Estimation of Salt and Temperature Effects on Ion Product of Water in Aqueous Solution

Masunobu Maeda,* Osamu Hisada, Yoshiaki Kinjo,† and Kaname Ito
Department of Applied Chemistry, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya 466
†Chemical Laboratory, College of Education, University of the Ryukyus, Okinawa 903-01
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The ion product of water at 298.15 K was evaluated according to the Pitzer ionic interaction theory in LiCl, NaCl, KCl, KNO_3, $LiClO_4$, and $NaClO_4$ media of different concentrations (0.1—5 mol kg^{-1}) and in artificial seawaters at different salinities (20—44‰). The Pitzer approach was also applied to the estimation of the ion products of water in NaCl media at temperatures (288—373 K) different from 298.15 K. The theoretically evaluated values showed reasonable agreement with experimental ones.

In studying ionic equilibria over an alkaline range in an aqueous solution, a knowledge of the ion product of water in that solution is indispensable. By inspection of the ion products of water available (see Tables 1—9),[1—3] it is apparent that they are influenced in diverse manners by the type and concentration of the electrolyte as well as by the temperature. Thus, the theoretical evaluation of the ion product of water in an aqueous electrolyte solution at a desired composition and temperature, where the experimental information is absent or difficult to be obtained, is of crucial importance.

In a previous paper[4] the enthalpy changes for ionization of water were determined at 298.15 K in

Table 1. Comparison between Observed and Estimated Ion Products of Water in LiCl Media at 298.15 K (pK_w Values in Molal Units)[a]

Ionic strength/mol kg^{-1}	Obsd[15]	Est		
		Without[b]	With[c]	With[d]
0.110	13.759(1)	13.769	13.766	13.766
0.200	13.705(1)	13.725	13.719	13.718
0.500	13.636(1)	13.665	13.650	13.648
1.010	13.599(1)	13.649	13.618	13.610
2.010	13.609(1)	13.708	13.647	13.614
3.000	13.670(1)	13.819	13.728	13.654

a) The numbers in parentheses are uncertainties of the last decimal place. b) Without θ's and Ψ's, c) with θ_{HLi}, θ_{OHCl}, and Ψ_{HLiCl} available in the literature, d) with all the needed θ's and Ψ's (θ_{HLi}, θ_{OHCl}, and Ψ_{HLiCl} available and Ψ_{OHClLi} determined from observed pK_w values).

Table 2. Comparison between Observed and Estimated Ion Products of Water in NaCl Media at 298.15 K (pK_w Values in Molal Units)[a]

Ionic strength/mol kg^{-1}	Obsd[15]	Est	
		Without[b]	With[c]
0.110	13.780(1)	13.784	13.782
0.210	13.742(1)	13.747	13.744
0.510	13.708(1)	13.719	13.712
1.010	13.725(1)	13.746	13.730
2.010	13.839(1)	13·879	13.837
3.000	13.980(1)	14.056	13.981

a) The numbers in parentheses are uncertainties of the last decimal place. b) Without θ's and Ψ's, c) with all the needed θ's and Ψ's.

Table 3. Comparison between Observed and Estimated Ion Products of Water in KCl Media at 298.15 K (pK_w Values in Molal Units)[a]

Ionic strength/mol kg^{-1}	Obsd[15]	Est	
		Without[b]	With[c]
0.110	13.788(1)	13.793	13.788
0.210	13.756(1)	13.763	13.755
0.510	13.724(1)	13.754	13.733
1.010	13.769(1)	13.808	13.762
2.010	13.893(1)	13.984	13.879
3.000	14.020(1)	14.196	14.020

a) The numbers in parentheses are uncertainties of the last decimal place. b) Without θ's and Ψ's, c) with all the needed θ's and Ψ's.

