blood. It is known that the average pH of human blood equals 7.36–7.44. Although the average value of the acid-base balance in blood is a strict constant of the organism, local pH values are not constant owing to the blood saturation with oxygen or carbon dioxide, metabolites, and salt ions. Therefore, as a far-sighted task, we consider the comparison of the properties of the processes that govern the establishment of equilibrium pH values in the human body and other natural objects, in particular, their dependence on the temperature and, especially, the NaCl concentration.

Therefore, the purposes of the work were as follows:

- to study the time behavior of the acid-base balance in aqueous NaCl solutions and its dependence on the temperature and salt concentration;
- to determine regularities in the temperature and concentration dependences of the time required for the establishment of equilibrium pH values in aqueous NaCl solutions;
- to make an attempt to construct a theoretical basis for explaining the studied regularities.

To achieve those purposes, we performed experimental studies of temporal changes of the acid-base balance in diluted aqueous NaCl solutions at various temperatures and NaCl concentrations, when atmospheric CO_2 was dissolved in them. An attempt was made to construct a rigorous theoretical substantiation of the observed processes.

We emphasize that the experimental measurements of the time dependences of the acid-base balance in aqueous NaCl solutions, which were carried out for the first time, were aimed at studying the non-equilibrium properties of aqueous solutions. First of all, the matter concerns the determination of the time values required for the establishment of the equilibrium pH in aqueous solutions, which provides information about the mobility of hydrogen ions.

2. Experimental Part

Freshly prepared distilled water of purity grade II according to DSTU ISO 3696:2003 was used. It was produced on an Adrona Crystal EX Double Flow water purification system (Adrona SIA, Latvia). Sodium chloride infusion solution of pharmaceutical grade (Darnytsya, Ukraine) was used as the initial solution. In what follows, the solution concentration will be denoted as ζ . This quantity is defined as the number of water molecules N_w per salt ion N_s , i.e.,

$$\zeta = \frac{N_w}{N_s}. \quad (1)$$

The initial solution was diluted with distilled water to the concentrations corresponding to $\zeta = 540, 675, 900,$ and 1620 water molecules per sodium or chlorine ion. The solutions were prepared gravimetrically using a balance Radwag AS 220.R2 (Radwag, Poland) with an accuracy of ± 0.1 mg.

Experimental measurements of the acid-base balance were carried out at the temperatures $T = 21.0, 25.0, 30.0, 35.0, 37.0, 40.0, 42.0,$ and 50.0 °C, i.e., within a temperature interval of 294–323 K. Thermostating with an accuracy of ± 0.1 K was provided making use of a UTU-10 ultra-thermostat (Krakow, Poland).

The values of pH of pure water and aqueous NaCl solutions were measured under the same conditions for each indicated temperature. The specimens of distilled water and the examined solutions, each 30 g in mass, were put into identical laboratory glasses and placed in the thermostat; the measurements of the acid-base balance were started after a time lapse of 20 min.

The acid-base balance was measured in accordance with the current IUPAC recommendations [17] using an AZ Bench Top Water Quality Meter 86505 (AZ Instrument Corp., Taiwan) equipped with a temperature-sensitive probe. The total relative error of pH measurements was found to equal 0.5% [18]. Before the measurements, the pH meter was calibrated using reference buffer solutions with pH values of 4.00 and 7.00 at 25.0 °C.

3. Results of Experimental Measurements of Time Dependences of the Acid-Base Balance in Water and Aqueous NaCl Solutions

The results of experimental measurements obtained for the time dependences of pH in water and aqueous

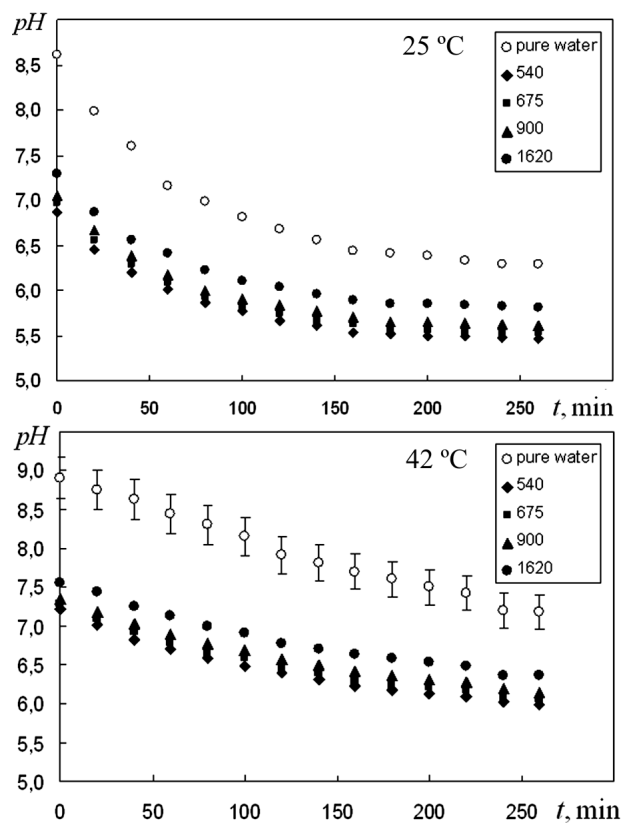


Fig. 1. Results of experimental measurements of the time dependences of the acid-base balance (pH) in water and aqueous NaCl solutions at temperatures of 25.0 and 42.0 °C and at concentrations corresponding to 540, 675, 900, and 1620 water molecules per sodium or chlorine ion

NaCl solutions at temperatures of 25.0 and 42.0 °C are presented in Fig. 1.

