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The Ionic Product of Water in Highly Concentrated Aqueous Electrolyte Solutions

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Summary. The ionic product of water, $K_w = [H^+][OH^-] = 10^{-pK_w}$, has been determined in aqueous NaCl (0.5–5.0 *M*), KCl (3.0 *M*), $NaNO_3$ (3.0 and 5.0 *M*), and KNO_3 (2.5 *M*) at 25 °C from high-precision potentiometric titrations carried out in cells with liquid junction using either glass or hydrogen electrodes. Measurements of K_w provide a set of self-consistent data that can be used in the estimation of activity coefficient changes and liquid junction potentials in the study of extremely concentrated electrolyte solutions. Where comparison is possible, results obtained by hydrogen electrode measurements are in excellent agreement (*ca* ± 0.005 in pK_w) with other reliable experimental values and the predictions of the *Pitzer* activity-coefficient model. The glass electrode results are, as expected, routinely lower (by 0.03–0.05 pK_w units), owing to interference by Na^+ ions. This effect virtually disappears in solutions of potassium salts. Comparison of the experimental results with the *Pitzer* predictions shows that knowledge of the ternary interaction parameters is essential to account for specific ionic effects in the concentration dependence of pK_w.

Keywords. Aqueous electrolyte solutions; Glass electrode; Hydrogen electrode; Ionic product of water; *Pitzer* model; Potentiometric titration.

Das Ionenprodukt des Wassers in hochkonzentrierten wäßrigen Elektrolytlösungen

Zusammenfassung. Das Ionenprodukt des Wassers, $K_w = [H^+][OH^-] = 10^{-pK_w}$, wurde in wässerigen Lösungen von NaCl (0.5–5.0 *M*), KCl (3.0 *M*), $NaNO_3$ (3.0 and 5.0 *M*) und KNO_3 (2.5 *M*) bei 25 °C gemessen. Dazu wurden potentiometrische Titrationen unter Verwendung von Glas- oder Wasserstoffelektroden in Zellen mit Überführung durchgeführt. Mit diesen pK_w-Werten kann man Änderungen der Aktivitätskoeffizienten in hochkonzentrierten Elektrolytlösungen ermitteln sowie Diffusionspotentiale abschätzen. Die mit Wasserstoffelektroden erhaltenen pK_w-Werte stimmen mit verläßlichen Literaturdaten innerhalb von *ca.* ± 0.005 überein. Bei Messungen mit Glaselektroden führt der Na^+-Fehler zu um 0.03–0.05 kleineren pK_w-Werten. Dieser Effekt wurde in Kaliumsalzlösungen nicht beobachtet. Der Vergleich der experimentellen Resultate mit Voraussagen des *Pitzer*-Modells unterstreicht die Bedeutung ternärer Wechselwirkungsparameter für die exakte Berechnung des Ionenproduktes.

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Introduction

Highly concentrated electrolyte solutions play a significant role in many hydrometallurgical processes. Perhaps the economically most important is the *Bayer* process for the extraction of alumina by dissolution of bauxite in concentrated NaOH. In addition to being directly relevant to the development of thermodynamic models for such industrial processes, the thermodynamic characterization of concentrated electrolytes is of more general interest, since investigations of reaction equilibria in aqueous solution are widely carried out in the presence of an inert or supporting electrolyte of sufficiently high concentration that ionic activity coefficients remain virtually constant.

Since the pioneering studies by *Harned* and coworkers [1–3] in the 1930s and 1940s, relatively few studies have focussed on the determination of pK_w. Indeed, most pK_w values in the concentrated electrolytes considered in the present work [4–21] (summarized in Table 1) have been reported as a minor part of studies of protonation, metal-ligand complexation, or solubility studies. Not surprisingly, little information is usually provided and it is often difficult to assess the reliability of such values. This is especially true since the introduction of computer methods for the least-squares analysis of experimental data. Consequently, pK_w is not known at all for many electrolytes and even for those that are commonly used as "inert" electrolytes in solution chemistry, the data are not entirely consistent and are missing over some ranges of ionic strength. In particular, relatively few data are available for concentrated solutions (3 *M* or above). It is also apparent from Table 1 that the influence of ionic strength on the value of pK_w is clearly different for each electrolyte, although these differences are not so great as to obscure the overall qualitative trend observed in the ionic-strength dependence of pK_w.

This work forms part of our continuing thermodynamic investigations of chemical equilibria in concentrated electrolytes where, in particular, we need systematic and internally-consistent measurements of pK_w. These are required for the estimation of activity coefficient changes, liquid junction potentials, and metal-ligand formation constants. Accordingly, the main aim of this paper is to describe some new determinations of the ionic product of water in aqueous NaCl, KCl, $NaNO_3$, and KNO_3, by application of glass- and hydrogen-electrode potentiometry. The data obtained are then related to published values for more dilute solutions and to calculated values obtained by the *Pitzer* concentrated electrolyte activity coefficient model. In addition to being directly useful for the description of chemical equilibria in these electrolytes, the measurement of pK_w over a range of concentrations is of obvious value in characterizing the electrolyte specificity in the ionic strength dependence.

Results and Discussion

The titrations involved measuring the potential of a cell that may be represented schematically as

$$\mathrm{Ag}|\mathrm{AgCl(s)}|5M\mathrm{NaCl(aq)}\underset{E_{j1}}{\|}5M\mathrm{NaCl(aq)}\underset{E_{j2}}{\|}x\ \mathrm{HX},\ (c\text{-}x)\ \mathrm{MX}|\mathrm{HE} \qquad 1$$

Table 1. Literature values of the ionic product of water (pK_w) in concentrated electrolytes at 298.15 K and 1 atm*

