

V.R. GAJEVSKIY

National University of Water Management and Nature Resources Use
(11, Soborna Str., Rivne 33028, Ukraine; e-mail: gur63@list.ru)**ELECTRIC CONDUCTIVITY
OF CARBON DIOXIDE AQUEOUS SOLUTIONS**

PACS 82.45.Rr

The system $CO_2 + H_2O$ with the concentration of free carbon dioxide varying from those close to the saturation one to the equilibrium one under environmental conditions has been studied. The dependences of ionic component concentrations on the solution pH are determined. Simultaneous measurements of the electric conductivity and the pH of the solution show that the contributions of ionic components in the carbonate-water system to the electric conductivity of the solution are additive and satisfy the Kohlrausch law with an error not exceeding $\pm 0.5\%$.

Keywords: aqueous solutions of electrolytes, conductivity, carbonate-water system, potentiometric method.

1. Introduction

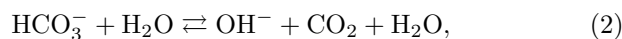
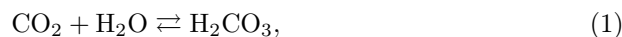
Researches of the transport properties in the aqueous solutions of electrolytes are important for the development of the theory of those systems in the framework of ionic-molecular, electron-nuclear, and other modern models [1, 2]. The electric conductivity is one of such physico-chemical transport properties. The methods of its measurement are considered to be exact and reliable [3]. However, the modern theory of electric conductivity in electrolyte solutions does not provide universal relations, which could be used in a wide interval of concentrations. Therefore, empirical relations are often applied [4]. This means that the theory of the aqueous solutions of electrolytes has to be improved both at the theoretical (the development of models) and instrumental levels. From this viewpoint, the correlation between the results of theoretical calculations and experimental ones is valuable. The magnitude of electric conductivity in the aqueous solutions of electrolytes is also an important physico-chemical parameter, which is standardized practically in all technological normative documents dealing with water systems and is used to monitor a lot of technological processes, in particular, the treatment of distilled and deionized water in the power, chemical, metallurgical, and other industries [5].

Recently, together with the conductometric method, potentiometric ones have been used more and more intensively for the determination of ion (ion-

selective electrodes) and gas (gas-selective electrodes) components in aqueous systems. Since water-treatment installations are not hermetic (they are isolated from the atmosphere), the simultaneous multi-parameter monitoring of such aqueous systems described in this work makes it possible to determine the contribution of free carbon dioxide to the total electric conductivity and, in such a manner, to facilitate the analysis of unwanted ionogenic factors that worsen the quality of distilled (deionized) water. The results of this work can also be useful, while searching for the reference measures and media for the measurement equipment [6].

2. Theory

The number of components in a carbonate-water system (CWS) is determined by the reactions describing the hydrolysis of carbonic acid components,



the equation of water dissociation,



and the equations describing the dissociation of carbonic acid,





Quantitative relationships between the CWS components under thermodynamic equilibrium conditions are established on the basis of expressions for the first- and second-stage dissociation constants of carbonic acid,

$$K_1 = \frac{\text{HCO}_3^- \text{H}^+}{\text{CO}_2}, \quad (7)$$

$$K_2 = \frac{\text{CO}_3^{2-} \text{H}^+}{\text{HCO}_3^-}, \quad (8)$$

the dissociation constant of water,

$$K_w = \text{H}^+ \text{OH}^-, \quad (9)$$

and the electroneutrality equation,

$$[\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-]. \quad (10)$$

In Eqs. (7)–(10), the components in brackets mean the corresponding concentrations, and those without the brackets stand for their activities. The temperature dependences of the constants K_1 , K_2 , and K_w can be found in work [7]. At $t = 25^\circ\text{C}$, they are equal to $K_1 = 1.72 \times 10^{-4}$, $K_2 = 4.40 \times 10^{-11}$, and $K_w = 1.00 \times 10^{-14}$. The system of equations (7)–(10) can be solved to determine the quantitative values for the components CWS (HCO_3^- , CO_3^{2-} , and CO_2) in terms of the independent parameter H^+ .

