Determination of the Activity of H^+ Ions Within and Beyond the pH Meter Range

Eva Rodil, Karin Persson, and Juan H. Vera
Dept. of Chemical Engineering, McGill University, Montreal, Quebec, Canada

Grazyna Wilczek-Vera
Dept. of Chemistry, McGill University, Montreal, Quebec, Canada

This work confirms that the activities of individual ions measured with ion-selective electrodes are physically meaningful. The individual activities of the Cl^-, Na^+ and K^+ ions in single-electrolyte aqueous solutions of HCl, NaOH and KOH were measured at 298.2 K in the range from 0 to 2 molal. In the pH range from 1 to 13, the pH values calculated from the measured activities of the ions are in good agreement with the values obtained with a pH probe. In agreement with previous results for potassium ions, and opposite to the behavior of other cations in 1:1 electrolyte solutions, the K^+ and the H^+ ions were found to have smaller activities than their conjugate anions. The experimental activity coefficients of the ions were correlated with the Khoshkbarchi-Vera equation and with the New Hydration Theory, and compared with the predictions given by the Pitzer theory.

Introduction

The motivation for this study originates from the observation by Pradhan and Vera (1998) that in aqueous diluted solutions of acids and bases, in the range of pH measurements, there is no noticeable effect of the nature of different counterions on the solubility of the amino acids. The solubility at a particular pH is independent of whether NaOH or KOH are used in the high pH region or whether the pH is adjusted with HNO_3 or HCl in the low pH region. At high concentrations of the acid or base, however, a distinctive effect is observed. The solubility of DL-alanine in the presence of potassium hydroxide is higher than in the presence of sodium hydroxide. Similarly, the solubility of DL-alanine is higher in the presence of HNO_3 than in the presence of HCl. Thus, the nature of the counterion of the H^+ or of the OH^- ions, has a distinct effect.

The purpose of this study is to explore the possibility of obtaining the pH of an aqueous solution of a single acid or base by measuring the activity of the counterion of the acid or the base. The agreement or disagreement between the pH directly measured with a pH meter and the pH indirectly determined from the activity of the counterions provides a further test of the validity of the assumptions that form the base of a method proposed to determine the activities of individual ions (Khoshkbarchi and Vera, 1996a,b; Marcos-Arroyo et al., 1996; Rabie et al., 1999; Taghikhani et al., 1999, 2000; Rodil and Vera, 2001). This method combines the measurement of the potential of an ion-selective electrode. E_{ISE}, vs. potential of a single-junction reference electrode, E_{REF}, with a data treatment that reduces the error originated by the presence of junction potential. Admittedly, this is a nonthermodynamic technique, as it uses a transport process to measure an equilibrium property. However, the use of nonthermodynamic methods to measure thermodynamic properties is not new in chemical engineering. Among other possible examples, gas chromatography has long been known to produce reliable values of second virial coefficients and of activity coefficients (Everett et al., 1968). Moreover, electrochemical cells have been used to measure mean ionic activity coefficients of electrolytes in aqueous solutions (Robinson and Stokes, 1959). The use of ion-selective electrodes to measure mean ionic activity coefficients of electrolytes have also been a standard practice in chemical engineering (Haghtalab and

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Correspondence concerning this article should be addressed to J. H. Vera.

E. Rodil is currently on leave from Dept. of Chemical Engineering, University of Santiago de Compostela, Santiago de Compostela, Spain.

Vera, 1991a,b; Khoshkbarchi and Vera, 1996c). As the thermodynamic properties measured in the cases quoted earlier were also accessible through thermodynamic methods, it was possible to verify directly the validity of the nonthermodynamic approach. In the case of the individual activity of ions, which until now are not accessible through thermodynamic methods, the validation was established through the reproduction of the values of the mean ionic activity coefficient of the electrolyte reported in the literature (Khoshkbarchi and Vera, 1996a; Taghikhani et al., 2000). However, it may be argued that the liquid junction potential of the reference electrode cancels out in the calculation of the mean ionic activity coefficient (Haghtalab and Vera, 1991a), while it does not cancel in the calculation of the activity coefficients of the individual ions. A recent study addressed this problem and demonstrated that the approximation made to estimate the junction potential has a small effect on the values of the activity coefficients of the individual ions (Rabie et al., 1999). The present study contributes additional evidence in support of the validity of this technique by the calculation of the pH of acid and basic solutions, starting from independent measurements of the activity of ions other than the hydrogen ion.

Discussion of the Method

Briefly stated, in this method the potential of an ion-selective electrode is measured against a single junction reference electrode, $E_k = (E_{\mathrm{ISE}} - E_{\mathrm{REF}})_k$, at a particular concentration k of the electrolyte. This potential is corrected for the presence of the junction potential, E_{Jk}, and written as φ_k, with a Nernst expression of the form:

$$\varphi_k = E_k - E_{Jk} = E^0 + S \ln \left(m_k \gamma_k / m^0 \right) \tag{1}$$

where $E^0 = E^0_{\mathrm{ISE}} - E_{\mathrm{REF}}$ and S are the standard potential and the slope characteristic of the electrochemical cell. In Eq. 1, m_k and γ_k are the molality and the activity coefficient of the ion under investigation, and $m^0 = 1$ mol/kg is the standard state concentration. The standard potential groups all effects independent of the molality of the solution studied. The problematic term in Eq. 1 is the liquid-junction potential of the reference electrode. In the absence of electric current, for the continuous-mixture junction between the standard solution r inside the reference electrode, and a sample solution k, the junction potential can be evaluated using the relation (Bates, 1965):

$$E_{Jk} = -\frac{RT}{F} \int_r^k \sum \left(\frac{\tau_i}{z_i} d \ln m_i \gamma_i \right), \tag{2}$$

