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Standardization of pH measurements based on the ion interaction approach

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The Pitzer method was used to calculate the pH values on the conventional and "true" scales for the TRIS—TRIS · HCl—NaCl—H_2O buffer system in the 0—40 °C temperature region and 0—4 NaCl molality interval. This buffer can be used as a standard for pH measurements in a wide range of ionic strengths. The conventional scale is used in cells without a salt bridge. The "true" scale is recommended for pH measurements using cells with a salt bridge. At the same concentrations of the buffer solution, the "true" scale is essentially transformed into the scale of the National Bureau of Standards (NBS) of the USA.

Key words: pH standardization, Pitzer method, TRIS buffer, activity coefficient of an individual ion.

The pH value is the most important parameter of the acid-base equilibrium in solutions. The pH scale of the National Bureau of Standards (NBS) of the USA is widely used presently.[1] This scale has been recommended for practical measurements in the USSR.[2] The disadvantages of the scale, including the fact that the residual potential of the liquid bridge (ΔE_j) cannot be taken into account in the procedures of measurement and calculation of pH, have previously been discussed.[3]

The concentration SWS (sea water scale) for measuring pH of sea water was developed by the minimization of the ΔE_j value using buffer standards close in composition and pH to the solutions under study. The concentrations of hydrogen ions have been ascribed[4] to buffer solutions close to sea water in composition, ionic strength, and pH. The cell with the liquid bridge (*A*) is also used in the SWS:

$$\text{Ag,AgCl}\;\left|\;\begin{matrix}\text{Solution of KCl,}\\ m \ge 3.5\end{matrix}\;\right\|\;\begin{matrix}\text{Studied solution}\\ \text{(standard solution)}\end{matrix}\;\left|\;\text{H}^+\text{-GE}(A)\right.$$

(GE is the glassy electrode),

as well as the commonly known equation

$$\text{pH}_X = \text{pH}_S + \frac{F(E_S - E_X)}{RT\ln(10)} \qquad (1)$$

In this case, the exact expression for pH has the form

$$\text{pH}_X(\text{SWS}) = \text{pH}_S(\text{SWS}) + {} + \frac{F(E_S - E_X + \Delta E_j)}{RT\ln(10)} + \log\left[\frac{(\gamma_H)_X}{(\gamma_H)_S}\right], \qquad (2)$$

i.e., an additional source of theoretical errors arises for the concentration scale due to the difference in the activity coefficients of hydrogen ions in the solution under study and the standard when the concentrations of salts in them are different. This error is insignificant for the range of salt content of 30—40%, where the activity coefficients of the ions weakly depend on the ionic strength. However, for dilute solutions (with the ionic strength lower than 0.2), the error noticeably increases and can achieve[5] 0.06 pH units.

The theory of ion interaction (the Pitzer method) has recently been proposed[6—10] as a theoretical basis for the new pH scale. In the framework of this approach, the concepts about the conventional and "true" pH scales have been developed.[3] The "true" scale is recommended for pH measurements using cell *A* and buffer solutions with a variable ionic strength. It does not contain the theoretical error due to the last term in Eq. (2). The conventional pH scale can be used for pH measurements using only the cell without a liquid bridge of the *B* type:

$$\text{ISE-Cl}^-\;\left|\;\begin{matrix}\text{Studied solution}\\ \text{(standard solution)}\end{matrix}\;\right|\;\text{H}^+\text{-GE}\ (B)$$

(ISE is the ion-selective electrode).

For the NaH_2PO_4—Na_2HPO_4—NaCl—H_2O buffer system, the pH values have been determined by the Pitzer method.[3] However, the phosphate buffer is not always convenient in the work because it can form insoluble salts in reaction with the solutions under study. The buffer based on 2-amino-2-(hydroxymethyl)propane-1,3-diol (TRIS) is widely used for measuring pH for medicinal, biological, and oceanological purposes. In this work, we calculated the standard pH values on the "true" and conventional scales for TRIS—TRIS · HCl—NaCl—H_2O buffer solutions in

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a wide interval of ionic strengths (0.05—4) and temperatures (0—40 °C). It was shown that in the numerical respect the scale changed insignificantly.