In the zeroth approximation, the time dependences of the acid-base balance in aqueous NaCl solutions can be expressed in the form:

$$\text{pH}(t) = \text{pH}(\text{eq}) + A \exp\left(-\frac{t}{\tau_s}\right). \quad (2)$$

Here, $\text{pH}(0) = \text{pH}(\text{eq}) + A$ is the initial pH value of the solution; $\text{pH}(\text{eq})$ is the final pH value of the solution (this is the pH value of the solution that is in equilibrium with atmospheric CO_2); t is the time passed since the solution was prepared; and $\tau_s(T, p, \zeta)$ is the relaxation time of the solution pH, which is a function of the temperature, pressure, and salt concentration. The analysis of Fig. 1 testifies that the dependencies $\text{pH}(t)$ for pure water in a temperature

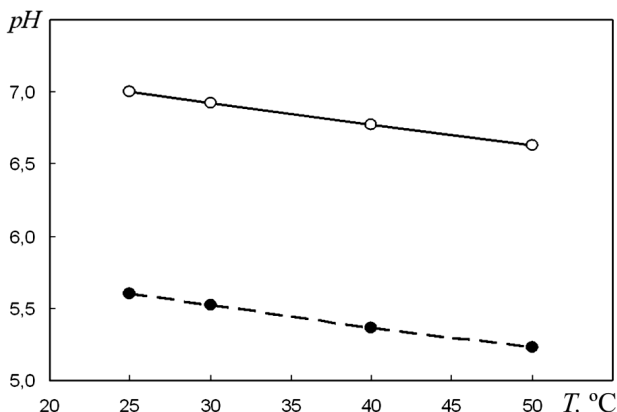


Fig. 2. Temperature dependences of the equilibrium components of pH in pure water (the upper curve) [20, 21] and in water that is in equilibrium with atmospheric CO₂ (the lower curve, constructed according to formula (3))

interval of 40–45 °C can be approximated by linear ones.

At $t \rightarrow \infty$, the curves in Fig. 1 tend to corresponding equilibrium pH values, the latter being presented in Fig. 2. In the studied temperature interval, the equilibrium pH values vary linearly, and the nonlinear character of the curves shown in Fig. 1 testifies to the non-equilibrium character of the processes in the solutions. Here, we considered that the acid-base balance is the sum of two contributions corresponding to the reducible and non-reducible pH components [19]. Therefore, the linear variations of the equilibrium components of the acid-base balance in Fig. 2 correspond to the temperature dependences of the reducible part of pH in aqueous NaCl solutions and pure water, whereas the nonlinear dependences in Fig. 1 correspond to the non-reducible part of pH.

The pH values for aqueous NaCl solutions that are in equilibrium with atmospheric CO₂ can be calculated according to the formula

$$\text{pH}(\text{eq}) = a - bT, \tag{3}$$

where $a = 5.97$, $b = 0.015$, and T is the solution temperature in Celsius degrees.

Formula (3) was used to calculate the equilibrium values of pH in aqueous NaCl solutions. At the equilibrium, this quantity is a function of the temperature and pressure. In other words, if we slowly vary the temperature or pressure, we get equilibrium pH values. But if the temperature or pressure is varied

quickly, the system ceases to be in the equilibrium state, and the instantaneous pH values substantially depend on the parameters (α, β, \dots) that characterize the degree of imbalance. This remark is important in view of the fact that these are the non-equilibrium values of $\text{pH}(t)$ that will be discussed below.

The temperature dependences of the pH relaxation time in water and aqueous NaCl solutions with various concentrations are depicted in Fig. 3. Table contains the equilibrium pH values for aqueous NaCl so-

Values of the pH relaxation time in aqueous NaCl solutions calculated for various solution concentrations ζ and temperatures T

$T, \text{ }^\circ\text{C}$	pH(eq)	ζ	$\tau_s, \text{ min}$
21.0	5.67	540	149
		675	170
		900	191
		1620	245
25.0	5.60	540	185
		675	202
		900	227
		1620	273
30.0	5.52	540	145
		675	171
		900	200
		1620	282
35.0	5.44	540	274
		675	299
		900	375
		1620	450
37.0	5.41	540	74
		675	84
		900	106
		1620	144
40.0	5.37	540	61
		675	77
		900	95
		1620	151
42.0	5.34	540	103
		675	117
		900	142
		1620	189
50.0	5.23	540	223
		675	248
		900	283
		1620	377

lutions, $\text{pH}(\text{eq})$, calculated according to formula (3), as well as the values of the pH relaxation time in them, τ_s , for the NaCl concentrations corresponding to $\zeta = 540, 675, 900,$ and 1620 water molecules per sodium or chlorine ion.