where τ_i is the transference number of species i. As discussed by Rabie et al. (1999), there is no computational problem to solve by iteration the loop created by needing to know γ_i in order to calculate E_{Jk} with Eq. 2, while needing E_{Jk} to calculate γ_i with Eq. 1. The main impediment to using Eq. 2 is the lack of information on transference numbers in concentrated solutions containing different ions. For dilute solutions, as a first approximation to Eq. 2, Henderson obtained the following expression (Bates, 1965):

$$E_{Jk} = \frac{RT}{F} \frac{\sum_i z_i \lambda_i^0 \left(c_i^k - c_{i,k}^r \right)}{\sum_i z_i^2 \lambda_i^0 \left(c_i^k - c_{i,k}^r \right)} \ln \frac{\sum_i z_i^2 \lambda_i^0 c_{i,k}^k}{\sum_i z_i^2 \lambda_i^0 c_i^r}, \tag{3}$$

where λ_i^0 is the limiting molar ionic conductance, c_i is the concentration of species i in equivalents per liter, and the superscript r and k designate the reference and the test solution, respectively. Values of the activity coefficients of ions calculated by Rabie et al. (1999) using Eq. 2, with an extrapolation of the transference numbers, produced results for the activity coefficients that only differ in the second decimal place from those calculated using Eq. 3. The activity coefficients for individual ions reported previously have all been obtained using Eq. 3 as a working approximation.

Thus, due to the unavailability of transference numbers for concentrated KCl and NaOH solutions, the values of junction potential are approximated in this work by the modified Henderson equation, Eq. 3. In the dilute region, at 298.2 K, the activity coefficients of the individual monovalent ions are approximated by the Guntelberg equation (Robinson and Stokes, 1959):

$$\log \gamma_k^{\mathrm{dil}} = \frac{-1.1762\sqrt{I_m}}{1+\sqrt{I_m}}, \tag{4}$$

where I_m is the dimensionless, molality based, ionic strength defined as:

$$I_m = 0.5 \sum_i \left(m_i z_i^2 / m^0 \right), \tag{5}$$

where z_i is the charge of ion i, and the summation extends over all ions present in the solution. The values of E^0 and S are evaluated from measurements of potentials in the dilute region according to the following specialization of Eq. 1:

$$\varphi_k^{\mathrm{dil}} = E^0 + S \ln \left(m_k \gamma_k^{\mathrm{dil}} / m^0 \right), \tag{1a}$$

using the fact that at low electrolyte concentrations, φ_k^{dil} is a linear function of the natural logarithm of $(m_k \gamma_k^{\mathrm{dil}} / m^0)$. Knowledge of the values of E^0 and S, together with a realistic estimate of the junction potential, allows for the determination of activity coefficients of the individual ion. As shown previously (Khoshkbarchi and Vera, 1996a; Rabie et al., 1999; Taghikhani et al., 2000), the activity coefficients of individual ions determined in this way reproduce within experimental accuracy the mean ionic activity coefficients of the electrolyte obtained independently by other experimental techniques.

The three basic assumptions of the method described earlier are that: (1) the ion-selective electrodes measure the activities of the individual ions; (2) the Guntelberg equation, Eq. 4, represents properly the activity coefficients of the individual ions at high dilution; and (3) the main junction potential is at the reference electrode and it is well represented by the Henderson equation, Eq. 3. The fact that the activity coefficients of the individual ions measured with ion-selective electrodes reproduce well the mean ionic activity coefficient of the electrolyte (Khoshkbarchi and Vera, 1996a; Rabie et al., 1999; Taghikhani et al., 2000), clearly validates the first and second of the preceding assumptions. It is not surprising that the Guntelberg equation, Eq. 4, represents well the activity coefficients of the individual ions at high dilution. It is known that this equation represents well the mean ionic activity coefficients at high dilution, and theory indicates that, for 1:1 electrolytes at high dilution, the activity coefficients of the individual ions converge to the value of the mean ionic activity coefficient of the electrolyte (Robinson and Stokes, 1959). More surprising, perhaps, is the fact that the measurements of the potential generated by ion-selective electrodes reproduce the mean ionic activity up to concentrations as high as 4 m. This agreement is in spite of all the complex mechanisms implied in the sensing of the ions by ion-selective electrodes and in spite of all the complexities of the physical chemistry of the ions in solution, like the formation of ion pairs and ion triplets, and the hydration of ions. The third assumption, however, is not covered by the good reproduction of the mean ionic activity coefficient from measurements with ion-selective electrodes. As stated earlier, the junction potential cancels out when calculating the mean ionic activity coefficient of the electrolyte (Haghtalab and Vera, 1991a). The effect of this assumption was discussed in a previous study (Rabie et al., 1999), and it was shown that the use of the Henderson equation affects the second place of the activity coefficients of the individual ions. Thus, the estimated accuracy of the activity coefficients obtained by this method is about ± 0.03. A different test of this approximation is to measure independently the activity coefficients of two different ions, using two independent ion-selective electrodes each with its own reference electrode, and to compare the results by transforming one activity into the other through thermodynamic relations. This is the procedure followed here.