Electrolyte	molarity	molality	Method	pK_w (molar)	pK_w (molal)	Reference
KCl[a]	2.0	2.1332	H	13.97(3)	13.91	4
	3.0	3.3131		14.18(3)	14.09	
	sat.			14.39(3)		
KCl	0.1	0.1006	H	13.78(1)	13.77	5
	0.5	0.5087		13.76(1)	13.74	
	1.0	1.0329		13.80(1)	13.77	
	2.0	2.1332		13.96(1)	13.90	
	2.99	3.3008		14.17(1)	14.08	
	3.72	4.2186		14.34(1)	14.23	
KNO_3[b]	0.06	0.0603	G	13.809(2)	13.805	6
	0.10	0.1007		13.778(2)	13.772	
	0.14	0.1412		13.753(2)	13.746	
	0.18	0.1818		13.749(2)	13.740	
KNO_3	0.1	0.1007	G	13.78	13.77	7
KNO_3	0.0087	0.0087	G	13.91(1)	13.91	8
	0.0182	0.0183		13.88(1)	13.88	
	0.262	0.2655		13.73(1)	13.72	
	1.010	1.0557		13.73(1)	13.69	
	2.000	2.1870		13.88(1)	13.80	
NaCl[c]	0.4	0.4041	G	13.75	13.76	9
	0.6	0.6084		13.76	13.75	
	0.8	0.8144		13.78	13.74	
NaCl	1	1.0220	G	13.78	13.76	10
	3	3.2030		14.03	13.97	
NaCl		1	Na(Hg)		13.62	11
		3			13.88	
		6			14.22	
NaCl	0.05	0.0502	H	13.805(10)	13.802	12
	0.1	0.1005		13.775(1)	13.771	
	0.2	0.2013		13.749(8)	13.743	
	0.4	0.4041		13.733(4)	13.724	
	0.6	0.6084		13.727(1)	13.715	
	2.0	2.0873		13.866(3)	13.829	
NaCl	0.5	0.5060	G	13.62	13.61	19
	1.0	1.0220		13.7267(4)	13.7078	
	3.0	3.2030		14.02	13.96	

(continued)

Table 1 (*continued*)

Electrolyte	molarity	molality	Method	pK_w (molar)	pK_w (molal)	Reference
NaCl	0.5	0.5060	G	13.6742(3)	13.6638	20
	1.0	1.0220		13.714(2)	13.695	
	3.0	3.2030		13.989(2)	13.932	
$NaClO_4^d$	1	1.0504	G	13.77(1)	13.73	10
	3	3.4956		14.17(1)	14.04	
$NaClO_4$	0.260	0.2638		13.73(1)	13.72	8
$NaClO_4$	1	1.0504	H	13.77(1)	13.73	13
$NaClO_4$	3	3.4956	H	14.22(2)	14.09	14
$NaClO_4$	0.1	0.1007	H	13.78(1)	13.77	5
	0.5	0.5130		13.74(1)	13.72	
	1.0	1.0504		13.80(1)	13.76	
	2.0	2.2083		13.97(1)	13.88	
	2.99	3.4820		14.20(1)	14.07	
	3.8	4.6369		14.42(2)	14.25	
$NaClO_4$	0.3	0.3050	G	13.76	13.75	15
$NaClO_4$	0.1	0.1007	H	13.75(3)	13.74	4
	0.4	0.4085		13.78(3)	13.76	
	1	1.0504		13.77(3)	13.73	
	3	3.4956		14.20(3)	14.07	
	5	6.5755		14.94(3)	14.70	
$NaClO_4$	1.5	1.6146	G	13.95	13.89	16
	3.0	3.4956		14.09	13.96	
$NaClO_4$	3.0	3.4956	G	14.184(2)	14.051	21
$NaClO_4$	3.0	3.4956	G	14.15(1)	14.02	18
$NaNO_3^e$	2.0	2.1382	G	13.86	13.80	17

*H: hydrogen electrode; G: glass electrode; numbers in parentheses indicate the standard deviation in the last decimal place quoted. The conversion of pK_w to the molal scale employed the formula pK_w (molal) = pK_w (molar) + $2\log_{10}(c_i/m_i)$, where c_i/m_i is the ratio of molarity to molality for the particular electrolyte i, as estimated from published volumetric data. Sources of volumetric data: [a,c]*Gonçalves* and *Kestin* [43]; [b]*Halasey* [44]; [d]*Hölemann* and *Kohner* [45]; [e]*Isono* [46] where HE represents a hydrogen ion responsive glass (GE) or platinum ($H_2(g)|Pt$) electrode, and E_{j1} and E_{j2} are liquid junction potentials. E_{j1} is essentially constant and may be incorporated into the potential E_{ref} of the silver–silver chloride reference electrode. The potential of the cell is then

$$E_{cell} = E_{HE} - E_{ref} - E_{j2} \qquad 2$$

If it is assumed that throughout the course of a titration E_{ref}, E_{j2}, the activity coefficients of trace species (H^+ and OH^-), and the hydrogen fugacity (pressure) are constant, then it is readily shown by the usual methods of electrochemical thermodynamics that, at 25 °C, the relationship between the cell potential and the hydrogen ion concentration is

$$E_{cell}/\text{mV} = E^{0'}/\text{mV} + 59.16 \log([H^+]/\text{mol}\cdot\text{l}^{-1}) \qquad 3$$

where $E^{0'}$ is the "formal" cell potential, which includes the standard cell potential, the liquid junction potential E_{j2}, and activity coefficient and hydrogen fugacity terms.

Least-squares analysis of emf data given by equation 3 can be carried out with respect to either the values of the potential (to obtain an estimate of the formal potential) or of the concentration of H^+ ions (to obtain an estimate of K_w). These least-squares optimizations were carried out by use of the ESTA library of computer programs [24–26]. Results of such optimizations are summarized in Table 2. It should be noted that the stated precisions in parentheses refer to the internal consistency of the titration data. The real errors in the equilibrium constant (pK_w) are generally an order of magnitude greater than the internal precision [26].

Table 2. Present results for pK_w at 298.15 K and 1 atm*

Electrolyte	Molarity	Molality	Method	pK_w (molar)	pK_w (molal)
NaCl	0.5	0.5060	G	13.7004(3)	13.6900
			H	13.7319(3)	13.7215
	1.0	1.0220	G	13.7169(4)	13.6980
			H	13.7560(2)	13.7371
	3.0	3.2030	G	14.0248(6)	13.9680
			H	14.0887(3)	14.0318
	5.0	5.6124	G	14.4890(6)	14.3872
			H	14.5383(3)	14.4379
$NaNO_3$	3.0	3.3259	G	13.9527(3)	13.8631
	5.0	6.0231	G	14.2734(6)	14.1117
KCl	3.0	3.3131	G	14.1462(3)	14.0600
			H	14.1574(4)	14.0712
KNO_3	2.5	2.8020	G	13.9820(5)	13.8830

* Abbreviations and details as for Table 1; see also text

Since ions are produced by the dissociation of water, the Gibbs energy change and equilibrium extent of this reaction in an electrolyte solution depend significantly on the ionic strength. The experimental data obtained in the present study (Table 2) and previous work (Table 1) show that the value of pK_w is influenced not only by the ionic strength but also by the identity of the ions present. This reflects the specificity in the interactions between various combinations of ions. The experimentally measurable quantity that results most directly from ionic interactions in an electrolyte solution is the mean activity coefficient, which is a geometric mean of the activity coefficients of an electroneutral combination of individual ions. Knowledge of this quantity is of critical importance in the prediction or correlation of thermodynamic properties of electrolytes, including the ionic product of water.