The analysis of the data presented in Table demonstrates that the pH relaxation times in aqueous NaCl solutions are shorter for higher solution concentrations. At the same time, the temperature behavior of the pH relaxation times in aqueous NaCl solutions is somewhat more complicated (Fig. 3). We emphasize that the quantity τ_s was introduced by us for the first time, so it seems impossible to compare it now with the results of other authors.

It is worth noting the similarity of the temperature dependences of the pH relaxation time in pure water and NaCl solutions (Fig. 3). A characteristic difference between those dependences is the appearance of local extrema in the curves, with the positions of those extrema being more noticeable at higher salt concentrations.

In order to elucidate the role of water in the behavior of the temperature dependence of the pH relaxation time in NaCl solutions, let us normalize the considered quantities. In particular, let us change to the dimensionless quantity

$$\tilde{\tau}(T, \zeta) = \lambda(\zeta) \frac{\tau_s(T, \zeta)}{\tau_w(T)}, \quad (4)$$

where $\tau_s(T, \zeta)$ is the pH relaxation time in the NaCl solution with the salt ion concentration ζ at the temperature T ; $\tau_w(T) = \lim_{\zeta \rightarrow \infty} \tau_s(T, \zeta)$ is the pH relaxation time in pure water at the temperature T ; and $\lambda(\zeta)$ is a constant depending on the NaCl concentration in the solution (for the concentrations $\zeta = 540, 675, 900,$ and 1620 water molecules per sodium or chlorine ion, it takes the values $\lambda = 1.81, 1.60, 1.34,$ and 1.01 , respectively).

Figure 4 shows the dependences $\tilde{\tau} = f(T, \zeta)$ of the dimensionless pH relaxation time in NaCl solutions on the temperature for the concentrations corresponding to $\zeta = 540, 675, 900,$ and 1620 water molecules per Na or Cl ion. The analysis of Fig. 4 shows that the curves $\tilde{\tau} = f(T)$ can be to some extent superimposed within the calculation error for the pH relaxation time.

Furthermore, the change to the dimensionless pH relaxation time $\tilde{\tau} = f(T, \zeta)$ according to formula (4)

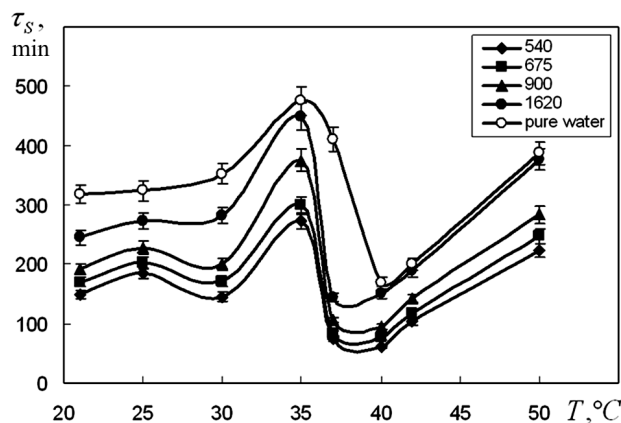


Fig. 3. Temperature dependences of the pH relaxation time in pure water and aqueous NaCl solutions with concentrations corresponding to 540, 675, 900, and 1620 water molecules per sodium or chlorine ion

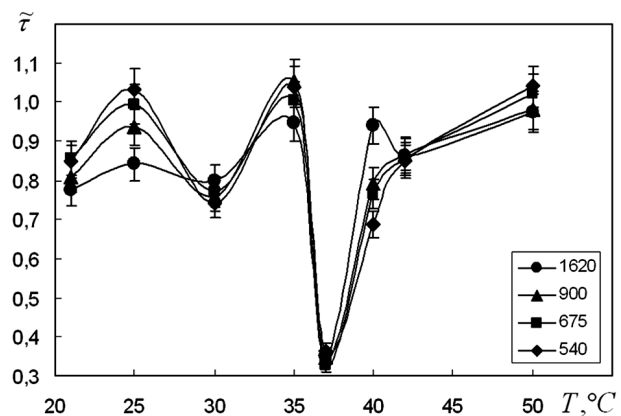


Fig. 4. Temperature dependences of the dimensionless pH relaxation time in NaCl solutions calculated according to formula (4) for concentrations corresponding to 540, 675, 900, and 1620 water molecules per sodium or chlorine ion

and to the dimensionless time interval that has passed since the solution preparation,

$$\tilde{t} = \lambda(\zeta) \frac{t}{\tau_w(T)}, \quad (5)$$

together with the subsequent substitution of the obtained quantities into Eq. (2) lead to the virtual superposition of the pH time dependences for aqueous NaCl solutions (see Fig. 1) into a single characteristic curve $\text{pH}(\tilde{t}) = f(\tilde{t}/\tilde{\tau})$ within the errors of both experimental measurements and the calculation of the average $\lambda(\zeta)$ values (Fig. 5). These considerations convincingly testify to the *similarity* in the