Standard pH values of TRIS—TRIS · HCl—NaCl—H$_2$O solutions

The TRIS—TRIS · HCl—NaCl—H$_2$O system is the simplest buffer solution with a variable ionic strength. The desirable ionic strength of the buffer solution is adjusted by an indifferent electrolyte. The pH value for the TRIS buffer is determined by the chemical equilibrium

$$\mathrm{TRIS \cdot H^+} \rightleftharpoons \mathrm{TRIS} + \mathrm{H^+}. \quad (3)$$

According to this, we can write the expression for the pH value of the buffer solution:

$$\mathrm{pH} = \mathrm{p}K_{\mathrm{bh}} + \log(m_{\mathrm{B}}/m_{\mathrm{BH}}) + \log(\gamma_{\mathrm{B}}/\gamma_{\mathrm{BH}}), \quad (4)$$

where pK_{bh} = $-\log K_{\mathrm{bh}}$, K_{bh} is the thermodynamic equilibrium constant (3), and m_{B} and m_{BH} are the molalities of TRIS and TRIS · H$^+$, respectively. The equation for the activity coefficient of the TRIS molecule follows from the theory of ion interaction[11]:

$$\ln\gamma_{\mathrm{B}} = 2m_{\mathrm{B}}\lambda_{\mathrm{B.B}} + 2m_{\mathrm{BH}}L_{\mathrm{B.BH.Cl}} + \\ + 2m_{\mathrm{Na}}L_{\mathrm{B.Na.Cl}} + 3m_{\mathrm{B}}^2\mu_{\mathrm{B.B.B}}. \quad (5)$$

For the conventional activity coefficient of the TRIS · H$^+$ ion, the Pitzer method gives the equation

$$\ln\gamma_{\mathrm{cBH}} = f^{\gamma} + 2m_{\mathrm{Cl}}(B_{\mathrm{BH.Cl}} + m_{\mathrm{Cl}}C_{\mathrm{BH.Cl}}) + \\ + 2m_{\mathrm{Na}}\theta_{\mathrm{Na.BH}} + m_{\mathrm{Na}}m_{\mathrm{BH}}\theta'_{\mathrm{Na.BH}} + \\ + m_{\mathrm{Na}}m_{\mathrm{Cl}}(B'_{\mathrm{Na.Cl}} + C_{\mathrm{Na.Cl}} + \psi_{\mathrm{Na.BH.Cl}}) + \\ + m_{\mathrm{BH}}m_{\mathrm{Cl}}(B'_{\mathrm{BH.Cl}} + C_{\mathrm{BH.Cl}}) + m_{\mathrm{B}}L_{\mathrm{B.BH.Cl}}. \quad (6)$$

The definition of the conventional pH scale for the TRIS—TRIS · HCl—NaCl—H$_2$O buffer solution follows from Eqs. (4)—(6):

$$\mathrm{pH}(P_{\mathrm{c}}) \equiv \mathrm{p}K_{\mathrm{bh}} + \log(m_{\mathrm{B}}/m_{\mathrm{BH}}) + \\ + [2m_{\mathrm{B}}\lambda_{\mathrm{B.B}} + (2m_{\mathrm{BH}} - m_{\mathrm{B}})L_{\mathrm{B.BH.Cl}} + \\ + 2m_{\mathrm{Na}}L_{\mathrm{B.Na.Cl}} + 3m_{\mathrm{B}}^2\mu_{\mathrm{B.B.B}} - f^{\gamma} - \\ - 2m_{\mathrm{Cl}}(B_{\mathrm{BH.Cl}} + m_{\mathrm{Cl}}C_{\mathrm{BH.Cl}}) - m_{\mathrm{Na}}m_{\mathrm{BH}}\theta'_{\mathrm{Na.BH}} - \\ - m_{\mathrm{Na}}m_{\mathrm{Cl}}(B'_{\mathrm{Na.Cl}} + C_{\mathrm{Na.Cl}} + \psi_{\mathrm{Na.BH.Cl}}) - \\ - m_{\mathrm{BH}}m_{\mathrm{Cl}}(B'_{\mathrm{BH.Cl}} + C_{\mathrm{BH.Cl}}) - 2m_{\mathrm{Na}}\theta_{\mathrm{Na.BH}}]/\ln(10). \quad (7)$$