The variation of the mean activity coefficient with concentration for dilute (say, $\leq 10\,\mathrm{m}M$) electrolytes is represented quite well by the *Debye-Hückel* theory (discussed, for example, by *Bockris* and *Reddy* [27]). Although the introduction of a characteristic ion-size parameter (or distance of closest approach) increases the range of validity of the *Debye-Hückel* theory to about $0.1\,M$, the extended *Debye-Hückel* theory is incapable of describing the activity coefficient behaviour of electrolytes at the concentrations of interest in the present work.

As a result of the complexity of the underlying statistical-mechanical problem, attempts to predict the specificities in the activity coefficient behaviour of concentrated electrolytes in terms of an ionic interaction model have met with rather limited success. However, several empirical activity coefficient models (discussed in detail in the monograph by *Zemaitis et al.* [28]) have been found to correlate such behaviour quite well. Three essential components of these models can be identified. The first is a formula constructed to reproduce the mean activity coeficient for a single electrolyte as a function of concentration. The electrolyte specific parameters (usually 1–4 for each cation–anion pair) in such formulae are obtained by regression analysis of experimental data. The second component is a mixing rule relating the model dependent parameters for a mixed electrolyte to the parameters pertinent to each constituent neutral electrolyte. The remaining component, which follows directly from the activity coefficient formula by application of the *Gibbs-Duhem* relation, is an expression for the osmotic coefficient. This is of particular importance in the consideration of the ion product, since the osmotic coefficient is simply related to the activity of the solvent.

Nowadays, the most widely used of these empirical activity-coefficient models is that developed by *Pitzer* [29]. According to this model, each cation-anion interaction is characterized by an empirical function containing up to four parameters. In addition, ternary ionic interactions and interactions between ions of the same sign are considered. These higher-order interactions are characterized by additional empirical constants. The comparatively large number of empirical constants gives the *Pitzer* model considerable flexibility in correlating the thermodynamic properties of ternary electrolyte mixtures (*i.e.*, solvent plus two salts having one common ion). If all ternary subsystems have been parametrized, the *Pitzer* model is capable of predicting the thermodynamic properties of more complex electrolyte mixtures of geochemical [30] and industrial [31] interest.

To apply the *Pitzer* model to the calculation of the ionic product (as in the interesting study by *Maeda et al.* [32] of aqueous LiCl, NaCl, KCl, KNO_3, $LiClO_4$, and $NaClO_4$) it is necessary to know the interaction parameters pertinent to the various two- and three-ion combinations in the solution. Thus, a solution containing a single strong electrolyte MX is regarded as a mixture of the three electrolytes M^+OH^-, H^+X^- and M^+X^-. In addition to the binary electrolyte interaction parameters for M^+OH^-, H^+X^-, and M^+X^-, constants q and y describing the interactions between ions of the same sign and ternary ionic interactions, respectively, are required. The formulae for the activity coefficients of cation M and anion X in a mixed electrolyte, and the corresponding result for the osmotic coefficient are given in the Appendix.

The ionic product is determined by applying the condition of chemical equilibrium to the ionization reaction

$$H_2O(aq) = H^+(aq) + OH^-(aq) \tag{4}$$

with the result

$$K_w^0 = \frac{(\gamma_{H^+} m_{H^+})(\gamma_{OH^-} m_{OH^-})}{a_w} \tag{5}$$

The thermodynamic equilibrium constant is therefore

$$K_w^0 = \exp\left[-\frac{\mu_{H^+}^0 + \mu_{OH^-}^0 - \mu_{H_2O}^0}{RT}\right] \tag{6}$$

and can be evaluated by making the identification [33]

$$\mu_i^0 \equiv \Delta_f H_i^0 - TS_i^0 \tag{7}$$

where $\Delta_f H_i^0$ and S_i^0, are, respectively, the standard enthalpy of formation and standard entropy of species i at 298.15 K. The use of data from the NBS tables [34] summarized in Table 3 produces K_w^0 (298.15) = 1.009×10^{-14}.

Denoting the equilibrium molality of the hydrogen and hydroxide ions by x, the equilibrium equation is solved in the form

$$f(x) \equiv \frac{K_w^0 a_w}{\gamma_{H^+}\gamma_{OH^-} x^2} - 1 = 0 \tag{8}$$

Calculations were also carried out with the Gibbs energy minimization program "ChemSage" [35, 37] which incorporates the *Pitzer* model in the version of *Harvie*

Table 3. Conventional reference thermodynamic data for the ionization of water [34]

Species	$\Delta_f H_i^0 (kJ \cdot mol^{-1})$	$S_i^0 (J \cdot K^{-1} \cdot mol^{-1})$
$H^+(aq)$	0	0
$OH^-(aq)$	− 229.99	− 10.75
$H_2O(aq)$	− 285.83	69.91

et al. [36]. Comparison between experimental values of pK_w and those calculated according to the above scheme requires the conversion of the electrolyte concentration from the molar to the molal scale. This conversion can be effected by application of tabulated conversion factors (such as those given by *Millero* [38] for the more commonly used supporting electrolyte molarities), or by numerical interpolation from tabulated density data for each electrolyte.

The results obtained in the present study will be discussed with reference to (i) their agreement with published experimental values, (ii) agreement between values measured by hydrogen- and glass-electrode potentiometry, and (iii) comparison with pK_w values calculated from *Pitzer's* equations.

NaCl media

In Fig. 1, our experimental results for pK_w in aqueous NaCl are plotted against molality, together with selected data from the literature. Our hydrogen electrode results (●) are seen to agree very well (to within 0.01) with those of *Harned* and *Mannweiler* [3] (△) and quite well with those of *Sjöberg et al.* [12] (□), also obtained with the hydrogen electrode but over a more limited concentration range. This level of agreement is very rare for independent determinations of equilibrium constants.