Table 4. Comparison between Observed and Estimated Ion Products of Water in KNO_3 Media at 298.15 K (pK_w Values in Molal Units)[a]

Ionic strength/mol kg^{-1}	Obsd[3]	Est		
		Without[b]	With[c]	With[d]
0.060	13.809(2)	13.823	13.823	13.818
0.105	13.778(2)	13.791	13.792	13.784
0.140	13.753(2)	13.775	13.776	13.765
0.182	13.749(2)	13.762	13.763	13.749
0.262	13.730(2)	13.746	13.747	13.727
1.056	13.730(2)	13.770	13.775	13.711
2.187	13.880(2)	13.924	13.933	13.853

a) The numbers in parentheses are uncertainties of the last decimal place. b) Without θ's and Ψ's, c) with θ_{HK} available in the literature, d) with all the needed θ's and Ψ's (θ_{HK} available and θ_{OHNO_3}, Ψ_{HKNO_3}, and Ψ_{OHNO_3K} determined from observed pK_w values).

concentrated aqueous single electrolyte solutions of several kinds, and compared with those predicted in terms of the Pitzer ionic interaction model.[5,6] The observed and estimated values agreed fairly well. It was also found that the free energy and enthalpy changes for dissociation of ammonium ion determined at 298.15 K in concentrated single electrolyte solutions and in artificial seawaters[7-9] showed good agreement with those estimated via the Pitzer approach.

In the present work, the free energy changes for ionization of water (ion products of water) at 298.15 K were evaluated according to the Pitzer approach in LiCl, NaCl, KCl, KNO_3, $LiClO_4$, and $NaClO_4$ media with different concentrations (0.1—5 mol kg^{-1}) and in artificial seawaters at various salinities (20—44‰). The Pitzer approach was also applied to the estimation of the ion products of water in NaCl media at temperatures (288—373 K) different from 298.15 K. The theoretical values thus evaluated were compared with the experimental ones available in the literature.

The experimental values of the ion products, which are subjected to the comparison with the predicted values, are given in Tables 1—9. The ion products of water at 298.15 K in $LiClO_4$ media, which have not been reported, were experimentally determined in a usual way by acid-base titrations with hydrogen

Table 5. Comparison between Observed and Estimated Ion Products of Water in $LiClO_4$ Media at 298.15 K (pK_w Values in Molal Units)[a]

Ionic strength/mol kg^{-1}	Obsd[b]	Est Without[c]	Est With[d]	Est With[e]
0.512	13.66(1)	13.656	13.663	13.66
1.049	13.64(1)	13.636	13.649	13.64
2.202	13.66(1)	13.711	13.737	13.67
3.481	13.74(1)	13.879	13.915	13.74

a) The numbers in parentheses are uncertainties of the last decimal place. b) Experimentally obtained in the present work, c) without θ's and Ψ's, d) with θ_{HLi} and Ψ_{HLiClO_4} available in the literature, e) with all the needed θ's and Ψ's (θ_{HLi} and Ψ_{HLiClO_4} available and θ_{OHClO_4} and Ψ_{OHClO_4Li} determined from observed pK_w values).

Table 6. Comparison between Observed and Estimated Ion Products of Water in $NaClO_4$ Media at 298.15 K (pK_w Values in Molal Units)[a]

Ionic strength/mol kg^{-1}	Obsd[15]	Est Without[b]	Est With[c]	Est With[d]
0.100	13.77(1)	13.789	13.792	13.79
0.510	13.72(1)	13.717	13.732	13.72
1.050	13.76(1)	13.748	13.773	13.75
2.210	13.88(1)	13.913	13.948	13.88
3.000	14.03(1)	14.061	14.092	14.00
3.500	14.07(1)	14.165	14.189	14.07
4.660	14.24(1)	14.429	14.424	14.25

a) The numbers in parentheses are uncertainties of the last decimal place. b) Without θ's and Ψ's, c) with θ_{HNa} and Ψ_{HNaClO_4} available in the literature, d) with all the needed θ's and Ψ's (θ_{HNa} and Ψ_{HNaClO_4} available and θ_{OHClO_4} and Ψ_{OHClO_4Na} determined from observed pK_w values).