Hence, in accordance with Eqs. (2)–(6), the components of the ionic subsystem that give contributions to the solution conductivity are HCO_3^- , CO_3^{2-} , H^+ , and OH^- . From Eq. (1)–(6), one can see that, when CO_2 approaches the saturation, the electric conductivity of the solution grows and, as the solution is degassed, decreases (see Fig. 1). On the basis of the Kohlrausch law, we obtain

$$\chi = (C_{\text{HCO}_3^-} \lambda_{\text{HCO}_3^-} + 2C_{\text{CO}_3^{2-}} \lambda_{\text{CO}_3^{2-}} + C_{\text{H}^+} \lambda_{\text{H}^+} + C_{\text{OH}^-} \lambda_{\text{OH}^-}), \quad (11)$$

where C_i and λ_i are the concentration and the ionic mobility, respectively, of the i -th component. The values for the latter were taken from work [8].

Between the cases of CO_2 -saturated and CO_2 -degassed deionized water, the hydrogen index in our experiments changed in the interval $\text{pH} = 4 \div 5.6$

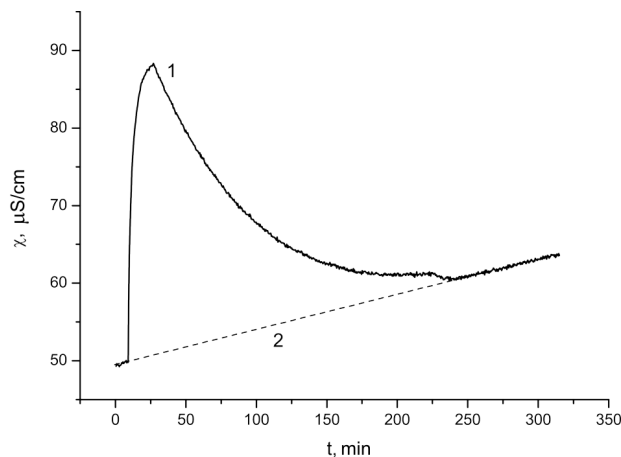


Fig. 1. (1) Electric conductivity change during the CO_2 -saturation and CO_2 -degassing of the solution; (2) change owing to the electrolyte leakage from the reference electrode

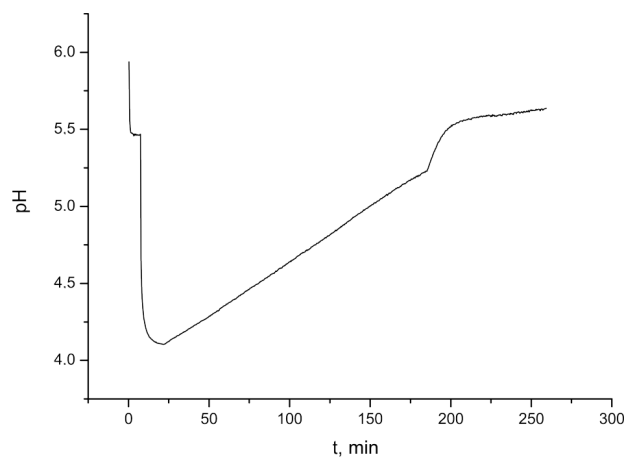


Fig. 2. Hydrogen index change during the CO_2 -saturation and CO_2 -degassing of the solution

(Fig. 2). Accordingly, the concentrations of the components in the carbonate system also changed following the relations

$$[\text{OH}^-] = \frac{K_w}{\text{H}^+ \gamma_{\text{OH}^-}}, \quad (12)$$

$$[\text{HCO}_3^-] = \frac{\frac{\text{H}^+}{\gamma_{\text{H}^+}} - \frac{K_w}{\text{H}^+ \gamma_{\text{OH}^-}} + \left(\sum_i A_i - \sum_j K_j \right)}{1 + \frac{K_2 \gamma_{\text{HCO}_3^-}}{\text{H}^+ \gamma_{\text{CO}_3^{2-}}}}, \quad (13)$$