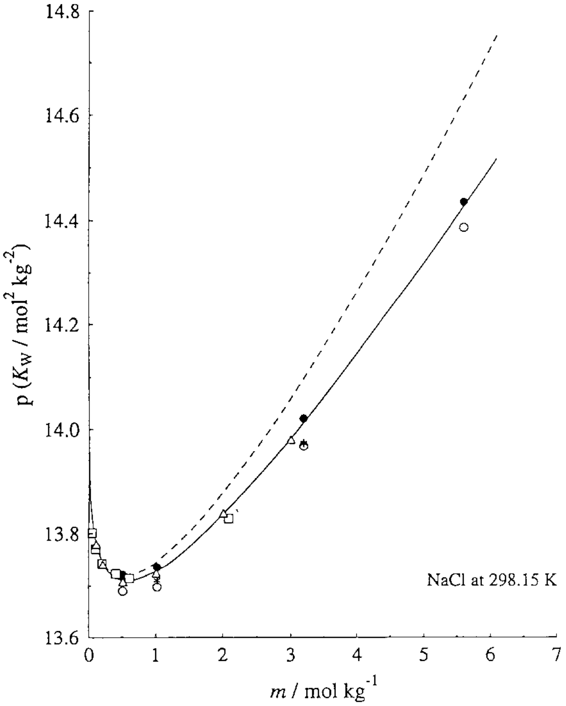

Fig. 1. Experimental and calculated values of pK_w for aqueous NaCl at 25 °C. ○: present investigation, glass electrode; ●: present investigation, hydrogen electrode; △: *Harned* and *Mannweiler* [3]; *: *Näsänen* and *Meriläinen* [10]; □: *Sjöberg et al.* [12]; ———: *Pitzer model;* --------: *Pitzer* model, neglecting higher-order terms

Our glass electrode results (○) are also in excellent agreement with literature data (Table 1), although the independent determinations vary more than for the hydrogen electrode (as perhaps might be expected). More important, it is apparent from Fig. 1 that there is a systematic difference between the glass and hydrogen electrode results at high ionic strengths. This appears to be outside the experimental error and is almost certainly due to interference of Na^+ with the glass membrane for large values of $-\log[H^+]$. Support for this interpretation comes from the increasing discrepancy with increasing concentration, and comparison of these results with those obtained in KCl (see below). Since the overwhelming majority of equilibrium constants are determined by glass electrode potentiometry in high concentrations of Na^+ containing media, further work is necessary to quantify these effects with modern glass electrodes.

Maeda et al. [32] compared literature values of pK_w in NaCl with those calculated from the *Pitzer* equations and showed that the extent of agreement is significantly dependent on the availability of the constants characterising the ternary (Ψ) and same-sign (θ) ionic interactions. This is illustrated in Fig. 1, which includes the *Pitzer*-predicted pK_w values with (solid curve) and without (dashed curve) the ternary and same-sign terms. It is of interest to note that the effect of the higher order interaction terms begins to be significant at molalities as low as $0.2\,\mathrm{mol\cdot kg^{-1}}$. At about $6\,m$, they contribute about 0.2 logarithmic units to pK_w.

KCl media

Our experimental data in $3\,M$ KCl (●, ○) are shown in Fig. 2, along with literature values [4, 5]. Whereas the discrepancy between our value and those of *Carpéni et al.* [4] (◆) and *Fischer* and *Byé* (◇) is significantly smaller (about 0.02) than the reported experimental precisions, it is noteworthy that the literature data are scattered about the *Pitzer* prediction (solid curve), whereas our value falls exactly on it. This and the fact that the earlier data are surprisingly imprecise for hydrogen electrode work (Table 1) suggests that a complete reinvestigation of pK_w in KCl media might be worthwhile. As for NaCl, the same-sign and ternary interaction parameters have a significant effect on the accuracy of the *Pitzer* prediction; indeed, this effect is even slightly larger than in NaCl. Unlike NaCl, however, our glass- and hydrogen-electrode results (Table 2) are in good agreement. As the K^+ interference with the glass membrane is known to be markedly lower than for Na^+, this observation supports the interpretation given above for the difference between the glass and hydrogen electrode results.

KNO_3 media

Results for KNO_3 solutions are shown in Fig. 3a. Data were obtained by use of glass electrodes, owing to the well-known instability of hydrogen electrodes in the presence of nitrates [39]. For KNO_3 media, our result (○) at $2.5\,M$ is consistent with the general trend of the results of *Näsänen* and *Meriläinen* [8] (◇) and *Jameson* and *Wilson* [6] (■). In contrast to NaCl and KCl media, a complete set of same-sign and ternary interaction parameters are not available to describe pK_w in KNO_3 solutions. As would be expected (cf. Figs. 1 and 2), the *Pitzer* predictions (Fig. 3a)

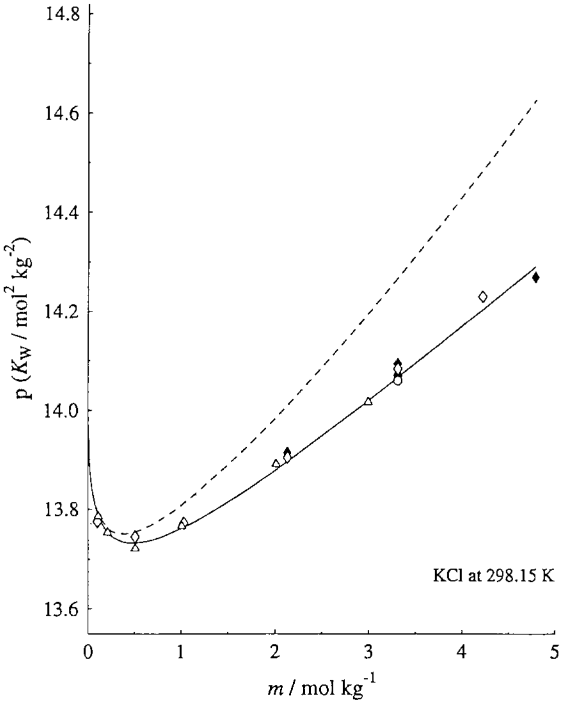

Fig. 2. Experimental and calculated values of pK_w for aqueous KCl at 25 °C. ○: present investigation, glass electrode; ●: present investigation, hydrogen electrode; △: *Harned* and *Hamer* [1]; ◆: *Carpéni et al.* [4], ◇: *Fischer* and *Byé* [5]; ———: *Pitzer* model; --------: *Pitzer* model, neglecting higher-order terms

are in relatively poor agreement with the experimental values (in comparing Fig. 3a with Figs. 1 and 2, differences in the axis scales should be noted.) The difference between the solid and dashed curves in Fig. 3a results only from the same-sign interaction parameter for K^+ and H^+, which has the value 0.005 [28].