Table 8. Comparison between Observed and Estimated Ion Products of Water in 1.019 mol kg^{-1} NaCl Medium at Temperatures Higher than 298.15 K (pK_w Values in Molal Units)[a]

Temperature/K	Obsd[20]	Est
303.15	13.535(5)	13.583
313.15	13.234(5)	13.288
323.15	12.955(5)	13.012
333.15	12.698(5)	12.745
343.15	12.461(5)	12.486
353.15	12.243(5)	12.238
363.15	12.038(5)	12.026
373.15	11.854(5)	11.879

a) The numbers in parentheses are uncertainties of the last decimal place.

Table 7. Comparison between Observed and Estimated Ion Products of Water in Artificial Seawaters of Different Salinities at 298.15 K (pK_w Values in Molal Units)

Salinity/‰		19.90		26.87		34.82		44.00	
		Obsd[19]	Est	Obsd[19]	Est	Obsd[19]	Est	Obsd[19]	Est
pK_w		13.31	13.26	13.23	13.14	13.17	13.03	13.09	12.92
Composition[a] /mol kg^{-1}	Na^+	0.2768		0.3793		0.4960		0.6319	
	Mg^{2+}	0.0302		0.0416		0.0546		0.0695	
	Ca^{2+}	0.00598		0.00820		0.01073		0.01365	
	Cl^-	0.3168		0.4345		0.5690		0.7242	
	SO_4^{2-}	0.0162		0.0222		0.0288		0.0370	
Ionic strength[b] /mol kg^{-1}		0.4016		0.5509		0.7208		0.9184	

a) Estimated in the present work, b) calculated with neglect of ion-pairing.

Table 9. Comparison between Observed and Estimated Ion Products of Water in NaCl Media at 308.15 and 288.15 K (pK_w Values in Molal Units)[a)]

Ionic strength/mol kg^{-1}	308.15 K			288.15 K	
	Obsd[3)]	Est[b)]	Est[c)]	Obsd[3)]	Est
0.500	13.37(1)	13.402	13.395	14.07(1)	14.074
1.02	13.38(1)	13.434	13.421	14.06(1)	14.103
2.08	13.46(1)	13.588	13.559	14.15(1)	14.247

a) The numbers in parentheses are uncertainties of the last decimal place. b) Estimated with parameter values in Table 13, c) estimated with parameter values in Table 14.

Table 10. Ion Products of Water at Ionic Strength=0 and Different Temperatures[3)]

Temperature/K	pK_w
288.15	14.345(1)
298.15	13.997(1)
303.15	13.834(1)
308.15	13.680(1)
313.15	13.535(1)
323.15	13.263(1)
333.15	13.016(1)
343.15	12.800(1)
353.15	12.598(1)
363.15	12.422(1)
373.15	12.266(1)

The numbers in parentheses are uncertainties of the last decimal place.

electrodes.[10)] The pK_w values originally expressed in molar concentration units were converted to the values with the molality scale by the use of the densities of the salt solutions. The densities of electrolyte solutions, when not available in the literature, were measured pycnometrically.

Procedures for Theoretical Estimation of Ion Product. The autoprotolytic reaction of water is denoted by Eq. 1,

$$H_2O = H^+ + OH^-. \tag{1}$$

The relation of the ion product, $K_w(I,T)$, with the activity coefficients of the relevant ionic species, γ, and the water activity, a_{H_2O}, in solution at ionic strength I mol kg^{-1} and temperature T K is represented by Eq. 2,

$$pK_W(I,T) = pK_W(0,T) + (\ln\gamma_H + \ln\gamma_{OH} - \ln a_{H_2O}) / \ln 10, \tag{2}$$

where $pK_w(0,T)$ denotes the ion product in a salt-free solution. Since the $pK_w(0,T)$ value is usually available in the literature, the present problem is reduced to estimating the γ values of H^+ and OH^- ions and the a_{H_2O} in the solution at ionic strength I and temperature T. The accepted $pK_w(0,T)$ values at temperatures of interest are given in Table 10.[3)]

According to Pitzer's approach,[11)] the trace activity coefficients of the ionic components of unit charge, H^+ and OH^-, and the water activity in the solution containing cations c's and anions a's of ionic strength I can be determined from Eqs. 3, 4, and 5, respectively.