In this work, we determine the activity coefficients of individual chloride ions in aqueous solutions of HCl and of the Na^+ and K^+ ions in aqueous solutions of NaOH and KOH, respectively, at concentrations up to 2 m. Thus, the correction for the junction potential is applied to the calculation of the activity coefficient of one ion only. The activity coefficient of the counterion, H^+ in the case of HCl, or OH^- in the cases of NaOH and KOH, is then evaluated from a knowledge of the mean ionic coefficient. For the case of HCl, for example, the activity coefficient of the hydrogen ion is evaluated from the knowledge of γ_{Cl^-} and $\gamma_\pm(\mathrm{HCl})$ as:

$$\gamma_{H^+}^{\text{calculated}} = \frac{\gamma_\pm^2(\mathrm{HCl})}{\gamma_{Cl^-}^{\text{measured}}}. \tag{6}$$

The pH is defined as the negative decimal logarithm of the relative activity of the hydrogen ion in the solution:

$$\mathrm{pH} = -\log a_{H^+} = -\log\left(m_{H^+}\gamma_{H^+}/m^0\right). \tag{7}$$

The idea, then, is to compare the calculated value of pH with experimental values of pH measured directly with a glass pH electrode. Because the pH probe has its own reference electrode, no cancellation of errors is possible in this case. Accordingly, an agreement of both sets of pH values in the concentration region in which the glass electrode is believed to be reliable would provide an additional validation of the method used to measure the activity coefficients of the individual ions. Before proceeding further, however, it is necessary to discuss briefly the elements on which the conventional scale of pH is based.

Conventional pH Scale

Covington (1993–1994) made a clear difference between the "notional" definition of pH, based on Eq. 7 using the actual activity coefficient of the hydrogen ion, and the "operational" definition of pH, in which Eq. 7 is used with well-defined assumptions for the activity coefficient of the hydrogen ion. In fact, as the activity coefficient of the hydrogen ion could not be independently determined, additional nonthermodynamic assumptions had to be made. MacInnes (1919) assumed that the activity coefficient of the chloride ion is the same in any solution containing chloride ions, and it is equal to the mean ionic activity coefficient of potassium chloride at the same chloride concentration. After accepting this step, the activity coefficient of the hydrogen ion can be calculated from Eq. 6. Guggenheim (1930) proposed an alternative assumption in which the individual activity coefficients of the cation and the anion of a 1:1 electrolyte are considered to be equal to the mean ionic activity coefficient of the electrolyte. In the case of the HCl solution, this assumption can be written as:

$$\gamma_{H^+} = \gamma_{Cl^-} = \gamma_{\pm(\mathrm{HCl})} \tag{8}$$

The Bates-Guggenheim approach (Bates, 1965), on the other hand, utilizes the knowledge of the mean ionic activity coefficient of HCl together with an approximation for the activity coefficient of chloride ions. For a concentration of less than 0.1 molal at 298.2 K, the following assumption is made:

$$\log \gamma_{Cl^-} = \frac{-1.1762\sqrt{I_m}}{1+1.5\sqrt{I_m}}. \tag{9}$$

Similarly, Butler and Cogley (1998) suggested that it is advantageous to use the Davies (1962) equation which, for the chloride ion at 298.2 K, takes the form:

$$\log \gamma_{Cl^-} = -1.1762\left(\frac{\sqrt{I_m}}{1+\sqrt{I_m}} + 0.2 I_m\right). \tag{10}$$

Notably, for 1:1 electrolytes, either the use of Eq. 9 or of Eq. 10 implies that the activity coefficient of the cation is considered equal to the activity coefficient of the anion and thus, necessarily, it is assumed that both are equal to the mean ionic activity coefficient. In practice both Eqs. 9 and 10 reproduce reasonably well the experimental values of the mean ionic activity coefficients of 1:1 electrolytes up to concentrations 0.1 m. Thus, the net result of either the Guggenheim-Bates approximation or Butler's proposal is that the activity coefficient of the hydrogen ion, at low molalities, is considered to have values close to the experimental value of the mean ionic activity coefficient of HCl. As discussed below, for the evaluation of pH in solutions of bases it is necessary to additionally consider the ionic product of water.

The experimental determination of the activity coefficients of the hydrogen ion through the measurement of the activity of the chloride ion in HCl solutions and of the activity of the cations in NaOH and KOH solutions, provides a unique opportunity to verify both the assumptions inherent to the experimental method and those inherent to the establishment of the operational pH scale. The results obtained in this work are expected to contribute to a better understanding of the relation between the activity of the hydrogen ion and the operational scale of pH in highly acidic and highly basic solutions. Clearly stated, the purpose of this work is not to propose a modification to the operational scale of pH, which is well defined and universally accepted (Bates, 1965; Christian, 1994; Gardner et al., 1997).

Experimental Measurements

Hydrochloric acid, potassium hydroxide 1.00 ± 0.01 N (at 20°C), and sodium hydroxide 1.00 ± 0.01 N and 10.00 ± 0.05 N (at 20°C) Acculute standard volumetric concentrates were received from Anachemia Chemicals Inc. (New York).

Three ion-selective electrodes manufactured by ORION were used: a chloride-ion-selective electrode (94-17B), the sodium-ion-selective electrode (ROSS 84-11), and the potassium-ion-selective electrode (93-19). All the measurements were conducted against the single junction Accumet silver chloride reference electrode (Fisher Scientific 13-620-46), which was filled with 4 molar KCl solution saturated with AgCl. The outgoing flow of the solution from the reference electrode was less than 8 μL/h.

The pH measurements were performed with an accupHast Reference/pH electrode (Fisher Scientific 13-620-116) filled with saturated potassium chloride solution (SP138-500). An OAKTON pH/mV Benchtop Meter model WD-35616-00 with a resolution of 0.1 mV and accuracy of ± 0.2 mV was used to monitor pH measurements, and an Orion milivoltimeter model 420A was used to monitor the response of the ion-selective electrodes. During the measurements, the solutions were stirred continuously and the temperature was kept constant at 298.2 ± 0.1 K using a thermostatic bath. A moderate rate of stirring was used to avoid the generation of air bubbles. The presence of air bubbles on the surface of electrodes causes errors in the electromotive force (emf) readings. Measurements were taken when the drift of the potentiometer was less than 0.1 mV in 10 min.