If reliable independently determined values for the binary interaction parameters β_0, β_1, and C are available, it is possible in principle to estimate the relevant ternary interaction parameters in any electrolyte MX by optimization of pK_w data such as those in Fig. 3a. It should, however, be noted that only combinations such as $(\Psi_{H,M,X} + \Psi_{M,OH,X})$ can be unambiguously determined in this way, because the concentrations of M^+ and X^- cannot be varied independently. Application of the optimization technique developed recently by *Königsberger et al.* [37] to the experimental data shown in Fig. 3a yields a good fit only if the binary interaction parameters β_0, β_1, and C are determined simultaneously with the ternary parameters. If the values tabulated by *Pitzer* [29] are used, the fit is poor (see Fig. 3b). On the other hand, use of values of β_0, β_1, and C determined from pK_w data in Figs. 3a and 3b by such simultaneous optimization results in predictions of the mean activity coefficient for KNO_3 that are seriously (~ 50%) in error. There are two possible explanations for this.

The most direct and convenient method of estimating the values of binary *Pitzer* parameters involves regression analysis of experimental activity or osmotic coefficient (ϕ) data for simple electrolytes [40]. This is because for a binary

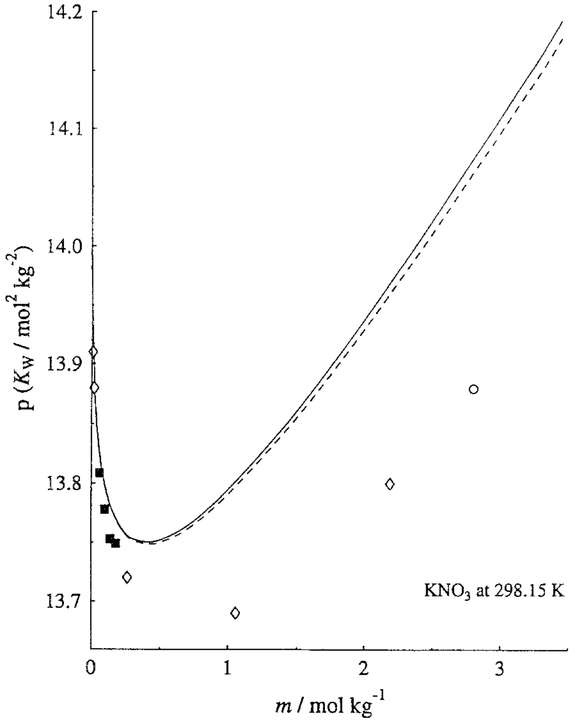

Fig. 3a. Experimental and calculated values of pK_w for aqueous KNO_3 at 25 °C. ○: present investigation, glass electrode; ◇: *Nasanen* and *Merilainen* [8]; ■: *Jameson* and *Wilson* [6]; ———: limited *Pitzer* model (see text); --------: *Pitzer* model, neglecting higher-order terms

electrolyte such as KNO_3, the expressions for ϕ and $\log\gamma_{\pm}$ are not only relatively simple but also linear with respect to the *Pitzer* parameters. In contrast, the connexion between the *Pitzer* parameters of pK_w is more complicated (since the *Pitzer* parameters influence the activity of the water as well as that of the ions), and relatively few data are available, so that errors in pK_w (of even a few hundredths of a unit) can exert large effects. Thus, regardless of the accuracy of the pK_w data in Figs. 3a and 3b, the binary *Pitzer* parameters derived from such data are unlikely to be as reliable as those determined from activity/osmotic coefficient data.

The second possible explanation for the discrepancy between the experimental and calculated data for KNO_3 concerns the published *Pitzer* parameters. *Kim* and *Frederick* [41] have observed that the *Pitzer* parameters determined by regression of ϕ and $\log\gamma_{\pm}$ depend strongly on the range of molality. They further pointed out [42] that osmotic coefficient data for mixtures of two electrolytes with a common ion are represented well by *Pitzer*'s model only if the interaction parameters for the constituent binary electrolytes are determined over the same concentration range represented by mixed-electrolyte data. For KNO_3 the upper limit of the molality range of the data given in Fig. 3 (about 3 mol·kg^{-1}) is clearly less than the maximum molalities in the data from which *Pitzer* [29] derived parameters for KNO_3 (3.8 mol·kg^{-1}), HNO_3 (6 mol·kg^{-1}) and KOH (5.5·mol kg^{-1}). These mismatches in the molality ranges are a less plausible explanation of the failure of the model than errors in the pK_w data. It appears that reliable measurements of osmotic

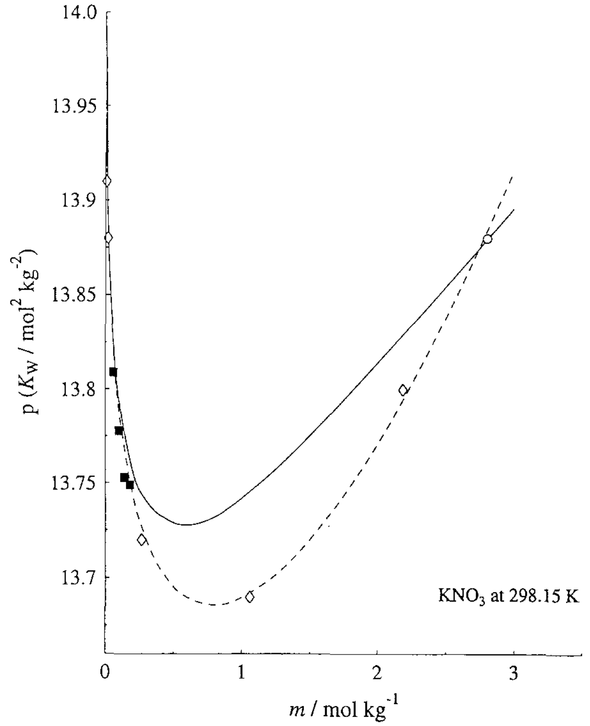

Fig. 3b. Experimental and calculated values of pK_w for aqueous KNO_3 at 25 °C. ○: present investigation, glass electrode; ◇: *Näsänen* and *Meriläinen* [8]; ■: *Jameson* and *Wilson* [6]; ———: *Pitzer* model, with binary parameters taken from *Pitzer* [29] and $\theta_{H,K} = 0.005$ (literature value [28]), $\theta_{OH,NO_3} = -0.0553$ (determined by optimization) and $\Psi_{H,K,NO_3} + \Psi_{K,OH,NO_3} = -0.0177$ (determined by optimization); --------: *Pitzer* model, with binary and ternary parameters optimized

coefficients in KNO_3/HNO_3 and KOH/KNO_3 mixtures and a redetermination of pK_w in KNO_3 over a wide concentration range are desirable.