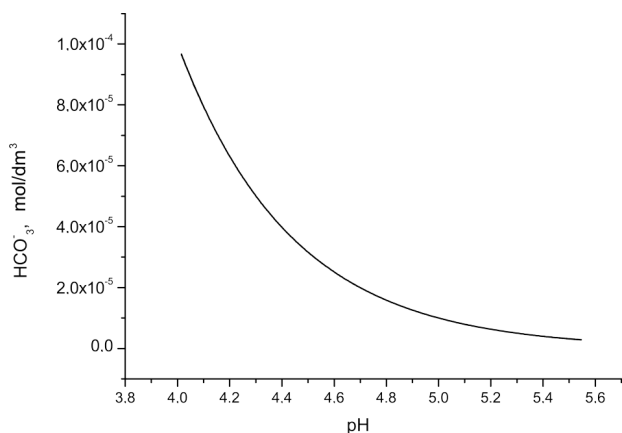


Fig. 3. Dependence of the hydrocarbonate ion concentration on pH

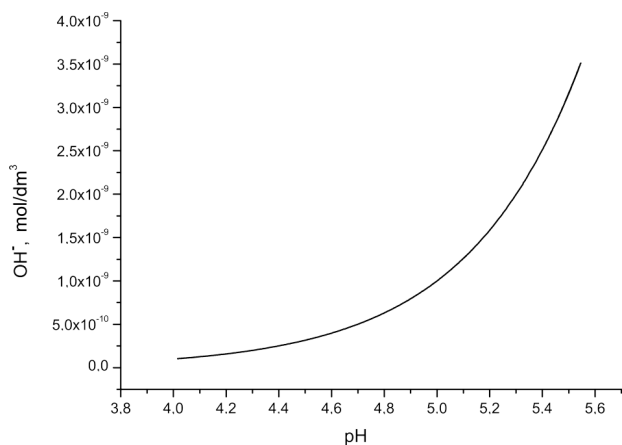


Fig. 4. Dependence of the hydroxyl ion concentration on pH

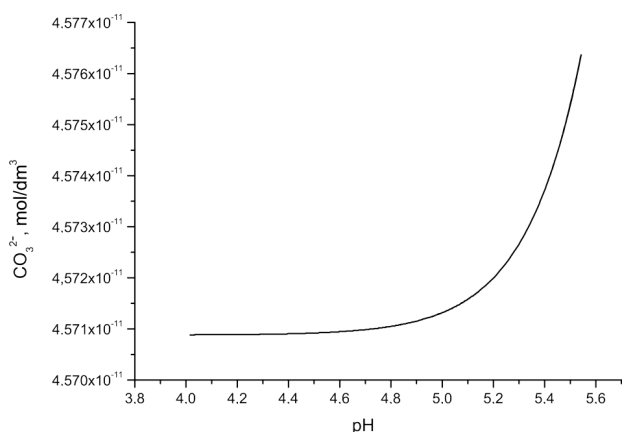


Fig. 5. Dependence of the carbonate ion concentration on pH

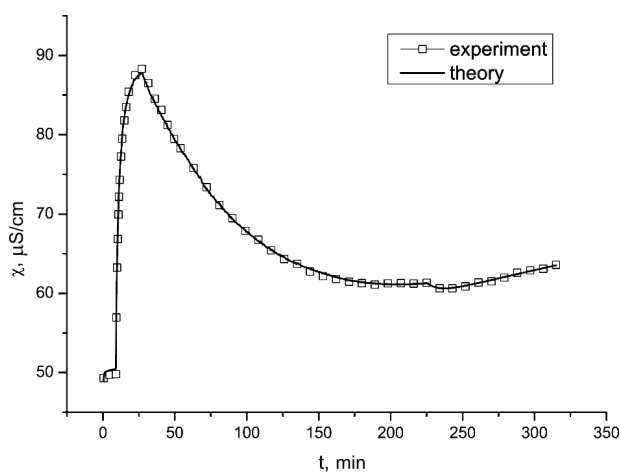


Fig. 6. Experimental and calculated values of the electric conductivity during the CO₂-saturation and the CO₂-degassing of the solution