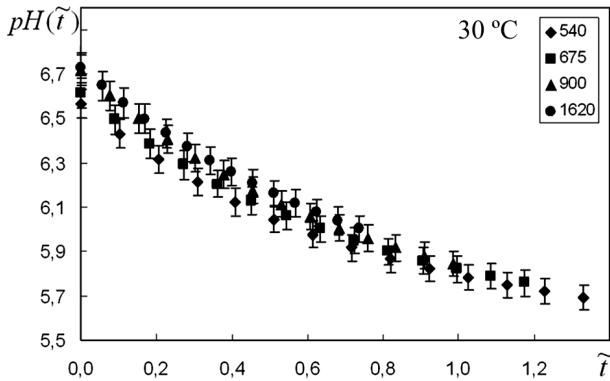


Fig. 5. Dependences of the normalized pH in NaCl solutions on the dimensionless time at a temperature of 30.0 °C for concentrations corresponding to 540, 675, 900, and 1620 water molecules per sodium or chlorine ion

behavior of the temperature dependences of the pH relaxation times in NaCl solutions with various salt concentrations.

It is worth noting that all curves in Fig. 4 demonstrate a minimum of the pH relaxation time in NaCl solutions in a vicinity of the temperature of 36.6 °C, which is optimal for the functioning of human and mammalian organisms [19]. Qualitatively, this result is consistent with the fact that the equilibrium in the water environment at a temperature of 36.6 °C is established during a minimum time interval, as it should be for living organisms. In addition, two local extrema at temperatures of 35 and 42 °C correspond to the minimum and maximum, respectively, ends of the temperature interval, where the living matter exists [19–28]. The shortest lifetime reflects the specific features of thermal motion in water itself, since the minimum is observed at all concentrations, and the concentration growth does not lead to its displacement. The revealed feature is completely associated with the properties of water and should play an extremely important role in biophysics, because it is exactly the mobility of hydrogen ions that determines the essence of physiological processes.

When discussing the influence of the NaCl concentration on the acid-base balance in solutions, it should be taken into account that the electric fields of ions can modify the equilibrium characteristics of electrolyte solutions. The concentration of CO₂ in the NaCl solution is somewhat lower than in water, because the solubility of CO₂ depends on the electron pair of an oxygen atom, which attracts the positively

charged hydrogen atom in the water molecule. Water molecules in electrolytes are less stable, because the electric fields of salt ions favor the dissociation of water molecules. Let us consider this issue in more details.

4. Influence of Electrostatic Interactions Between Ions on Molecular Processes in NaCl Solutions

An important issue is the influence of electrostatic fields generated by salt ions on the establishment of the pH equilibrium values in aqueous NaCl solutions. The analysis of this issue should be started by comparing the average distances between the salt ions (they can be evaluated from geometric considerations) with the average distances over which the electrostatic field of charged salt ions extends.

From the geometric point of view, the average number of water molecules between sodium or chlorine ions in a NaCl solution with the corresponding concentration can be evaluated as $\zeta^{1/3}$. Assuming that the diameter of water molecule equals $r_w = 3 \text{ \AA}$ and multiplying half of the average number of water molecules between the ions by the diameter of water molecule, we obtain the quantity

$$r_\zeta = \frac{1}{2} \zeta^{1/3} r_w. \tag{6}$$

In order to evaluate the average distances over which the electrostatic field of charged ions extends, let us calculate the Debye radius for aqueous NaCl solutions using the formula

$$\frac{1}{r_D^2} = 8\pi\gamma n_+^{2/3}, \quad n_+ = n_{\text{Na}} + n_{\text{H}}, \tag{7}$$

where $n_{\text{Na}} = x_{\text{Na}} n_w$ and $n_{\text{H}} = x_{\text{H}} n_w$ are the concentrations of sodium and hydrogen ions, respectively; n_w is the concentration of water molecules; and γ is the parameter of solution non-ideality [14]. The quantity γ is the ratio between the energy of ionic electrostatic field and the energy of molecular thermal motion in the solution,

$$\gamma = \frac{e^2 n_{\text{Na}}}{\epsilon k_B T}, \tag{8}$$

The concentration of Na⁺ ions $n_{\text{Na}} \sim 10^{19} \text{ cm}^{-3}$ exceeds the concentration of H⁺ ions $n_{\text{H}} \sim 10^{13} \text{ cm}^{-3}$ by six orders of magnitude, i.e., $n_{\text{Na}} \gg n_{\text{H}}$. Therefore,

the concentration of H^+ ions in formula (7) can be neglected, so $n_+^{2/3} \approx n_{Na}^{2/3}$. It is easy to get convinced that

$$x_{Na} = \frac{1}{\zeta + 1} \approx \frac{1}{\zeta}, \quad (9)$$

where ζ is the average number of water molecules per Na or Cl ion. Figure 6 shows the Debye radii in angströms calculated for various concentrations ζ and temperatures T .