$NaClO_4$ media

The pK_w values in $NaClO_4$ are of interest in view of the widespread use of this substance as a supporting electrolyte. As shown in Fig. 4, the agreement between the predictions of the *Pitzer* model and experimental measurements by *Carpéni et al.* [4] (◆) and *Fischer* and *Byé* [5] (◇) is poor, despite the fact that one of the ternary interaction parameters Ψ (for H^+–Na^+–ClO_4^-) is known. This shows the importance of knowing *both* ternary parameters. Clearly this system warrants further study, especially as the high solubility of $NaClO_4$ enables its use as a supporting electrolyte at very high ionic strengths. We are currently determining pK_w in concentrated $NaClO_4$ solutions.

$NaNO_3$ media

Our experimental values (○) for the pK_w in aqueous $NaNO_3$ are shown in Fig. 5, and are broadly consistent with the only available literature value for this medium,

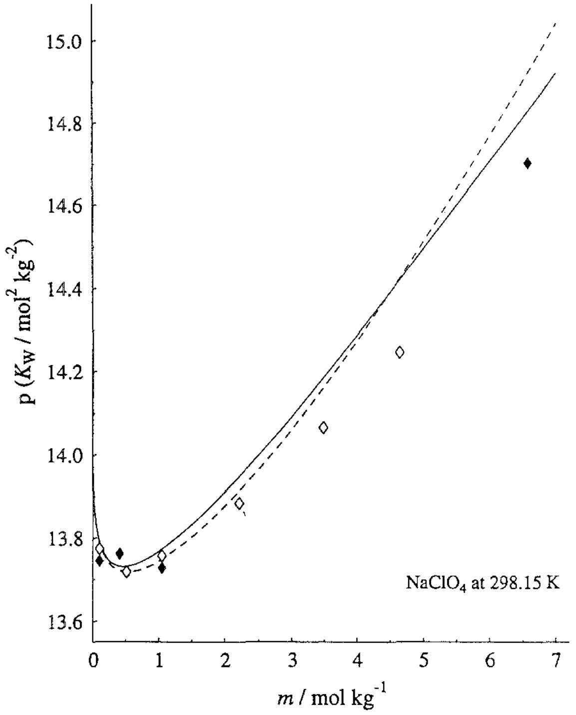

Fig. 4. Experimental and calculated values of pK_w for aqueous $NaClO_4$ at 25 °C. ◆: *Carpéni et al.* [4]; ◇: *Fischer* and *Byé* [5]; ———: limited *Pitzer* model (see text); --------: *Pitzer* model, neglecting higher-order terms

also measured by glass-electrode potentiometry [17]. The agreement with *Pitzer*'s theory is again poor, which can again be explained by the absence of ternary and same-sign interaction parameters for this system. In view of the poor quality of the results obtained for KNO_3 (see above), the limited data available, and the Na^+ error, it does not seem worthwhile attempting to estimate these parameters from the pK_w data.

Conclusions

The data obtained for concentrated solutions of NaCl, KCl, KNO_3, and $NaNO_3$ are in good agreement with the published values for pK_w as a function of molality. Measurements of pK_w by hydrogen and glass electrode potentiometry enables a correction to be made for the sodium ion error that arises with the use of glass electrodes. This is particularly important for the case of nitrate-containing electrolytes, for which the hydrogen electrode cannot be used.

Experimental results obtained in the present study and published work have also been compared with the predictions made on the basis of *Pitzer*'s activity coefficient model for concentrated electrolytes. Such comparisons indicate the importance of the same-sign and ternary ionic interaction parameters. Where values for the necessary parameters are available, the *Pitzer* model provides an excellent correlation of the experimental data.

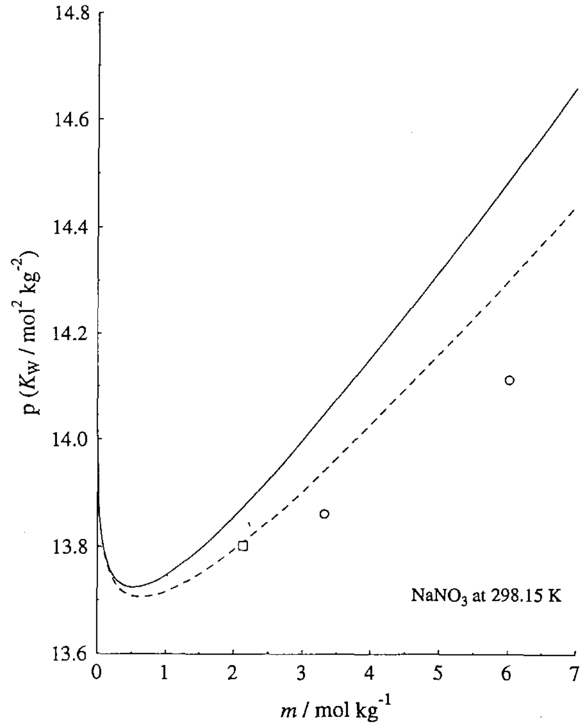

Fig. 5. Experimental and calculated values of pK_w for aqueous NaNO$_3$ at 25 °C. ○: present investigation, glass electrode; □: *Hugel* [17]; ———: limited *Pitzer* model (see text); --------: *Pitzer* model, neglecting higher-order terms

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Experimental

General Procedure

To measure the ionic product of water in an electrolyte M^+X^- of concentration c (mol·dm^{-3}, M), mixtures consisting of the strong acid HX (0.02 M) and the salt MX (c-0.02 M) were titrated potentiometrically with the strong base MOH (0.1 M) in MX (c). All titrations were performed in standard jacketed cells on the high precision automated titration systems previously developed in our laboratories [20, 22]. In experiments involving glass electrodes (Metrohm, model 6.0101.000), the solutions were blanketed by high purity nitrogen delivered through a carbon dioxide trap and a presaturator containing the electrolyte concentration of interest. The burettes were Metrohm 665 Model Dosimat units driven by an IBM PC computer. The calibrated precision of the burettes was ± 0.1%. All volumetric glassware was grade "A" and calibrated. The emf was measured to ± 0.1 mV by high impedance digital voltmeters of in-house construction, connected to the computer. The temperature in the cells was maintained at 25 ± 0.01 °C by use of a circulator thermostat (Haake Model

N3B). Temperatures were periodically checked with a calibrated ITS 90 platinum resistance thermometer.