$$\begin{aligned}\ln\gamma_H = {} & F + \sum_{a=1}^{N_a} m_a(2B_{Ha} + ZC_{Ha}) \\ & + \sum_{c=1}^{N_c} m_c(2\theta_{Hc} + \sum_{a=1}^{N_a} m_a\Psi_{Hca}) \\ & + \sum_{a=1}^{N_a-1}\sum_{a'=a-1}^{N_a} m_a m_{a'}\Psi_{aa'H} + \sum_{c=1}^{N_c}\sum_{a=1}^{N_a} m_c m_a C_{ca},\end{aligned} \tag{3}$$

$$\begin{aligned}\ln\gamma_{OH} = {} & F + \sum_{a=1}^{N_c} m_c(2B_{cOH} + ZC_{cOH}) \\ & + \sum_{a=1}^{N_a} m_a(2\theta_{OHa} + \sum_{c=1}^{N_c} m_c\Psi_{OHac}) \\ & + \sum_{c=1}^{N_c-1}\sum_{c'=c-1}^{N_c} m_c m_{c'}\Psi_{cc'OH} + \sum_{c=1}^{N_c}\sum_{a=1}^{N_a} m_c m_a C_{ca},\end{aligned} \tag{4}$$

$$\ln a_{H_2O} = -0.0180\phi \sum_i m_i. \tag{5}$$

For use in Eqs. 3—5 the following terms are defined.

$$\begin{aligned}F = {} & -A^\phi[I^{1/2}/(1+1.2I^{1/2}) + (2/1.2)\ln(1+1.2I^{1/2})] \\ & + \sum_{c=1}^{N_c}\sum_{a=1}^{N_a} m_c m_a B'_{ca} + \sum_{c=1}^{N_c-1}\sum_{c'=c+1}^{N_a-1} m_c m_a \theta'_{cc'} \\ & + \sum_{a=1}^{N_a-1}\sum_{a'=a+1}^{N_a} m_a m_{a'}\theta'_{aa'}\end{aligned} \tag{6}$$

$$C_{ca} = C^\phi_{ca}/2|z_c z_a|1/2 \tag{7}$$

$$Z = \sum_i z_i m_i \tag{8}$$

$$\begin{aligned}\sum_i m_i(\phi-1) = {} & 2(-A^\phi I^{3/2}/(1+1.2I^{1/2}) \\ & + \sum_{c=1}^{N_c}\sum_{a=1}^{N_a} m_c m_a(B^\phi_{ca} + ZC_{ca}) \\ & + \sum_{c=1}^{N_c-1}\sum_{c'=c+1}^{N_c} m_c m_{c'}(\theta^\phi_{cc'} + \sum_{a=1}^{N_a} m_a\Psi_{cc'a}) \\ & + \sum_{a=1}^{N_a-1}\sum_{a'=a+1}^{N_a} m_a m_{a'}(\theta^\phi_{aa'} + \sum_{c=1}^{N_c} m_c\Psi_{aa'c})\end{aligned} \tag{9}$$

In Eq. 3 m_c is the molality of cation c, and N_c the total number of cations. Similar definitions apply for anions a's. A^ϕ in Eqs. 6 and 9 is the Pitzer-Debye-Hückel limiting slope given by Eq. 10,

$$A^\phi = (1/3)(2\pi N_0 d_w/1000)^{1/2}(e^2/DkT)^{3/2}, \tag{10}$$

where N_0 is Avogadro's number, d_w and D are the density and dielectric constant of water, respectively. The second virial coefficients B in Eqs. 3, 4, 6, and 9 are given by the following ionic strength dependence.

$$B^{\phi}_{ca} = \beta^{(0)}_{ca} + \beta^{(1)}_{ca} \exp(-\alpha_{ca} I^{1/2}) + \beta^{(2)}_{ca} \exp(-12 I^{1/2}) \quad (11)$$

$$B_{ca} = \beta^{(0)}_{ca} + \beta^{(1)}_{ca} g(\alpha_{ca} I^{1/2}) + \beta^{(2)}_{ca} g(12 I^{1/2}) \quad (12)$$

$$B'_{ca} = \beta^{(1)}_{ca} g'(\alpha_{ca} I^{1/2})/I + \beta^{(2)}_{ca} g'(12 I^{1/2})/I \quad (13)$$