How strongly does the electrostatic interaction between the salt ions in the solution affect molecular processes in it? Let us analyze the non-ideality parameter γ , which is the ratio between the energy of the electrostatic field generated by ions and the energy of thermal motion of molecules in the solution (Fig. 7). As one can see from Fig. 7, in the studied concentration interval, the energy of thermal motion of molecules in the solution is approximately three times as high as the energy of the electrostatic field of ions, i.e., electrostatic interaction does not substantially affect molecular processes in the examined solutions.

Note that, at $\gamma \approx 1$, the energy of the electrostatic field of ions becomes comparable to the energy of the thermal motion of molecules in the solution, so the contribution of the electrostatic interaction between ions to molecular processes in the solution has to be taken into consideration. It occurs at the concentration $n = 2.77 \times 10^{21} \text{ cm}^{-3}$, i.e., at the concentration ζ corresponding to 6 water molecules per one Na or Cl ion. At $\gamma \geq 1$, the electrostatic interaction between ions dominates over the thermal motion of molecules, which leads to the formation of pairs of oppositely charged ions – i.e., NaCl molecules are formed – and the clustering process takes place – i.e., the salt precipitates in the saturated solution.

Thus, the contribution of the electrostatic interaction does not play a decisive role in the considered solutions. Therefore, it does not significantly affect molecular processes in NaCl solutions. However, as will be explained below, normal pH values arise owing to collisions between water molecules, and this is a manifestation of the thermal motion of molecules. The increase of the parameter γ with the salt concentration testifies to the increasing role of electric fields in the destruction of water molecules.

5. Calculation of pH in Pure Water

The obtained experimental results require a clear qualitative and quantitative substantiation of the mechanisms governing the establishment of the equilibrium pH values in pure water and in water contacting with atmospheric CO_2 . It is clear that the equilibrium pH values are mainly determined by the peculiarities of intermolecular collisions in water and in the solutions. In what follows, we pay attention, first of all, to the role of binary collisions between water molecules.

Consider the mechanism of pH formation in pure water. The concentration of hydrogen ions c_H will be determined by the fraction of molecules whose velocities are sufficient for their dissociation at a collision. The equation describing the dissociation of wa-

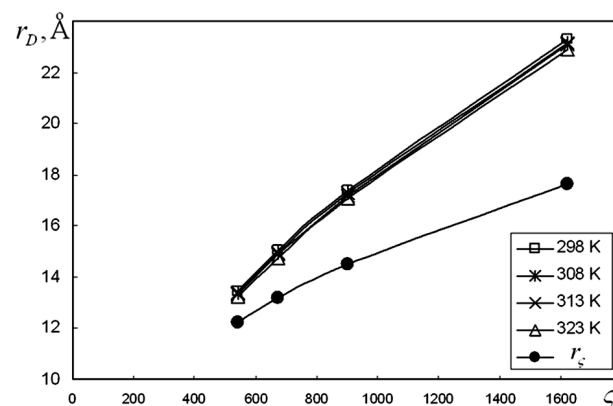


Fig. 6. Dependences of the Debye radius and the quantity r_ζ on the ionic concentration ζ in aqueous NaCl solutions at various temperatures

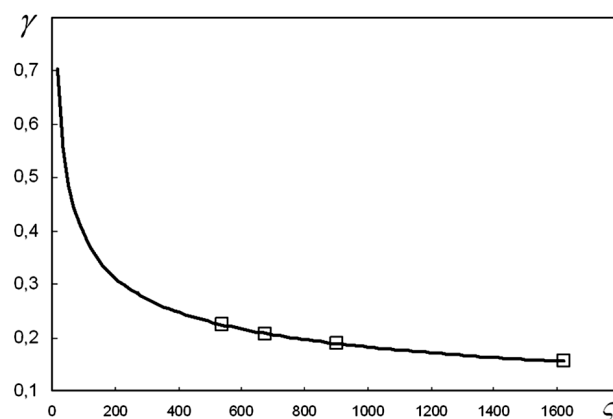


Fig. 7. Concentration dependence of the parameter γ at $T = 298 \text{ K}$. The solid curve is plotted according to formula (8)

ter molecules looks like



Let us evaluate the fraction of molecules that have energies sufficient for the dissociation of water molecules at room temperature. For this purpose, let us apply the Maxwell distribution over the magnitudes of relative velocities

$$\frac{\Delta n_D}{n} = \frac{\pi}{2} \left(\frac{m}{\pi k_B T} \right)^{3/2} \int_{v_D}^{\infty} \exp\left(-\frac{mv^2}{4k_B T}\right) v^2 dv, \quad (11)$$