Hydrogen electrode

The hydrogen electrode used was of the *Hildebrand* dip type but with a body made of teflon rather than glass. It consisted of a 10 × 7 × 0.1 mm foil welded to a 1 × 280 mm Pt wire. The wire was melt-coated with polyethylene. The electrode was housed in a teflon tube with a side inlet, which was perpendicular to the hydrogen outlets, and had a standard taper to match the cell top. Ultra-high purity hydrogen gas (CIG) was delivered *via* thickwalled copper tubing to a presaturator containing the solution of studied electrolyte. The cell was tightly sealed to minimize contamination by atmospheric oxygen and carbon dioxide. A flow rate of 2–3 bubbles per second emerging from one side of the immersed electrode was usually used.

Platinum electrodes were prepared in the following manner [23]. Old platinum black (when present) was dissolved by immersion in a 1:1 *aqua regia*—water mixture for 30 min at about 50 °C with magnetic stirring. The foil was abraded with emergy cloth (grit size 1200) to remove impurities and treated with fresh *aqua regia*—water mixture for 1 hour at about 50 °C with stirring. The electrode was washed with distilled water. The foil was placed flat on a glass plate and burnished with the rounded end of a glass rod. The glass plate had a channel (1 mm deep, 1 mm wide, and about 3 cm long) to accommodate the Pt wire during burnishing. The electrode was next treated in concentrated HNO_3 at about 50 °C for 1 h with stirring. After washing with distilled water the foil was again burnished and cleaned in concentrated HNO_3 for about 5 min with heating and stirring as before, then washed once more with distilled water. The final cleaning consisted of a cathodic electrolysis at $3\,mA \cdot cm^{-2}$ in $0.2\,M H_2SO_4$ for 10 min to remove surface oxides. During this cleaning procedure, hydrogen should be evolved as small bubbles from the whole surface of the foil; if not, the foil must be burnished and cleaned again. Washed electrodes were platinized without delay in 2% (originally in 3.5%) w/v chloroplatinic acid containing 0.003% (or 0.005%) w/v lead acetate trihydrate solution at 30 or $50\,mA \cdot cm^{-2}$ for 10 min in an H-type two compartment cell. Good stirring was found to be essential to achieve an even black coating. Surface lead was removed by soaking the electrode for at least 24 h in aerated 1 *M* perchloric acid. The finished electrode was stored in distilled water and handled with care. Electrodes were replatinized whenever they failed to stabilize properly, usually after 1–15 days of work.

Appendix

Although the *Pitzer* theory is widely regarded as the most general and flexible of the activity coefficient models suitable for concentrated electrolytes, the equations for the ionic activity and osmotic coefficients are quite involved. The implementation of these equations is not entirely straightforward and is further complicated by the existence of several versions of the theory in the literature. In particular, it is worth mentioning that the equations given by *Zemaitis et al.* [28, page 236] are incorrect, in that the concentration dependent contributions to the same-sign ionic interaction terms are missing. Accordingly, we provide in this Appendix a summary of the *Pitzer* activity and osmotic coefficient formulae used in the theoretical part of the present work. More detailed discussions of the underlying physical model are given by *Pitzer* [29] and *Harvie* and *Weare* [30].

The starting point for the derivation of *Pitzer*'s model is a virial expansion for the excess *Gibbs* energy of the solution (containing n_w kg of solvent) in terms of solute molalities *m*:

$$\frac{G_{ex}}{RT} = n_w \left[f(I) + \sum_i \sum_j \lambda_{ij}(I) m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k \right] \qquad \text{A1}$$

where f is a *Debye-Hückel* type function, depending only on ionic strength, $\lambda_{ij}(I)$ is the ionic strength dependent second virial coefficient between species i and j, and μ_{ijk} is the ionic strength independent third virial coefficient between species i, j, and k. In principle, these virial coefficients can be expressed in terms of the potential of mean force between the appropriate species. The essence of the *Pitzer* approach is to avoid the statistical-mechanical difficulties associated with doing this by representing measurable combinations of virial coefficients by empirical functions. These functions contain parameters which can be determined by regression analysis of experimental osmotic or activity coefficient data. On carrying out the required differentiations of equation A1 with respect to the molalities, the following expressions for the ionic activity coefficients and the osmotic coefficient result.

$$\ln \gamma_M = z_M^2 F + \sum_a m_a(2B_{Ma} + ZC_{Ma}) + \sum_c m_c\left(2\Phi_{Mc} + \sum_a m_a \Psi_{Mca}\right) + \sum_{a<a'}\sum m_a m_{a'} \Psi_{aa'M} + |z_M| \sum_c \sum_a m_c m_a C_{ca} \tag{A2}$$

$$\ln \gamma_X = z_X^2 F + \sum_c m_c(2B_{cX} + ZC_{cX}) + \sum_a m_a\left(2\Phi_{Xa} + \sum_c m_c \Psi_{Xac}\right) + \sum_{c<c'}\sum m_c m_{c'} \Psi_{cc'X} + |z_X| \sum_c \sum_a m_c m_a C_{ca} \tag{A3}$$

$$\phi - 1 = \frac{2}{\sum_i m_i}\left[-\frac{A_\phi I^{3/2}}{1 + bI^{1/2}} + \sum_c \sum_a m_c m_a (B_{ca}^\phi + ZC_{ca}) + \sum_{c<c'}\sum m_c m_{c'}\left(\Phi_{cc'}^\phi + \sum_a m_a \Psi_{cc'a}\right)\right.$$
$$\left. + \sum_{a<a'}\sum m_a m_{a'}\left(\Phi_{aa'}^\phi + \sum_c m_c \Psi_{aa'c}\right)\right] \tag{A4}$$

$$Z = \sum_i m_i |z_i|$$

where z_i is the algebraic charge number of ion i. In these formulae, we have followed closely the notation used by *Harvie* and *Weare* [30]. Thus, the summations expressions are over cations (c) and anions (a), and the double summation indices a < a′ and c < c′ refer to all distinguishable pairs of non-identical anions and cations, respectively.