The functions, g and g', are defined by the equations.

$$g(x) = 2(1-(1+x)\exp(-x))/x^2 \quad (14)$$

$$g'(x) = -2(1-(1+x+x^2/2)\exp(-x))/x^2 \quad (15)$$

with $x=\alpha_{ca}/I^{1/2}$ or $12I^{1/2}$. When either cation c or anion a is univalent, $\alpha_{ca}=2$. For 2:2 or higher valence pairs $\alpha_{ca}=1.4$. The second virial coefficients θ, which depend on the ionic strength, are given in the following form.

$$\theta^{\phi}_{ij} = \theta_{ij} + {}^{E}\theta_{ij}{}^{(I)} + I^{E}\theta'_{ij}{}^{(I)} \quad (16)$$

$$\theta_{ij} = \theta_{ij} + {}^{E}\theta_{ij}{}^{(I)} \quad (17)$$

$$\theta'_{ij} = {}^{E}\theta_{ij}{}^{(I)} \quad (18)$$

When the ions i and j are of the same charge, ${}^{E}\theta_{ij}(I)$ and ${}^{E}\theta'_{ij}(I)$ are set equal to zero. The third virial coefficients, C^{ϕ}_{ca} and ψ_{ijk} are assumed to be independent of the ionic strength.[6] Usually, the contributions of the higher order terms θ and ψ are small, and significant only at high ionic strength.

The values for $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^{ϕ} at 298.15 K have been calculated from the activity coefficient and osmotic coefficient data of single electrolytes, and the values for θ and ψ at 298.15 K from the data of mixed electrolytes.[12—14] The relevant parameter values used in the calculations by means of Eqs. 3—5 are collected in Tables 11 and 12.

Since the parameter values for the Mg^{2+}-OH^- interactions, which are needed for the theoretical calculations in artificial seawaters, are not available, they were estimated on the basis of hydrolysis data for Mg^{2+} and Ca^{2+} ions. The equilibrium constant for the reaction $M^{2+}(M=Mg \text{ or } Ca)+OH^-=MOH^+$ has been reported to be ca. 360 for Mg^{2+} and 14 for Ca^{2+} at 298.15 K in a salt-free solution,[15] while no data for their enthalpy changes having been reported. Thus, the $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^{ϕ} for the Mg^{2+}-OH^- interactions were estimated simply on the assumption that they were 360/14 times the corresponding values for the Ca^{2+}-OH^- interactions. These parameter values are given in Table 11.

The parameter values $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} for HCl,

Table 11. Single Electrolyte Parameters in Pitzer's Equations at 298.15 K

Catioa	Anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}
H	Cl	0.1775	0.2945		0.0008
H	NO_3	0.1119	0.3206		0.0010
H	ClO_4	0.1747	0.2931		0.00819
H	SO_4	0.0298			0.0438
Li	OH	0.015	0.14		
Na	OH	0.0864	0.253		0.0044
K	OH	0.1298	0.320		0.0041
Mg	OH	−4.49[a)]	−5.92[a)]	−147[a)]	
Ca	OH	−0.1747	−0.2303	−5.72	
Li	Cl	0.1494	0.3074		0.00359
Na	Cl	0.07650	0.2664		0.00127
K	Cl	0.04835	0.2122		−0.00084
Mg	Cl	0.35235	1.6815		0.00519
Ca	Cl	0.31590	1.6140		−0.00034
Li	NO_3	0.1420	0.2780		−0.0051
Na	NO_3	0.0068	0.1783		−0.00072
K	NO_3	−0.0816	0.0494		0.00660
Li	ClO_4	0.1973	0.3996		0.0008
Na	ClO_4	0.0554	0.2755		−0.00118
Na	SO_4	0.01958	1.1130		0.00497
Mg	SO_4	0.22100	3.3430	−37.25	0.025
Ca	SO_4	0.20000	2.650	−57.70	

a) Estimated by multiplying 360/14.0 the corresponding values for the Ca^{2+}-OH^- interactions.