The electrodes were conditioned prior to the measurement according to the manufacturer's procedure. In all experiments, the deionized water used was obtained by passing distilled water through ion-exchange columns type Easy pure RF, Compact Ultrapure Water System, Barnstead Thermoline.

In the HCl experiments, separate solutions were prepared prior to the measurements. The 2.00 ± 0.02 N (at 20°C) solutions were prepared by dissolving two ampoules of the standard volumetric concentrates in a $1{,}000.0 \pm 0.3$-mL volumetric flask. For more diluted solutions two methods of preparation were tested. In the first one, these solutions were prepared through the subsequent dilutions of the most concentrated solution using the standard glassware. The estimated error due to the dilution process was below 0.5%, that is, smaller than the error of the standard concentrated solutions. Alternatively, during some dilutions an analytical balance was used. The estimated error of this procedure does not exceed 0.02%. All experiments started with the lowest concentration of electrolyte.

In the NaOH and KOH series of determinations, the gravimetric method of solution preparation was used with a stepwise withdrawal of dilute solution and addition of concentrated NaOH or KOH solution, respectively. In this case, 4.00 ± 0.04 N (at 20°C) solutions were prepared by dissolving one ampoule of the standard volumetric concentrates in a 250.00 ± 0.24-mL volumetric flask. Additionally, for the higher concentrations of NaOH, the standard volumetric solution 10.00 ± 0.05 N was used. The CO_2 gas dissolved in deionized water was removed by bubbling with nitrogen (Extra Dry, Praxair, Montreal) for 4 h, and the whole setup, including beaker, electrodes, and meters, was placed in a nitrogen-filled glove box. Nitrogen saturated with water was circulated and the thermostated beaker was covered to prevent water evaporation.

For the pH measurements in the hydrochloric acid solutions, the electrode was calibrated with two buffers: the potassium hydrogen phthalate buffer (Fisher Scientific, SB101-500) of pH 4.00 ± 0.01 at 298.2 K and the potassium tetroxalate (Anachemia Science) of pH 1.68 ± 0.01 at 298.2 K. For the calibration of the pH electrode before the measurements of the sodium and potassium hydroxide solutions, the potassium phosphate monobasic/sodium hydroxide buffer (Fisher Scientific, SB107-500) pH 7.00 ± 0.01 at 298.2 K and the potassium carbonate/potassium tetraborate/potassium hydroxide buffer (Fisher Scientific, SB115-500) pH 10.00 ± 0.01 at 298.2 K were used. All the buffers are traceable to the U.S. National Institute of Standards and Technology. Corrections to the readings of the pH meter were made following the indications given in the manual for the pH electrode.

Summarizing, the activity coefficients of chloride in hydrochloric acid solution, of sodium ions in sodium hydroxide solution, and potassium ions in potassium hydroxide solution were measured. The experiments were replicated five times and the data presented are the average of the replicas. Additionally, the pH of all the systems investigated was also determined.

Results and Discussion

The averaged values of five series of measurements of activity coefficients of Cl^- ions in aqueous solutions of HCl are reported in Table 1, together with literature values of the mean ionic activity coefficients of HCl (Zaytsev and Aseyev, 1992) and the values of the activity coefficients of the H^+ ion calculated with Eq. 6. Table 2 presents the comparison of different possible values of pH, according to the definition adopted in Eq. 7. The experimental values of pH measured using the pH electrode and pH meter are designated as $pH^{measured}$, and for pH values below 4.0, the values were corrected according to Robinson's recommendation (1985–1986) as:

$$pH^{corrected} = pH^{measured} + 0.009(4.00 - pH^{measured}). \quad (11)$$

Table 1. Activity Coefficients in the HCl System at 298.2 K

m	Exp. γ_{Cl^-}	Lit.* $\gamma_\pm$	Calc. γ_{H^+}
0.003	0.956	0.942	0.928
0.005	0.907	0.928	0.950
0.008	0.908	0.915	0.922
0.01	0.911	0.894	0.877
0.03	0.942	0.859	0.783
0.05	0.948	0.834	0.734
0.07	0.958	0.819	0.700
0.1	0.961	0.793	0.655
0.3	1.153	0.765	0.507
0.5	1.350	0.761	0.429
0.7	1.573	0.774	0.381
0.9	1.829	0.797	0.347
1.2	2.262	0.845	0.316
1.7	2.955	0.928	0.291
2.0	3.932	1.032	0.271

Note: Estimated pooled standard deviation for the experimentally determined activity coefficient = 0.08.

*Zaytsev and Aseyev (1992).

The calculated activity coefficients for the hydrogen ion are those obtained from Eq. 6 with the experimental values for activity coefficients reported in Table 1:

$$\mathrm{pH}^{\text{calculated}} = -\log\left(m_{\mathrm{H}^+}\gamma_{\mathrm{H}^+}^{\text{calculated}}/m^0\right). \tag{12}$$

As discussed previously, the values of pH obtained with a glass electrode and a pH meter are based on a scale constructed using reasonable assumptions but not a precise knowledge of the activity coefficient of the hydrogen ion. Thus, these assumptions, reasonable as they may be, are built-in in the values obtained with the pH meter calibrated using prepared standard solutions. It is of interest to compare the values of pH measured and calculated with those obtained using some simple assumptions. Thus, for discussion purposes only, we have also included in Table 2 the values of pH obtained using two different assumptions for the activity coefficients of the H^+ ion. First, we assume the activity coefficient of the hydrogen ion to be equal to the mean ionic activity coefficient of HCl, and define a $\mathrm{pH}_\pm$ by:

$$\mathrm{pH}_\pm = -\log\left(m_{\mathrm{H}^+}\gamma_{\pm(\mathrm{HCl})}/m^0\right). \tag{13}$$