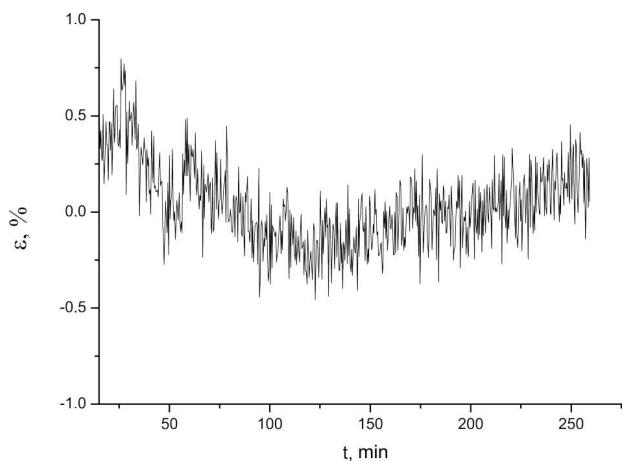


Fig. 7. Relative error of electroconductivity measurements

$$[\text{CO}_3^{2-}] = \frac{\frac{\text{H}^+}{\gamma_{\text{H}^+}} - \frac{K_w}{\text{H}^+ \gamma_{\text{OH}^-}} + \left(\sum_i A_i - \sum_j K_j \right)}{1 + \frac{\text{H}^+ \gamma_{\text{CO}_3^{2-}}}{K_2 \gamma_{\text{HCO}_3^-}}}. \quad (14)$$

Here, $[A_i]$ and $[K_i]$ are the concentrations of anions and cations, respectively, in the background electrolyte. The activity coefficients γ_i of the corresponding components were calculated from the first approximation of the Debye–Hückel equation, because their concentrations did not exceed 10^{-3} M.

From expressions (12)–(14), one can see that the contributions of CWS components to the conductivity

ity can be expressed only in terms of the activity of hydrogen ions, i.e. $\chi = \chi(a_{\text{H}^+})$. Therefore, the electric conductivity in this system can be calculated on the basis of the parameter a_{H^+} by measuring the pH. pH-dependences (12)–(14) are depicted in Figs. 3 to 5.

In the researches of this kind, the contribution of the electrolyte leakage from the reference electrode should be taken into account. In Fig. 1, the corresponding contribution is shown by the dotted line. The kinetics of electrolyte leakage from the reference electrode was analyzed separately. In every experiment, it was monitored on the basis of initial and final sections in the conductivity curve.

3. Experimental Part

The experiments were carried out on a specially designed measuring analyzer of the water system quality [9]. Deionized water was poured in a thermostated cuvette. If necessary, the KCl electrolyte could be added. The same cuvette contained the pH and reference electrodes and the conductivity and temperature sensors. The solution was thermostated at a temperature of 25 ± 0.1 °C. Carbon dioxide was blown through the solution until the CO_2 concentration reached a value close to the saturation. Simultaneously, the constant flow rate of carbon dioxide was monitored with the help of a rotameter. After achieving the CO_2 concentration close to the saturation, the solution was degassed by stirring it with a mechanical mixer. With the help of special converters and a multichannel ADC, signals from the sensors were registered in a PC database. As a result, the database for our experiment contained the electric conductivity (χ , $\mu\text{S}/\text{cm}$, see Fig. 1), pH (Fig. 2), and temperature values.