where n_D is the concentration of water molecules whose velocities are sufficient for their dissociation at collisions, n the concentration of water molecules, m the mass of the water molecule, and v the relative velocity of molecules. The minimum relative velocity sufficient for the dissociation of a water molecule at its collision equals

$$v_D = \left(\frac{6k_B T_D}{m} \right)^{1/2}, \quad (12)$$

where T_D is the dissociation energy of a water molecule in temperature units. After the asymptotic expansion of expression (11), the concentration of hydrogen ions in the first approximation looks like

$$c_H \approx \frac{2}{\sqrt{\pi}} \sqrt{\frac{3T_D}{2T}} \exp\left(-\frac{3T_D}{2T}\right). \quad (13)$$

Then the pH value for water is equal to

$$\text{pH} = -\lg(c_{\text{H}^+}). \quad (14)$$

According to work [29], the energy of water molecule dissociation into the H^+ and OH^- ions equals $E_D = 117.8$ kcal/mol. On the temperature scale, this value calculated per molecule corresponds to the temperature

$$T_D \approx 3.97 \times 10^3 \text{ K}. \quad (15)$$

In liquid water, the values of E_D and T_D change considerably owing to the screening effect. Its influence can be evaluated by the formula

$$T_D = \frac{E_D}{\varepsilon(\omega \sim 1/\tau_D) k_B}, \quad (16)$$

where $\varepsilon(\omega \sim 1/\tau_D)$ is the dielectric permittivity of water at the characteristic frequency of molecular rotation, $\varepsilon(\omega \sim 1/\tau_D) \approx 20$ [29]. Therefore, taking Eq. (16) into account, we obtain the following estimate for the concentration of hydrogen ions:

$$c_{\text{H}^+} \approx 8.55 \times 10^{-8}. \quad (17)$$

Then the acid-base balance acquires the following value at 25 °C:

$$\text{pH} = -\lg(c_{\text{H}^+}) \approx 7. \quad (18)$$

This result agrees with experimental values for the pH in pure water obtained at a temperature of 25°C and at the atmospheric pressure maintained with the help of argon.

6. Calculation of the Equilibrium Concentration of Atmospheric CO₂ in Water

In this section, the main attention is paid to the change of the equilibrium pH value in water under the influence of the interaction of water molecules with CO₂ admixture molecules.

The balance between carbon dioxide in water and air is established according to the equality of the chemical potentials of CO₂ molecules in water and air:

$$\mu_{\text{CO}_2}^{(w)} = \mu_{\text{CO}_2}^{(a)}, \quad (19)$$

where the chemical potential of CO₂ in water is the sum of three components: these are the components associated with the translational and rotational molecular motions and the contribution of the intermolecular interaction,

$$\mu_{\text{CO}_2}^{(w)} = \mu_{\text{tr}}^{(w)} + \mu_{\text{rot}}^{(w)} + \mu_{\text{int}}^{(w)}. \quad (20)$$

The superscripts (w) and (a) in Eq. (19) indicate the presence of CO₂ molecules in water and atmosphere, respectively.

The ideal component of the chemical potential of carbon dioxide in the solution is equal to

$$\mu_{\text{tr}}^{(w)}(T, p) = \varepsilon_0 - T \left[1 - \ln \frac{p_{cs}}{p_0} - \frac{5}{2} \ln \frac{T}{T_0} \right], \quad (21)$$

where the following notations are used:

$$p_0 = \frac{T_0}{v_{qu}(T_0)}, \quad v_{qu}(T_0) = \left(\frac{mT_0}{2\pi\hbar^2} \right)^{3/2}, \quad (22)$$

ε_0 is the energy of the molecule in the ground state; $p_{cs} = c_{cs}p_s$ is the partial pressure of CO_2 in the solution; p_s is the pressure in the solution; $c_{cs} = N_c/(N_w + N_c)$ is the fraction of CO_2 molecules in the solution; and N_c and N_w are the concentrations of CO_2 and water molecules, respectively. The contribution of ε_0 is small, so it will not be considered further.

The contribution of the rotational motion to the chemical potential of CO_2 is equal to

$$\mu_{\text{rot}}^{(w)} = -T \ln \frac{2IT}{h^2}, \quad (23)$$

where $I = \sum_i m_i r_i^2$ is the moment of inertia of the CO_2 molecule. This contribution is small as compared to the contributions made by the translational motion and the intermolecular interaction, so we ignore it in our calculations.