Second, we assume that the activity coefficient of the hydrogen ion is equal to unity and define a pH_m as:

$$\mathrm{pH}_m = -\log\left(m_{\mathrm{H}^+}/m^0\right). \tag{14}$$

For better visualization, the values of the experimentally measured pH and the values of pH calculated from the activity coefficients of the chloride ion are also presented in Figures 1 and 2. Figure 1 is confined to the diluted region from 0 to 0.1 m, and compares the pH values determined experimentally in this study and scarce literature data to the values calculated using Eq. 12. Additionally, Figure 1 presents the predictions obtained using the Bates-Guggenheim approach, Eq. 9, normally used in determining pH (Bates, 1965), and the predictions obtained from the Davies equation, Eq. 10. As can be seen in Figure 1, all the values coincide in the region of 0 to 0.01 molal. The usual value of standard deviation for the pH measurements, in the low ionic strength region, has been estimated as 0.05 pH units based on the results from 11 professional laboratories (Gardner et al., 1997), which is equivalent to a precision range of approximately ±0.1 pH units. In fact, some of the values of the interlaboratory test reported by Gardner et al. (1997) show a precision range as high as ±0.2 pH units. Thus, the discrepancy between the measured values of pH and the calculated values in the more concentrated region of 0.01 to 0.1 molal could, in principle, be attributed to experimental error, which can lead, at 95% confidence level, to an error of ±0.2 pH units. The Davies equation, Eq. 10, seems to compare better with the results of the present study than the Bates-Guggenheim approach, Eq. 9. In general, all the predicted and experimentally determined values of pH are below those obtained from the experimentally evaluated activity of hydrogen. This trend becomes much more pronounced for higher concentrations of HCl, as can be clearly seen on Figure 2. As discussed pre-

Table 2. Experimental pH Values in the HCl System vs. Calculated Values Based on Different Assumptions of Activity Coefficients

	pH		$\mathrm{pH} = -\log(m_{\mathrm{H}^+}\gamma/m^0)$		
m	Meas.	Corr. Eq. 11	$\gamma = \gamma_{\mathrm{H}^+}$ Eq. 12	$\gamma = \gamma_\pm$ Eq. 13	$\gamma = 1$ Eq. 14
0.003	2.53	2.54	2.56	2.55	2.52
0.005	2.30	2.32	2.32	2.33	2.30
0.008	2.11	2.13	2.13	2.14	2.10
0.01	2.02	2.04	2.06	2.05	2.00
0.03	1.60	1.62	1.63	1.59	1.52
0.05	1.38	1.41	1.44	1.38	1.30
0.07	1.23	1.26	1.31	1.24	1.15
0.1	1.06	1.09	1.18	1.10	1.00
0.3	0.53	0.56	0.82	0.64	0.52
0.5	0.30	0.33	0.67	0.42	0.30
0.7	0.15	0.19	0.57	0.27	0.15
0.9	0.04	0.08	0.51	0.14	0.05
1.2	−0.09	−0.06	0.42	−0.01	−0.08
1.7	−0.29	−0.25	0.31	−0.20	−0.23
2.0	−0.40	−0.36	0.27	−0.34	−0.30

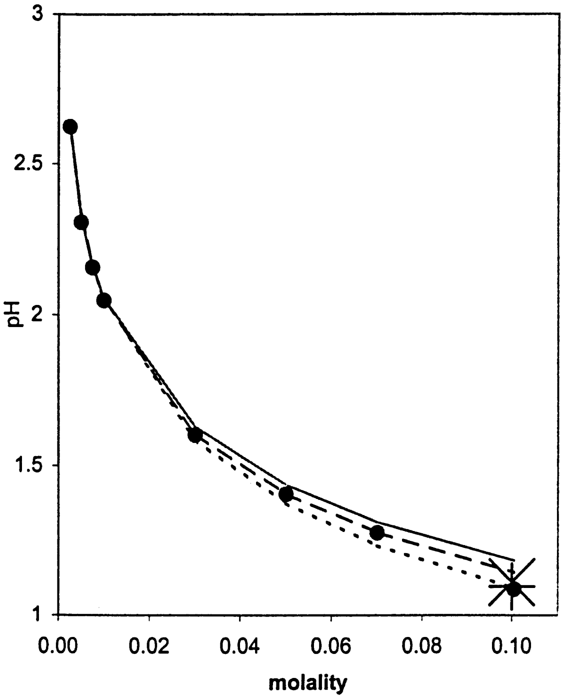

Figure 1. pH values in diluted aqueous solution of HCl at 25°C.

●—Experimental values; + Bates et al. (1950); × Bowler and Bates (1955); —— calculated from $\gamma_{H^+}^{calculated}$; ---- calculated from Bates-Guggenheim approximation; ———— calculated from Davies equation.

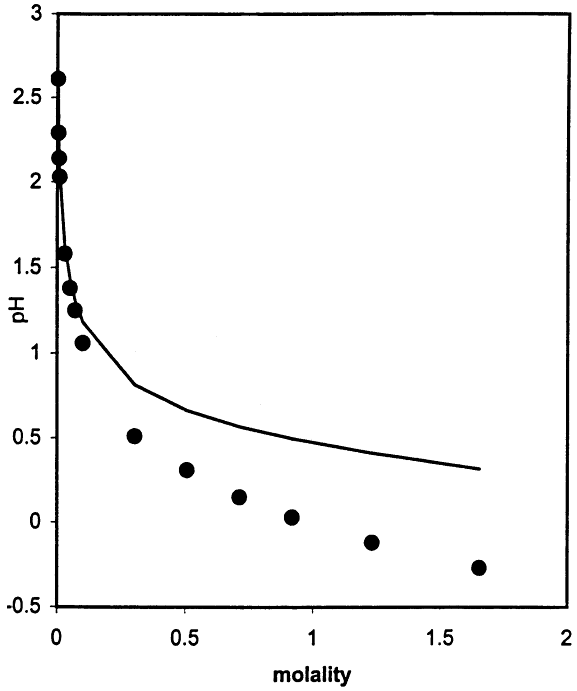

Figure 2. Concentrated region of aqueous HCl.