The quantities B_{ij}, B'_{ij}, Φ'_{ij}, and Φ'_i are empirical functions that represent measurable combinations of ionic second virial coefficient functions and their derivatives. The B_{ij}, B'_{ij} functions refer to cation-anion pairs, and are defined by

$$B_{ij} = \beta_0 + \frac{2\beta_1}{\alpha_1^2 I}\{1 - (1 + \alpha_1\sqrt{I})\exp(-\alpha_1\sqrt{I})\} + \frac{2\beta_2}{\alpha_2^2 I}\{1 - (1 - \alpha_2\sqrt{I})\exp(-\alpha_2\sqrt{I})\} \tag{A5}$$

$$B'_{ij} = \frac{2\beta_1}{\alpha_1^2 I^2}\left\{-1 + \left(1 + \alpha_1\sqrt{I} + \frac{\alpha_1^2 I}{2}\right)\exp(-\alpha_1\sqrt{I})\right\} + \frac{2\beta_2}{\alpha_2^2 I^2}\left\{-1 + \left(1 + \alpha_2\sqrt{I} + \frac{\alpha_2^2 I}{2}\right)\exp(-\alpha_2\sqrt{I})\right\} \tag{A6}$$

where β_0, β_1, and β_2 are adjustable parameters, and
$\alpha_1 = 2.0$ for 1:1, 2:1, 3:1, 4:1, 5:1, 3:2, and 4:2 electrolytes; or 1.4 for 2:2 electrolytes;
$\alpha_2 = 0.0$ for 1:1, 2:1, 3:1, 4:1, and 5:1 electrolytes; 12.0 for 2:2 electrolytes; or 50.0 for 3:2 and 4:2 electrolytes.
The last terms of equations A5 and A6 both vanish for all electrolytes in which $\alpha_2 = 0$.

The function F is given by

$$F = -A_\phi\left[\frac{\sqrt{I}}{1 + b\sqrt{I}} + \frac{2}{b}\ln(1 + b\sqrt{I})\right] + \sum_c \sum_a m_c m_a B'_{ca} + \sum_{c<c'}\sum m_c m_{c'} \Phi'_{cc'} + \sum_{a<a'}\sum m_a m_{a'} \Phi'_{aa'} \tag{A7}$$

where

$$A_\phi = \frac{A \ln 10}{3}$$

A is the *Debye-Hückel* constant, and $b = 1.2$. The Φ_{ij}, Φ'_{ij} functions refer to cation-cation or anion-anion pairs, and are defined by

$$\Phi_{ij} = \theta_{ij} + \theta^{E}_{ij}(I) \qquad \text{A8}$$

$$\Phi'_{ij} = \theta^{E'}_{ij}(I) \qquad \text{A9}$$

where θ_{ij} is an adjustable parameter, obtained from activity or osmotic coefficient data for mixtures of two binary electrolytes with a common ion. The functions θ^{E}_{ij} and $\theta^{E'}_{ij}$ represent the electrostatic energy contributions arising from differences in ionic charges. These functions are in turn represented in terms of virial coefficient integrals for the screened coulomb potential:

$$\theta^{E}_{MN}(I) = \frac{z_M z_N}{4I}\left[J_0(x_{MN}) - \tfrac{1}{2}J_0(x_{MM}) - \tfrac{1}{2}J_0(x_{NN})\right] \qquad \text{A10}$$

$$\theta^{E'}_{MN}(I) = \frac{z_M z_N}{8I^2}\left[J_1(x_{MN}) - \tfrac{1}{2}J_1(x_{MM}) - \tfrac{1}{2}J_1(x_{NN})\right] \qquad \text{A11}$$

where

$$x_{MN} = 6 z_M z_N A_\phi \sqrt{I}$$

$$J_0(x) = \frac{x}{4} - 1 + \frac{1}{x}\int_0^\infty \left[1 - \exp\left(-\frac{x}{y}e^{-y}\right)\right] y^2\,dy$$

$$J_1(x) = \frac{x}{4} - \frac{1}{x}\int_0^\infty \left[1 - \left(1 + \frac{x}{y}e^{-y}\right)\exp\left(-\frac{x}{y}e^{-y}\right)\right] y^2\,dy$$

It is clear from equations A10 and A11 that θ^{E} and $\theta^{E'}$ vanish identically if the ions have the same charge.

Measurable combinations of third virial coefficients are represented by the empirical constants C and Ψ. Values of C_{ca} corresponding to anion a and cation c, of respective charges z_a and z_c, are given by

$$C_{ca} = \frac{C^{\phi}_{ca}}{2\sqrt{|z_a z_c|}} \qquad \text{A12}$$

where C^{ϕ}_{ca} is in turn derived from analysis of osmotic coefficient data from solutions of a single electrolyte, while values of $\Psi_{cc'a}$, $\Psi_{aa'c}$, etc. are obtained from the corresponding data for mixed electrolytes. Calculation of the osmotic coefficient and the activity of water requires evaluation of the quantities B^{ϕ}_{ca} and Φ^{ϕ}_{ij}. For cation c and anion a, B^{ϕ}_{ca} is defined by

$$B^{\phi}_{ca} = \beta_0 + \beta_1 \exp(-\alpha_1\sqrt{I}) + \beta_2 \exp(-\alpha_2\sqrt{I}) \qquad \text{A13}$$

which for ions i and j of the same sign Φ^{ϕ}_{ij} is defined by

$$\Phi^{\phi}_{ij} = \theta_{ij} + \theta^{E}_{ij}(I) + I\frac{d\theta^{E}_{ij}(I)}{dI} \qquad \text{A14}$$

The activity of water can then be obtained from

$$a_w = \exp\left(-\frac{M_w \sum_i m_i}{1000}\phi\right) \qquad \text{A15}$$

where M_w is the molar mass of water (18.0153 g·mol^{-1}).

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