Table 12· Common-Ion Two Electrolyte Parameters in Pitzer's Equations at 298.15 K

Cation (c)	Cation (c′)	θcc′	Ψcc′Cl	Ψcc′NO_3	Ψcc′ClO_4
H	Li	0.015	0.000		-0.001_7
H	Na	0.036	−0.004		−0.016
H	K	0.005	−0.007	−0.015[a)]	
H	Mg	0.10	−0.011		
H	Ca	0.092	−0.015		

Anion (a)	Anion (a′)	θaa′	Ψaa′Li	Ψaa′Na	Ψaa′K	Ψaa′Ca
OH	Cl	−0.050	−0.019[a)]	−0.006	−0.008	−0.025
OH	NO_3	−0.094[a)]			0.062[a)]	
OH	ClO_4	0.0013[a)]	−0.037[a)]	−0.008[a)]		
OH	SO_4	−0.013		−0.009		

a) Estimated from observed pK_w values.

NaCl, and NaOH required to predict the pK_w values in NaCl media at temperatures higher than 298.15 K were estimated in the following.

Recently, Pitzer and coauthors[16,17] have estimated the ion-interaction parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} for several 1 : 1 electrolytes including HCl and NaCl as a function of temperature on the basis of the apparent molar heat capacities above 298.15 K, and represented the temperature dependence of the parameter values by simple empirical equations. The parameter values for $\beta^{(0)}$, $\beta^{(1)}$, and C at T K and 1.01×10^5 Pa are expressed by the following equations,

$$\begin{aligned}\beta^{(0)} = {} & A_\beta^c(T/2+298^2/2T-298) \\ & + B_\beta^c(T^2/6+298^3/3T-298^2/2) \\ & + C_\beta^c(T^3/12+298^4/4T-298^3/3) \\ & + (298-298^2/T)(\partial\beta^{(0)}(298)/\partial T) \\ & + \beta^{(0)}(298),\end{aligned} \tag{19}$$

$$\beta^{(1)} = (298-298^2/T)(\partial\beta^{(1)}(298)/\partial T) + \beta^{(1)}(298), \tag{20}$$

$$C = (298-298^2/T)(\partial C(298)/\partial T) + C(298), \tag{21}$$

where A_β^c, B_β^c, and C_β^c are the fitting parameters independent of temperature. The temperature derivatives of the parameter values at 298.15 K have been obtained from the heat of dilution data for the electrolytes.[6] The parameter values $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} for HCl at temperatures of interest were calculated with the values for A_β^c, B_β^c, and C_β^c and those for the temperature derivatives of $\beta^{(0)}$, $\beta^{(1)}$, and C. The values for NaCl were taken from Ref. 16. They are collected in Table 13. Since the three A_β^c, B_β^c, and C_β^c values for NaOH are not available, they were estimated on the basis of the observed pK_w data at three temperatures; i. e., Eqs. 19—21 were introduced into Eqs. 3—5, and the rearranged Eqs. 3—5 into Eq. 2. The observed pK_w values in 1.019 mol kg^{-1} NaCl medium at 353, 363, and 373 K in Table 8 and the p$K_w(0,T)$ values at the corresponding temperatures in Table 10 were then introduced into Eq. 2 to solve the three resultant equations for the A_β^c, B_β^c, and C_β^c values. In these calculations was made no introduction of the higher order terms θ and ψ, because their contributions are expected to be small at this level of concentration. The A_β^c, B_β^c, and C_β^c values for NaOH were estimated to be 21.6, −0.132, and 2.01×10^{-4}, respectively. In Table 13 are also shown the parameter values $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} for NaOH at temperatures in question calculated according to Eqs. 19—21 with the relevant parameter values.