Comparison of the experimental (●) pH values with those calculated from $\gamma_{H^+}^{calculated}$ (——), Eq. 12.

viously, however, the values of pH measured by the pH meter calibrated against standards, by construction of the operational pH scale, will be in close agreement with the values obtained with Eq. 13. This effect is clearly seen in Table 2 up to molality 0.1. Above molality 0.1 of the acid, the corrected pH values agree better with the values calculated with the assumption of activity coefficient equal to unity, Eq. 14. We believe that the values of pH calculated from the experimental activity of the chloride ions are closer to the notional value as defined by Covington (1993–1994).

Tables 3 and 4 contain the average values of activity coefficients of cations as determined experimentally from five series of measurements in aqueous systems of NaOH and KOH, respectively. From the knowledge of the individual activity coefficient of the cation, γ_{Me^+}, and of the mean ionic activity coefficients of a corresponding base, MeOH, the activity coefficient of the hydroxyl ion can be determined:

$$\gamma_{OH^-}^{calculated} = \frac{\gamma_{\pm}^{2}(\mathrm{MeOH})}{\gamma_{Me^+}^{measured}}. \tag{15}$$

These values are also reported in Tables 3 and 4. The activity of the hydrogen ion can then be evaluated from the expressions for the charge balance and the ionic equilibrium constant of water (Butler and Cogley, 1998). The thermodynamic equilibrium constant for the dissociation of water, in terms of activities, can be written as:

$$K_w = \frac{a_{H^+} a_{OH^-}}{a_w}. \tag{16}$$

As explained by Butler and Cogley (1998), while the value of the ionic product of water expressed in terms of concentrations changes with the total ionic strength of the solution at fixed temperature, the value of the thermodynamic constant K_w is only a function of temperature. In pure water, the activity of water is unity and, as the ionic strength is zero, the activity coefficients of OH^- and H^+ are equal to unity. Thus, the concentrations-based value of the ionic product of water in pure water is exactly the thermodynamic constant K_w that can be used, in terms of activities, even for concentrated solutions of electrolytes. For alkaline solutions, in the range of concentrations studied in this work, the final equation for pH takes the form:

$$\mathrm{pH}^{calculated} = -\log\left(\frac{K_w a_w m^0}{m_{OH^-}\gamma_{OH^-}^{calculated}}\right), \tag{17}$$

where, at high pH, the molality of the OH^- is equal to the molality of the base. The values of pH calculated from the activity coefficients of the cations in the hydroxide solutions are compared in Tables 5 and 6 with the experimental pH measured and the values corrected according to Robinson (1985–1986). For the preceding calculation, we have used the value of the base-ten logarithm of the ionic product of pure water, K_w, at 298.2 K equal to minus 13.997 ± 0.003 (Butler and Cogley, 1998). Values for the activity of water, a_w, required for Eq. 17, have been directly obtained or interpolated from the tabulations presented by Robinson and Stokes (1959).

Following Robinson (1985–1986), the experimental values of pH above 9.2 were corrected using the equation:

$$\mathrm{pH}^{\mathrm{corrected}} = \mathrm{pH}^{\mathrm{measured}} + 0.014\left(\mathrm{pH}^{\mathrm{measured}} - 9.2\right). \quad (18)$$

For comparison, in Table 5 and 6 we have also included the values of $\mathrm{pH}_{\pm}$ and pH_m calculated as

$$\mathrm{pH}_{\pm} = -\log\left(\frac{K_w a_w m^0}{m_{\mathrm{OH}^-}\gamma_{\pm(\mathrm{MeOH})}}\right) \quad (19)$$

and

$$\mathrm{pH}_m = -\log\left(\frac{K_w a_w m^0}{m_{\mathrm{OH}^-}}\right). \quad (20)$$

Notably, as seen in Tables 5 and 6, for concentrations up to 0.01 m the experimental values of pH measured with the pH probe agree closely with the values calculated using the mean ionic activity coefficients of NaOH and KOH (Eq. 19), respectively, while the corrected values of measured pH agree better with the results obtained assuming the activity coefficient of the OH^- ion equal to unity (Eq. 20). As seen from Tables 5 and 6, for aqueous solutions of NaOH and KOH at pH below 12.8, the pH values obtained from the activity of the hydrogen ion calculated from the readings of the sodium and potassium ion-selective electrodes fall between the experimental measurements of pH and the corrected values. For values of pH above 12.8, the corrected measured values are in better agreement with the values obtained from activity measurements. Notably, for the case of KOH, the values of Table 6 show that at high pH the corrected values of pH agree closely with the values calculated from Eq. 19, as can be expected from the construction of the operational pH scale. The experimental values of pH, together with the corresponding literature data and the pH results obtained from Eq. 17 are compared for the NaOH and KOH systems in Figure 3. Results are in good agreement up to the concentration of 0.05 m, that is, up to a pH of 12.6. As shown in Figure 4, for more concentrated solutions, the values of pH obtained from the activities of the cations were always higher than the experimental ones and the pH values of the KOH system consistently lay above those of NaOH. We believe that the values obtained from the measured activities of the cations are closer to the "notional" values as defined by Covington (1993–1994).