Here pH(P_{c}) on the pH on the conventional Pitzer scale, and the index "c" implies "conventional." Two groups of parameters of interaction of the components of the TRIS—TRIS · HCl—NaCl—H$_2$O system have been obtained previously.[12] For these two groups of parameters, we calculated the pH(P_{c}) values and found that the maximum difference is 0.005 pH units for a zero concentration of NaCl, which completely disappears at m_{NaCl} higher than 0.1. To find the standard pH values of TRIS—TRIS · HCl—NaCl—H$_2$O buffer solutions, we used the interaction parameters[12] that better agree with the experiment (the standard deviation of the experimental values from the theoretical ones is equal to 0.15 mV). Using Eq. (7), we calculated pH(P_{c}) for the range of NaCl molality of 0—4 and the temperature range of 0—40 °C. We approximated them by the empirical equation

$$\mathrm{pH} = a_0 + a_1m^{1/2} + a_2m + a_3m^{3/2} + \\ + a_4m^2 + a_5m^{5/2} + a_6m^3. \quad (8)$$

whose coefficients are presented in Table 1.

As already mentioned,[3] in the framework of the Pitzer method, we can develop the "true" pH value based on the equation for the activity coefficient of an individual ion containing immeasurable virial coefficients. For our buffer system, this scale is defined by the expression

$$\mathrm{pH}(P) \equiv \mathrm{pH_c} - [m_{\mathrm{B}}(\lambda_{\mathrm{B.BH}} - \lambda_{\mathrm{B.Cl}}) + \\ + m_{\mathrm{BH}}\lambda_{\mathrm{BH.BH}} + m_{\mathrm{Na}}\lambda_{\mathrm{Na.Na}} - m_{\mathrm{Cl}}\lambda_{\mathrm{Cl.Cl}} + \\ + 1.5m_{\mathrm{BH}}m_{\mathrm{Cl}}(\mu_{\mathrm{BH.BH.Cl}} - \mu_{\mathrm{BH.Cl.Cl}}) + \\ + 1.5m_{\mathrm{Na}}m_{\mathrm{Cl}}(\mu_{\mathrm{Na.Na.Cl}} - \mu_{\mathrm{Na.Cl.Cl}})]/\ln(10). \quad (9)$$

This pH scale can be established only by some simplifying assumptions. In many cases, the contribution of the second virial coefficients of the likely charged ions and the contribution of the third virial coefficients can be neglected. We assumed that only two terms in the brackets of Eq. (9), namely, $m_{\mathrm{B}}\lambda_{\mathrm{B.BH}}$ and $m_{\mathrm{BH}}\lambda_{\mathrm{BH.BH}}$, contribute noticeably to the pH value. It follows from this assumption and the definition of $L_{\mathrm{B.BH.Cl}}$[12] that

$$\lambda_{\mathrm{B.BH}} = L_{\mathrm{B.BH.Cl}}. \quad (10)$$

The relationship between $\lambda_{\mathrm{BH.BH}}$ and $\theta_{\mathrm{Na.BH}}$ has already been mentioned previously.[12] Neglecting the Na$^+$—Na$^+$ and Na$^+$—TRIS · H$^+$ interactions, we may assume that

$$\lambda_{\mathrm{BH.BH}} = -2\theta_{\mathrm{Na.BH}}. \quad (11)$$

It follows from Eqs. (9)—(11) that

$$\mathrm{pH}(P) \equiv \mathrm{pH}(P_{\mathrm{c}}) - (m_{\mathrm{B}}L_{\mathrm{B.BH.Cl}} - 2m_{\mathrm{BH}}\theta_{\mathrm{Na.BH}})/\ln(10). \quad (12)$$

Using Eq. (12), we ascribed the "true" pH(P) values to the buffer solutions in the 0—40 °C temperature region and the range of NaCl molality of 0—4, which were also approximated by Eq. (8). The coefficients of this equation for the calculation of the "true" pH are also presented in Table 1.

Acid-base equilibria of aqueous solutions of electrolytes depend on the activity rather than on the concentration of hydrogen ions. Therefore, the standardization of pH measurements should be based on a method describing the non-ideal behavior of the components of the solution. The Pitzer method, which has received wide recognition for the description of the non-ideal properties of multicomponent solutions of electrolytes, was used as a theoretical basis of standardization of pH measurements.