The ion-interaction parameter values $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} for HCl, NaOH, and NaCl at 308.15 K were calculated according to Eq. 22[6] on the basis of their activity coefficients at that temperature available in the literature.[18]

$$\ln\gamma_{ca} = f^{\gamma} + m_{ca}B_{ca}^{\gamma} + m_{ca}^2C_{ca}^{\gamma}, \tag{22}$$

where

$$\begin{aligned}f^{\gamma} = {} & -A^{\phi}[I^{1/2}/(1+1.2I^{1/2}) \\ & + (2/1.2)\ln(1+1.2I^{1/2})],\end{aligned} \tag{23}$$

$$\begin{aligned}B_{ca}^{\gamma} = {} & 2\beta^{(0)} + (\beta_{ca}^{(1)}/2I)[1 \\ & - \exp(-2I^{1/2})(1+2I^{1/2}-2I)],\end{aligned} \tag{24}$$

$$C_{ca}^{\gamma} = (3/2)C_{ca}^{\phi}. \tag{25}$$

The calculated ion-interaction parameter values at

Table 13. Single Electrolyte Parameters in Pitzer's Equations at Temperatures above 298.15 K

	$\beta^{(0)}$			$\beta^{(1)}$			$C^{\phi}\times10^3$		
Temperature/K	HCl	NaOH	NaCl	HCl	NaOH	NaCl	HCl	NaOH	NaCl
303.15	0.1782	0.0907	0.0788	0.2952	0.254	0.2814	1.1	3.4	0.88
308.15	0.1788	0.101	0.0817	0.2959	0.254	0.2833	1.4	2.6	0.40
313.15	0.1791	0.110	0.0846	0.2965	0.255	0.2893	1.6	1.7	−0.04
323.15	0.1793	0.120	0.0892	0.2977	0.256	0.2967	2.2	0.0	−0.80
333.15	0.1788	0.114	0.0927	0.2989	0.257	0.3038	2.7	−1.5	−1.46
343.15	0.1777	0.0848	0.0956	0.3000	0.258	0.3109	3.2	−3.0	−2.04
353.15	0.1767	0.0521	0.0977	0.3010	0.259	0.3180	3.6	−4.3	−2.52
363.15	0.1764	0.0326	0.0992	0.3020	0.260	0.3253	4.1	−5.7	−2.94
373.15	0.1778	0.0621	0.1002	0.3030	0.261	0.3326	4.5	−6.9	−3.30

Table 14. Single Electrolyte Parameters in Pitzer's Equations at 288.15 and 308.15 K

	$\beta^{(0)}$			$\beta^{(1)}$			$C^{\phi}\times10^3$		
Temperature/K	HCl	NaOH	NaCl	HCl	NaOH	NaCl	HCl	NaOH	NaCl
288.15	0.1782	0.0833	0.0675	0.2940	0.2434	0.2615	2.2	3.8	3.1
308.15	0.1746	0.0971	0.0790	0.2913	0.2507	0.2882	−0.6	0.1	1.7

308.15 K are given in Table 14. The observed pK_w values in NaCl media at 308.15 K (Table 9) were compared with both of the values predicted with the parameter values in Table 13 and with those in Table 14.

The parameter values for HCl, NaOH, and NaCl given in Table 13, which have been estimated by the use of the heat capacities at temperatures above 298 K, are not applicable to the prediction of pK_w values at temperatures below 298 K. Thus, for the prediction of pK_w values in NaCl media at 288.15 K (observed pK_w values in Table 9) the ion-interaction parameter values for HCl, NaOH, and NaCl were calculated in the same manner as for the case at 308.15 K according to Eq. 22 by using their activity coefficients at 288.15 K available in the literature.[18] The calculated parameter values are given in Table 14.