Table 3. Activity Coefficients in the NaOH System at 298.2 K

m	Exp. γ_{Na^+}	Lit.* $\gamma_{\pm}$	Calc. γ_{OH^-}
0.002	0.955	0.951	0.947
0.004	0.933	0.933	0.933
0.006	0.918	0.920	0.922
0.008	0.911	0.913	0.915
0.009	0.902	0.905	0.908
0.03	0.848	0.850	0.852
0.05	0.832	0.820	0.808
0.07	0.829	0.801	0.774
0.1	0.823	0.766	0.713
0.2	0.832	0.739	0.656
0.3	0.855	0.716	0.600
0.4	0.881	0.699	0.555
0.5	0.920	0.688	0.515
0.7	1.014	0.676	0.451
1.0	1.117	0.676	0.409
1.2	1.244	0.677	0.369
1.6	1.439	0.692	0.333
2.0	1.652	0.720	0.314

Note: Estimated pooled standard deviation for the experimentally determined activity coefficient = 0.09.
*Zaytsev and Aseyev (1992).

Table 4. Activity Coefficients in the KOH System at 298.2 K

m	Exp. γ_{K^+}	Lit.* $\gamma_{\pm}$	Calc. γ_{OH^-}
0.002	0.958	0.951	0.944
0.004	0.933	0.933	0.933
0.005	0.927	0.926	0.925
0.007	0.912	0.915	0.918
0.01	0.901	0.890	0.880
0.03	0.842	0.851	0.860
0.06	0.785	0.813	0.843
0.08	0.772	0.799	0.827
0.1	0.743	0.772	0.802
0.2	0.706	0.749	0.795
0.3	0.689	0.730	0.774
0.4	0.671	0.718	0.769
0.5	0.657	0.713	0.774
0.7	0.650	0.714	0.784
0.8	0.637	0.718	0.809
1.0	0.634	0.739	0.862
1.3	0.632	0.770	0.938
1.6	0.635	0.810	1.033
1.9	0.642	0.855	1.139

Note: Estimated pooled standard deviation for the experimentally determined activity coefficient = 0.02.
*Zaytsev and Aseyev (1992).

The values of individual activity coefficients determined in this study were correlated using the Koshkbarchi-Vera (1996a) equation:

$$\ln\gamma_i = \frac{-8.766 z_i^2\sqrt{I_x}}{1+9\sqrt{I_x}} + B_i\frac{I_x^{3/2}}{1+9\sqrt{I_x}} + C_i\ln\left(1+9I_x^{2/3}\right), \quad (21)$$

which proved itself much more suitable for this purpose than the New Hydration Theory (Rabie et al., 1999):

$$\ln\gamma_i = \frac{-8.766 z_i^2\sqrt{I_x}}{1+\rho_i\sqrt{I_x}} - h_i\ln a_w, \quad (22)$$

where ρ_i is a size parameter; h_i is the hydration number; a_w is the activity of water; and I_w is the ionic strength expressed in mole fractions:

$$I_x = 0.5\sum_i x_i z_i^2, \quad (23)$$

Table 5. Experimental pH Values in the NaOH System vs. Calculated Values Based on Different Assumptions of Activity Coefficients

	pH		$\mathrm{pH} = -\log\left(\frac{K_w a_w m^0}{m_{\mathrm{OH}^-}\gamma}\right)$		
m	Meas.	Corr. Eq. 18	$\gamma = \gamma_{\mathrm{OH}^-}$ Eq. 17	$\gamma = \gamma_{\pm}$ (NaOH) Eq. 19	$\gamma = 1$ Eq. 20
0.002	11.25	11.27	11.28	11.27	11.29
0.004	11.56	11.59	11.58	11.56	11.60
0.006	11.74	11.77	11.75	11.74	11.77
0.008	11.87	11.90	11.87	11.86	11.90
0.009	11.96	12.00	11.96	11.95	12.00
0.03	12.42	12.46	12.40	12.40	12.48
0.05	12.61	12.65	12.60	12.61	12.70
0.07	12.72	12.77	12.73	12.75	12.85
0.1	12.84	12.89	12.86	12.88	13.00
0.2	13.04	13.09	13.11	13.17	13.30
0.3	13.14	13.20	13.24	13.33	13.48
0.4	13.21	13.27	13.34	13.45	13.61
0.5	13.26	13.32	13.41	13.54	13.71
0.7	13.33	13.39	13.51	13.68	13.85
1.0	13.40	13.46	13.62	13.84	14.01
1.2	13.43	13.49	13.67	13.92	14.09
1.6	13.48	13.54	13.75	14.06	14.21
2.0	13.51	13.58	13.81	14.18	14.31

Table 7 contains the parameters of Eqs. 21 and 22 together with accompanying errors for the systems under investigation. The values of the parameters for Eq. 22 presented in Table 7 are devoid of any physical meaning.