The statistical integral for carbon dioxide in water is traditionally presented in the expansion form

$$Z_{\text{int}} = Z_{\text{id}} \left[1 - \frac{N_c(N_w - 1)}{V} B_{\text{int}}(T) + \dots \right]. \quad (24)$$

The second virial coefficient $B_{\text{int}}(T)$ depends on the average potential of interaction between water and CO_2 molecules $U_{wc}(R)$:

$$B_{\text{int}}(T) = 2\pi \int_0^\infty R^2 [1 - \exp(-\beta U_{wc}(R))] dR \approx b_{wc} - \frac{a_{wc}}{T}, \quad (25)$$

where

$$a_{wc} = 2\pi \int_{r_w+r_c}^\infty U_{wc}(R) R^2 dR, \quad (26)$$

$$b_{wc} = \frac{2\pi(r_w + r_c)^3}{3}. \quad (27)$$

Since the solution is dilute, which means a negligibly small number of CO_2 molecules in comparison with the number of water molecules, the first term in Eq. (25) is negligibly small. Then the second virial coefficient is equal to

$$B_{\text{int}}(T) \approx -\frac{a_{wc}}{T}. \quad (28)$$

The averaged interaction potential U_{wc} in Eq. (24) is determined by statistically averaging the microscopic potential $\Phi_{wc} = \Phi_{wc}(r, \Omega_1, \Omega_2)$ over the angular variables,

$$\exp(-\beta U_{wc}) = \oint_{\Omega_1=4\pi} \frac{d\Omega_1}{4\pi} \oint_{\Omega_2=4\pi} \frac{d\Omega_2}{4\pi} \exp(-\beta \Phi_{wc}). \quad (29)$$

The microscopic potential of interaction between CO_2 and water molecules in the first approximation is equal to the energy of dipole-quadrupole interaction,

$$\Phi_{wc} \approx W_D Q_{\alpha\beta}. \quad (30)$$

The vector components of the dipole moment of a water molecule equal $D_\alpha^{(w)} = D_w e_\alpha$, where D_w is the dipole moment magnitude, and e_α are the components of the unit vector directed along the dipole moment vector of the water molecule. By choosing the position of the carbon atom at the center of the CO_2 molecule, the components of the quadrupole moment tensor of the CO_2 molecule can be written in the form

$$Q_{\alpha\beta}^{(c)} = Q_0 n_\alpha n_\beta, \quad (31)$$

where

$$Q_0 = 2q_0 l^2, \quad (32)$$

n_α and n_β are the components of the unit vector specifying the orientation of the CO_2 molecule, q_0 is the effective charge of an oxygen atom, and l is the distance between the carbon and oxygen atoms in the CO_2 molecule.

Since the interaction energy of water molecules with the CO_2 molecule is much lower than the energy of thermal motion, let us expand the exponent in Eq. (29) in the series,

$$\exp(-\beta U_{wc}) = \oint_{\Omega_1=4\pi} \frac{d\Omega_1}{4\pi} \oint_{\Omega_2=4\pi} \frac{d\Omega_2}{4\pi} \left(1 - \beta \Phi_{wc} + \frac{1}{2} \beta^2 \Phi_{wc}^2 + \dots \right). \quad (33)$$

Let us also account for the influence of the environment on the interaction potential between the water and CO_2 molecules by including the dielectric constant of water, ε , into the interaction potential. Then

the averaged potential of interaction between the water and CO₂ molecules takes the form

$$U_{wc} = -\frac{1}{2\varepsilon}\beta \langle \Phi_{wc}^2 \rangle. \quad (34)$$

The value of $\langle \Phi_{wc}^2 \rangle$ is determined by the potential of the dipole-quadrupole interaction between the water and CO₂ molecules,

$$\langle \Phi_{wc}^2 \rangle \approx \langle W_{DQ}^2 \rangle. \quad (35)$$

After performing necessary substitutions in expression (34) and convoluting the tensors, the average interaction potential between the water and CO₂ molecules looks like

$$U_{wc} = -\frac{1}{2\varepsilon R^8} \beta D_w^2 Q_0^2. \quad (36)$$

Then the fraction of CO₂ molecules in the solution equals

$$c_{cs} = c_a \chi(T), \quad (37)$$

where

$$\chi(T) = \exp[-n_w B_{\text{int}}(T)]. \quad (38)$$

Accordingly, the second virial coefficient is equal to

$$B_{\text{int}}(T) = \frac{\pi D_w^2 Q_0^2}{5\varepsilon T^2 (r_w + r_c)^5}. \quad (39)$$

Hence, the expression for the fraction of carbon dioxide in water takes the form

$$c_{cs} = c_a \exp \left[-n_w \frac{\pi D_w^2 Q_0^2}{5\varepsilon T^2 (r_w + r_c)^5} \right]. \quad (40)$$