Results and Discussion

Evaluation of pK_w Values in Single Electrolyte Solutions at 298.15 K. In Tables 1—6 there are quantitative comparisons between the observed and predicted pK_w values in single electrolyte solutions at 298.15 K. The calculations were made with and without the higher order terms θ and ψ so that the need for considering the terms was examined. All the θ and ψ values required for the calculations are known only in NaCl and KCl media. As for the NaCl and KCl media it is apparent from Tables 2 and 3 that the values calculated with the higher order terms in Table 12 are in agreement with the observed ones within the experimental uncertainties, while the differences are fairly large, especially at high molalities in the calculations without them. These results point out the need to use θ and ψ values at high ionic strengths when they are available. The agreement between the values observed and those predicted with the higher order terms in the NaCl and KCl media demonstrates the validity of the Pitzer approach, and thus, suggests that unknown θ and ψ values are determinable from the observed pK_w values. With the other electrolyte solutions (Tables 1, 4—6), where all the higher order terms are not always available, it is seen that rather large discrepancies between the values observed and those calculated without the higher order terms occur at higher ionic strengths. The introduction of a partial set of the higher order terms leads to worse agreement between the observed and predicted values (an exception being the LiCl system). The higher order terms should be included when a full set of them are known. However, the omission of unknown θ and ψ values is unlikely to have a serious effect at low ionic strengths. Unknown θ and ψ values were estimated according to Eqs. 2—5 on the basis of the observed pK_w values in Tables 1 and 4—6. In Table 12 are also given the θ and ψ values thus estimated, which may be employed for the theoretical calculations of equilibrium constants in other systems where H^+ and/or OH^- ions participate.

Evaluation of pK_w Values in Artificial Seawaters at 298.15 K. The values observed and predicted with the parameter values in Tables 11 and 12 are compared each other in Table 7. Although the deviations are seen to exceed the experimental uncertainties, the agreement may be reasonable in view of the fact that the parameter values for the Mg^{2+}–OH^- interactions were estimated with the simple assumption (360/14 times the parameter values for the Ca^{2+}–OH^- interactions) and that the composition for each seawater, which was not given in Ref. 19, was deduced on the basis of the description about its preparation procedures. From a comparison of the pK_w values in Tables 2 and 7 it is apparent that the pK_w values in the seawaters are much smaller than the values in the NaCl solutions at the corresponding ionic strengths. An attempt was made to calculate the pK_w values in the seawaters on the assumption that the parameter values for the Mg^{2+}–OH^- interactions were the same as those for the Ca^{2+}–OH^- interactions. It was found that the calculated pK_w values were around 13.7(19.90‰)—13.5(44‰), which are much higher by 0.4 than the observed values. This result indicates that the main difference between the pK_w values in the seawaters and those in the NaCl media results from the Mg^{2+}–OH^- interactions in the seawaters.

Evaluation of pK_w Values in NaCl Media at Temperatures Different from 298.15 K. a) pK_w Values in 1.019 mol kg^{-1} NaCl Medium at Temperatures above 298.15 K. It is seen from Table 8 that the observed values are in reasonable agreement with the predicted ones in consideration of the fact that the activity coefficients of NaOH have been estimated by using the A_{β}^{ϕ}, B_{β}^{ϕ}, and C_{β}^{ϕ} values calculated from a limited number of pK_w values for lack of the apparent heat capacity data for NaOH.

b) pK_w Values at 308.15 K. The observed values are compared in Table 9 with both the values estimated with the parameter values in Table 13 and with those in Table 14. The observed values yield better agreement with the values estimated with the data in Table 14, which is reasonable, if one considers some uncertainties introduced in the calculations of the parameter values for NaOH in Table 13. The rather large discrepancy at 2.08 mol kg^{-1} may be due to the neglect of the higher order terms which are not available.

c) pK_w Values at 288.15 K. The observed and calculated values in Table 9 are seen to show good agreement each other.

In the light of the above results, it may be said that although the deviations between the observed and estimated values exceed in some cases by far the experimental uncertainties probably due to approximations made in the calculations and the unavailableness of higher order terms, the present results demonstrate the reliability of the ionic interaction model by Pitzer and co-workers to estimate free energy changes in concentrated salt solutions over a wide range of temperature. It is necessary to determine higher order terms by e.g., isopiestic measurements in mixed electrolyte solutions so that free energy changes at high ionic strengths should be predicted more accurately.

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