The application of cell A for pH measurements represents, as has been mentioned, a certain simplifica-

Table 1. Empirical coefficients in Eq. (8) for the calculation of $p(a_{H}\gamma_{Cl})$ and pH in the conventional and "true" scales for TRIS—TRIS · HCl—NaCl—H_2O buffer solutions (m_B = 0.04; m_{BH} = 0.04)

T/°C	a_0	a_1	a_2	a_3	a_4	a_5	a_6
				Conventional pH scale			
0	8.9233	0.0878	0.46950	−0.80598	0.61297	−0.225077	0.032464
5	8.7567	0.0884	0.46888	−0.80617	0.61401	−0.225634	0.032565
10	8.5956	0.0890	0.47019	−0.80749	0.61518	−0.226456	0.032702
15	8.4411	0.0896	0.47492	−0.80952	0.61646	−0.227400	0.032853
20	8.2932	0.0901	0.47945	−0.81335	0.61946	−0.228676	0.033046
25	8.1514	0.0907	0.48708	−0.81932	0.62301	−0.230295	0.033280
30	8.0148	0.0913	0.49407	−0.82647	0.62799	−0.232102	0.033536
35	7.8834	0.0919	0.49966	−0.83431	0.63326	−0.234033	0.033806
37	7.8325	0.0921	0.50090	−0.83638	0.63480	−0.234669	0.033900
40	7.7577	0.0925	0.50192	−0.84107	0.63791	−0.235863	0.034069
				"True" pH scale			
0	8.9244	0.0878	0.46948	−0.80595	0.61296	−0.225072	0.032463
5	8.7577	0.0884	0.46894	−0.80628	0.61411	−0.225673	0.032571
10	8.5965	0.0890	0.47015	−0.80742	0.61511	−0.226428	0.032697
15	8.4419	0.0896	0.47498	−0.80963	0.61655	−0.227438	0.032859
20	8.2938	0.0902	0.47938	−0.81323	0.61936	−0.228631	0.033039
25	8.1518	0.0907	0.48703	−0.81923	0.62293	−0.230262	0.033274
30	8.0151	0.0913	0.49407	−0.82646	0.62799	−0.232100	0.033535
35	7.8837	0.0919	0.49966	−0.83432	0.63328	−0.234041	0.033807
37	7.8327	0.0921	0.50090	−0.83637	0.63479	−0.234668	0.033900
40	7.7580	0.0925	0.50196	−0.84113	0.63795	−0.235875	0.034070
				$p(a_{H}\gamma_{Cl})$			
0	9.0100	0.1277	0.90926	−1.54150	1.14838	−0.419721	0.060110
5	8.8438	0.1288	0.90202	−1.54169	1.15093	−0.420831	0.060314
10	8.6831	0.1300	0.89855	−1.54443	1.15438	−0.422466	0.060585
15	8.5292	0.1312	0.90000	−1.54907	1.15863	−0.424466	0.060902
20	8.3819	0.1323	0.90223	−1.55599	1.16480	−0.426861	0.061266
25	8.2407	0.1335	0.90849	−1.56572	1.17189	−0.429734	0.061689
30	8.1048	0.1346	0.91496	−1.57724	1.18081	−0.432940	0.062154
35	7.9742	0.1358	0.92071	−1.58994	1.19030	−0.436378	0.062648
37	7.9235	0.1363	0.92232	−1.59430	1.19377	−0.437708	0.062845
40	7.8492	0.1371	0.92383	−1.60215	1.19951	−0.439833	0.063149