The acid-base balance in water with dissolved CO₂ can be presented as the logarithm of the sum of two contributions,

$$\text{pH} \approx -\lg \left(c^{(w)} + \Delta c^{(c)} \right), \quad (41)$$

where $c^{(w)}$ is the fraction of hydrogen ions in pure water [see Eq. (17)], and $\Delta c^{(c)}$ is a contribution to the ionic concentration that appears as a result of the CO₂ dissolution in water. Since the solution is dilute, we will assume that all carbon dioxide molecules chemically react with water ones and dissociate into

ions. Then the latter contribution is equal to the fraction of dissolved CO₂,

$$\Delta c^{(c)} \approx c_{cs}. \quad (42)$$

The fraction of hydrogen ions in pure water is much lower than $\Delta c^{(c)}$, so expression (41) can be approximately rewritten in the form

$$\text{pH} \approx -\lg(c_{cs}) + \frac{c^{(w)}}{c_{cs}}. \quad (43)$$

The fraction of CO₂ in atmospheric air equals $c_a \approx 3 \times 10^{-4}$, and the concentration of water molecules is $n_w = \frac{1}{3} \times 10^{23} \text{ cm}^{-3}$. Then the fraction of CO₂ molecules in the solution [see Eq. (40)] is equal to

$$c_{cs} \approx 10^{-5.6}, \quad (44)$$

which is two orders of magnitude less than the fraction of CO₂ molecules in air, and approximately two orders of magnitude larger than the fraction of hydrogen ions in pure water without admixtures.

By applying the obtained results (17) and (40), we can evaluate the acid-base balance of the CO₂ solution at a temperature of 25 °C:

$$\text{pH} \approx 5.6. \quad (45)$$

Hence, the obtained value testifies to a substantial influence of atmospheric CO₂ on the variation of pH in water and, therefore, in diluted aqueous NaCl solutions.

7. Conclusions

For the first time, the problem concerning the non-equilibrium properties of the acid-base balance in aqueous solutions has been formulated. This issue is important for the correct interpretation of the processes occurring in human and mammalian organisms. The time dependences of pH in aqueous NaCl solutions contacting with atmospheric CO₂ have been experimentally studied. The measurements were carried out at the NaCl concentrations corresponding to 540, 675, 900, and 1620 water molecules per sodium or chlorine ion and in a temperature interval of 294–323 K.

The pH relaxation times in aqueous NaCl solutions with dissolved atmospheric CO₂ and their dependences on the solution concentration and temperature have been calculated. It is shown that the pH

relaxation time in aqueous NaCl solutions decreases, if the concentration of NaCl in the solution increases.

The analysis of the temperature dependence of the pH relaxation time testifies that the corresponding curves can be superimposed to a certain extent within the calculation error limits for the pH relaxation time, which points to the *similar* behavior of the temperature dependences of the pH relaxation times in NaCl solutions with various salt concentrations.

In a vicinity of the temperature of 36.6 °C, which is optimal for the functioning of human and mammalian organisms, the pH relaxation time in NaCl solutions has a minimum. This result is qualitatively consistent with the fact that the equilibrium in the aqueous environment at the indicated temperature is established within a minimum time interval, which is important for physiological processes in blood plasma. The shortest lifetime reflects the specificity of thermal motion in water itself, since the minimum was observed at all concentrations, and the concentration growth is not accompanied by its displacement. The revealed specific feature is completely governed by water properties and should play an extremely important role in biophysics, since plenty of physiological processes are controlled by the mobility of hydrogen ions.

An attempt has been made to construct a rigorous theoretical justification of the mechanisms responsible for the establishment of the equilibrium pH value in pure water and in water contacting with atmospheric CO₂. It is shown that the results of calculations based on the derived relationships correlate well with experimental results. It is proved that atmospheric CO₂ has a substantial effect on the pH change in water and aqueous NaCl solutions.

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ВПЛИВ АТМОСФЕРНОГО ВУГЛЕКИСЛОГО ГАЗУ НА ПОКАЗНИК КИСЛОТНО-ЛУЖНОГО БАЛАНСУ ВОДНИХ РОЗЧИНІВ ХЛОРИДУ НАТРІЮ

У роботі експериментально досліджено вплив атмосферного вуглекислого газу на показник кислотно-лужного балансу розбавлених водних розчинів хлориду натрію в інтервалі температур (294–323) К для концентрацій, яким у середньому відповідає 540, 675, 900 і 1620 молекул води на один іон натрію або хлору. Розраховано часи релаксації показника кислотно-лужного балансу водних розчинів хлориду натрію при розчиненні у них атмосферного вуглекислого газу в залежності від температури та концентрації солі. Встановлено подібність поведінки температурної залежності часів релаксації показника кислотно-лужного балансу розчинів хлориду натрію різних концентрацій. Для з'ясування природи та особливостей подібності розраховано радіуси Дебая і показано, що у досліджених нами розчинах внесок електростатичної взаємодії не є визначальним, тому вона не буде відчутно впливати на молекулярні процеси. Здійснено спробу побудови строго теоретичного обґрунтування механізмів встановлення рівноважного значення показника кислотно-лужного балансу чистої води і води при її контакті з атмосферним вуглекислим газом. Показано, що розрахунки за отриманими співвідношеннями добре корелюють з експериментальними результатами. Доведено, що атмосферний вуглекислий газ має суттєвий вплив на зміну показника кислотно-лужного балансу води і водних розчинів хлориду натрію.

Ключові слова: водний розчин, хлорид натрію, показник кислотно-лужного балансу, вуглекислий газ, час релаксації.