4. Analysis of Results

In Figs. 1 and 2, the experimental curves for the electric conductivity χ and the pH index, respectively, of the examined solution are shown. As follows from Figs. 3 to 5, in our experiments, the hydrocarbonate ion made a main contribution among the ionic components of CWS to the conductivity of the carbon dioxide aqueous solution. At the same time, the total content of carbonate and hydroxyl ions did not exceed 0.1%.

Figure 6 demonstrates the electroconductivity curve that was measured with the help of a conductometer, as well as the conductivity values (squares) calculated from the activity of hydrogen ions by means of relations (11)–(14). One can see that, in the examined interval 50–90 $\mu\text{S}/\text{cm}$ of the electric conductivity, the calculated values adequately describe the results measured by a conductometer.

Figure 7 illustrates the time-dependence of measurement errors, which has a dynamic character. It is quite probable that the errors originated from nonequilibrium processes, as a response of the hydrocarbonate system to a change of CO_2 in it. From Fig. 7, it is evident that the relative error between the measured and calculated values does not exceed $\pm 0.5\%$, which is a completely satisfactory result for the measurement technique used in our conductometric and potentiometric studies.

5. Conclusions

The contributions of ionic components in the examined system to the electric conductivity were shown to be additive and satisfy the Kohlrausch law based on the independence of mobilities of separate ionic components. The results of our researches make it possible to assert that the simultaneous arrangement of the potentiometric and conductometric sensors in a galvanically coupled medium (electrolyte solutions belong to this class) does not result in their substantial (to within the error limits of $\pm 0.5\%$) interference and, therefore, allows complex potentiometric and conductometric measurements to be performed. The experimental researches enabled us to develop a procedure for the calibration of a conductometric sensor, in which a solution with a varying contents of carbon dioxide is used as a reference one, and an auxiliary measurement of the solution pH is applied [6].

1. I.R. Yukhnovskii and M.F. Golovko, *Statistical Theory of Classical Equilibrium Systems* (Naukova Dumka, Kyiv, 1987) (in Russian).
2. G.A. Krestov, *Thermodynamics of Ionic Processes in Solutions* (Khimiya, Leningrad, 1984) (in Russian).
3. V.M. Lobo, *Elektrokhimiya* **27**, 613 (1991).
4. B.P. Golubev, P.P. Shcherbakov, and S.N. Golubev, *Trudy Moskov. Energet. Inst.* (1978).
5. *Building Regulations (SNIIP) 2.04.02-84. Water supply. External network and constructions* (Izdat. Liter. Stroitel., Moscow, 1985) (in Russian).

6. V.Z. Kochmarskyi and V.R. Gajevsky, *Patent N 10423 Ukraine, G01N27/06. No. U2005 03925, 15.11.2005*, Bull. No. 11.
7. S.S. Zavodnov, *Carbonate and Sulphide Balance in Mineral Waters* (Gidrometeoizdat, Leningrad, 1965) (in Russian).
8. Ju. Lurie, *Handbook of Analytical Chemistry* (Mir Publ., Moscow, 1975).
9. V.G. Gajevsky and V.Z. Kochmarskyi, in *Proceedings of the 3rd Scientific and Engineering Conference* (UDAVG, 1997), Vol. 5, p. 7 (in Ukrainian).

Received 13.05.14.

Translated from Ukrainian by O.I. Voitenko

В.Р. Гаєвський

ЕЛЕКТРОПРОВІДНІСТЬ ВОДНИХ РОЗЧИНІВ ВУГЛЕКИСЛОТИ

Р е з ю м е

Досліджено систему $\text{CO}_2 + \text{H}_2\text{O}$ зі змінним вмістом вільної вуглекислоти від концентрацій близьких до насичення, до атмосферної. Встановлено залежності концентрацій іонних компонент такої системи від рН. Одночасними вимірюваннями електропровідності і рН показано, що внесок іонних компонент карбонатної водної системи в електропровідність розчину адитивний і задовольняє закон Кольрауша з похибкою, яка не перевищує $\pm 0,5\%$.