tion for which the potential of the liquid bridge of cell *A* can be a source of errors in the determination of pH values. The use of the conventional pH scale in the framework of the theory of ion interaction opens a new way for pH measurements. In this case, we should apply a cell without transfer, for example, *B*. Two reasonable definitions of the conventional pH scale are possible. One of them, the concentration definition ($pH(P_c) \equiv -\log m_H$), has already been discussed.[13,14] Another definition was proposed in the present work: $pH(P_c) \equiv -\log a_H$. We prefer the conventional activity scale, because an additional information on the parameters of ion interaction of the NaCl—HCl—H_2O and TRIS · HCl—HCl—H_2O systems is required for the determination of the concentration of the H^+ ion of standard buffer solutions. Additional experimental data and the introduction of the additional parameters of ion interaction entail an additional uncertainty in the ascribed $pH(P_c)$ values. However, these two definitions of the pH scale do not basically contradict. A cell without transfer is used in practice. It is calibrated with respect to the standard solution with the known molalities of the anion and the H^+ ion and the known for them mean-ion activity coefficient or with respect to the known product of the conventional activities of the anion and H^+ ion, which is, in essence, the same. Different types of cells without transfer, which were used for measurements of pH of various concentrated solutions, have been proposed.[7] A pseudo-buffer (HCl or NaOH in a solution of NaCl) was used for the calibration of cell *B*. Most industrial, natural, and physiological solutions have pH ~7; however, such a pseudo-buffer in this pH region does not possess buffer properties and is inconvenient in work. For this purpose, we proposed the TRIS—TRIS · HCl—NaCl—H_2O buffer. The conventional $pH(P_c)$ value of the solution under study can be calculated from the electromotive force of cell *B* by the equation

$$pH(P_c)_X = p(a_H\gamma_{Cl})_{cS} + \frac{F(E_S - E_X)}{RT\ln(10)} + \\ + \log\left[\frac{(m_{Cl})_X}{(m_{Cl})_S}\right] + \log(\gamma_{cCl})_X. \quad (13)$$

The subscripts "S" and "X" indicate the standard and studied solutions, respectively; $p(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})_{\mathrm{cS}} = -\log(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})_{\mathrm{cS}}$. For the TRIS—TRIS · HCl—NaCl—H_2O buffer solution, the $p(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})_{\mathrm{cS}}$ value can be determined by the equation

$$\begin{aligned} p(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})_{\mathrm{c}} \equiv \mathrm{pH}(P_{\mathrm{c}}) - [f^{\gamma} + 2m_{\mathrm{Na}}(B_{\mathrm{Na,Cl}} + m_{\mathrm{Cl}}C_{\mathrm{Na,Cl}}) + \\ + m_{\mathrm{B}}L_{\mathrm{B,Na,Cl}} + 2m_{\mathrm{BH}}(B_{\mathrm{BH,Cl}} + m_{\mathrm{Cl}}C_{\mathrm{BH,Cl}}) + \\ + m_{\mathrm{BH}}m_{\mathrm{Cl}}(B'_{\mathrm{BH,Cl}} + C_{\mathrm{BH,Cl}}) + \\ + m_{\mathrm{Na}}m_{\mathrm{Cl}}(B'_{\mathrm{Na,Cl}} + C_{\mathrm{Na,Cl}}) + \\ + m_{\mathrm{BH}}m_{\mathrm{Na}}(\theta'_{\mathrm{BH,Na}} + \psi_{\mathrm{Na,BH,Cl}})]/\ln(10). \quad (14) \end{aligned}$$

The $p(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})_{\mathrm{c}}$ values were calculated from Eq. (14) and also approximated by Eq. (8). The standard deviation of the theoretically calculated values from the experimental values[12] is equal to 0.15 mV, and the uncertainty in the $\mathrm{pH}(P_{\mathrm{c}})$ and $p(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})_{\mathrm{c}}$ values amounts to ±0.0075 pH units at the confidence level of 0.99. As follows from Eq. (13), the molality of the Cl^- ion and its conventional activity coefficient should be known for the analyzed solutions.

For solutions with unknown macrocomponent composition, pH measurements should be carried out using cell *A*. The cell is calibrated by standard solutions on the "true" pH scale. The concentration of the salt background (NaCl) is selected to be close to the concentration of the solution under study in such a manner that the condition $\Delta E_j \approx 0$ is fulfilled. At the zero concentration of the salt background, the "true" pH scale is transformed into the scale of the National Bureau of Standards (NBS) of the USA for the same concentrations of the buffer solutions. In fact, the pH values of the TRIS buffer in the NBS scale[15,16] are ~0.015 pH units higher than the pH(*P*) values calculated by Eq. (12) (Fig. 1). However, the values of the British standard $\mathrm{pH_B}$[13] are substantially lower (by 0.05 pH units) than our data. In essence, Fig. 1 demonstrates the divergences on the "true" scale based on three different postulates. For example, the TRIS buffer of the British standard has been established using a cell with a liquid junction calibrated relative to biphthalate buffer. We explain the difference between this and our data by the indefinite potential of the liquid bridge at the TRIS buffer/KCl bridge boundary.[15] The Bates—Guggenheim convention has been used[15,16] for the determination of the pH value on the NBS scale:

$$\ln\gamma_{\mathrm{Cl}} = -A^{\gamma}\sqrt{I}/(1 + 1.5\sqrt{I}). \quad (15)$$

It is assumed that the activity coefficient of the Cl^- ion in a dilute solution is independent of the nature of the counterion. However, this is not true: the author of Ref. 12 showed the existence of associates of TRIS · H^+ with Cl^-, due to which the activity coefficient of the Cl^- ion decreases. In fact, the mean ion activity coefficients of NaCl and TRIS · HCl in individual solutions are equal to 0.820 and 0.799, respectively, at $m = 0.05$ and 25 °C. Asymmetry in the activity coefficients of the counterions in the individual solutions can appear only due to the strong specific interaction of the likely charged ions, in the given case, Cl^-—Cl^-, Na^+—Na^+, and TRIS · H^+—TRIS · H^+. Assumptions (10) and (11) result in the insignificant (~0.001 pH units) difference between the "true" and conventional scales (see Table 1, coefficients a_0). Therefore, we assume that the nonideal properties of the counterions in the individual electrolytes NaCl and TRIS · HCl are symmetrical, *i.e.*, $\gamma_{\mathrm{Cl}} \approx \gamma_{\mathrm{NaCl}}$ and $\gamma_{\mathrm{Cl}} \approx \gamma_{\mathrm{TRIS\cdot HCl}}$. Thus, the observed (see Fig. 1) difference between NBS and the "true" scale can be explained by the difference in the activity coefficients of the Cl^- ion equal to ~0.02. From this it follows that the commonly accepted[1,14] universalism of the Bates—Guggenheim convention is not valid.

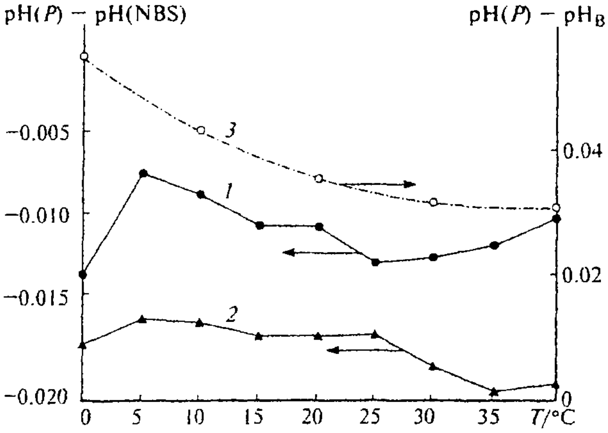

Fig. 1. Comparison of the pH values of TRIS buffer on different scales: *1*, pH(*P*) − pH(NBS)[16] for $m_{\mathrm{B}} = 0.05$, $m_{\mathrm{BH}} = 0.05$; *2*, pH(*P*) − pH(NBS)[15] for $m_{\mathrm{B}} = 0.01667$, $m_{\mathrm{BH}} = 0.05$; and *3*, pH(*P*) − $\mathrm{pH_B}$[13] for $m_{\mathrm{B}} = 0.01667$, $m_{\mathrm{BH}} = 0.05$.

The role of the third virial coefficients in Eq. (14) can be evaluated by the parameters $C_{\mathrm{Na,Cl}} = 6.67 \cdot 10^{-4}$ and $C_{\mathrm{BH,Cl}} = -6.95 \cdot 10^{-4}$, which represent the electroneutral sum of the third virial coefficients. Evidently, the difference between these virial coefficients, which were neglected in the calculation of pH(*P*), should be a value of the same order. Based on this assumption, we may suggest that the maximum error due to the neglect of the third virial coefficients in Eq. (9) should not exceed 0.01 pH unit for a NaCl molality of 4. Neglecting the second virial coefficients, $\lambda_{\mathrm{Na,Na}}$ and $\lambda_{\mathrm{Cl,Cl}}$, can result, most likely, in an error that does not exceed several thousandths of a pH unit.

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