Due to the lack of experimental data, many attempts were made in the past to approximate the values of the activity coefficients of individual ions. The Pitzer theory (1991) is one of the most commonly used models for this purpose. It has the form:

$$\ln \gamma_i = \frac{-1.176 z_i^2 \sqrt{I_m}}{1 + b_i \sqrt{I}_m} + c_i I_m. \qquad (24)$$

The values given by Pitzer (1991) for the parameters b_i and c_i of ions of interest here are presented in Table 8. Pitzer

Table 6. Experimental pH Values in the KOH System vs. Calculated Values Based on Different Assumptions of Activity Coefficients

	pH		$\mathrm{pH} = -\log\left(\frac{K_w a_w m^0}{m_{\mathrm{OH}^-}\gamma}\right)$		
m	Meas.	Corr. Eq. 18	$\gamma = \gamma_{\mathrm{OH}^-}$ Eq. 17	$\gamma = \gamma_{\pm}$ (KOH) Eq. 19	$\gamma = 1$ Eq. 20
0.002	11.28	11.31	11.27	11.27	11.29
0.004	11.55	11.59	11.56	11.56	11.60
0.005	11.65	11.68	11.66	11.66	11.69
0.007	11.79	11.83	11.80	11.80	11.84
0.01	11.94	11.98	11.96	11.95	12.00
0.03	12.40	12.44	12.42	12.41	12.48
0.06	12.67	12.72	12.70	12.69	12.78
0.08	12.78	12.83	12.82	12.80	12.91
0.1	12.86	12.91	12.91	12.89	13.00
0.2	13.11	13.17	13.19	13.17	13.31
0.3	13.26	13.32	13.36	13.33	13.49
0.4	13.37	13.43	13.49	13.46	13.61
0.5	13.46	13.52	13.59	13.56	13.71
0.7	13.61	13.67	13.76	13.71	13.86
0.8	13.67	13.73	13.83	13.77	13.91
1	13.77	13.84	13.95	13.88	14.01
1.3	13.91	13.97	14.11	14.02	14.13
1.6	14.02	14.09	14.24	14.14	14.22
1.9	14.12	14.19	14.36	14.23	14.29

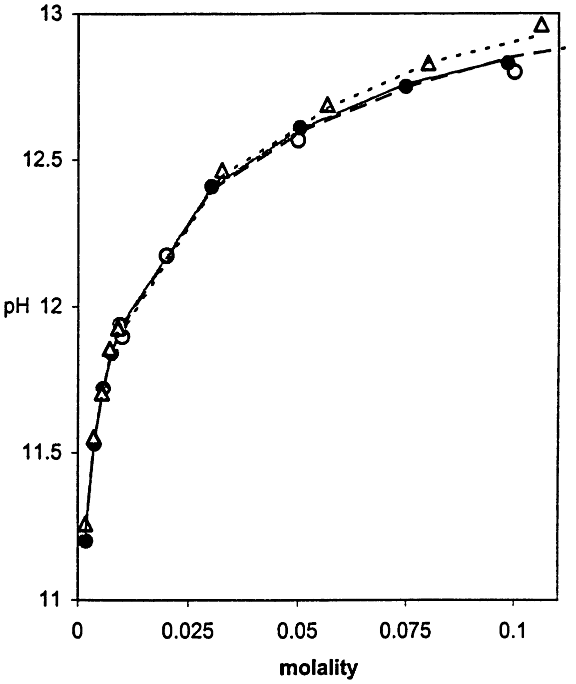

Figure 3. pH values in the diluted region of aqueous NaOH and KOH systems at 25°C.

NaOH: ●—experimental data; ○—(Bates et al., 1950), —— calculated from Eq. 17; KOH: Δ—experimental data; ---- calculated from Eq. 17; — — — — calculated from Davies equation.

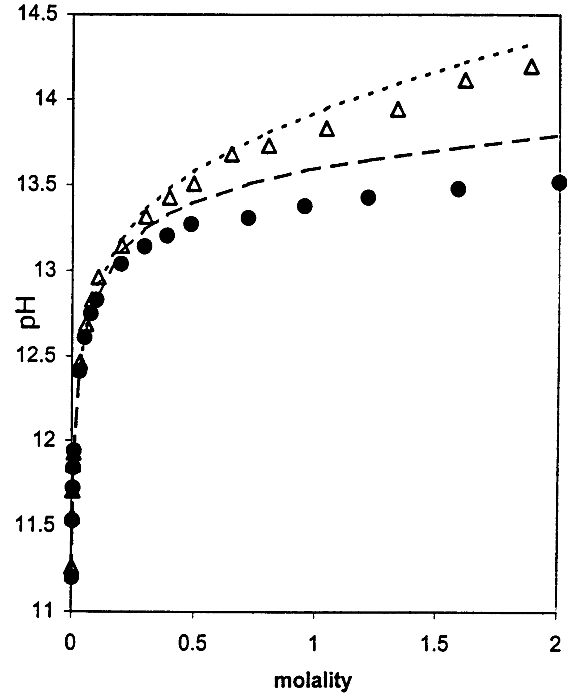

Figure 4. pH values in concentrated aqueous solutions of NaOH and KOH at 25°C.

NaOH: ●—experimental data; ---- calculated from Eq. 17; KOH: Δ—experimental data; ···· calculated from Eq. 17.

(1991) introduced the following assumptions for the evaluation of these parameters:

1. The activity coefficient of an ion was assumed to be independent from the nature of counterions and dependent solely on the total ionic strength and the values of coefficients b_i and c_i.
2. The MacInnes assumption (1919) was adopted.

Figure 5 compares the prediction of the Pitzer model with the experimental values of individual activity coefficients determined in the present work and their correlation with Eq. 21. It is interesting to observe that not only the calculated values differ in magnitude from the experimental ones, but also that the qualitative prediction fails. The Pitzer model predicts that the activity coefficients of the chloride ions are smaller than the mean ionic activity coefficients and that of hydrogen ions are larger. The experimentally determined activity coefficients show the reverse trend. As shown in Figure 6, the same is true for the NaOH system. Only for the case of the activity coefficients in the KOH system presented in Figure 7, Pitzer's model gives correct qualitative predictions. On the other hand, for both KOH and HCl, the Pitzer's model reproduces the mean ionic activity coefficients, since, as shown in Table 8, these values were used to calculate the activity coefficients of the single ions. For NaOH, as individual ionic activity coefficients were obtained with independent assumptions, Pitzer's model fails to reproduce the mean ionic activity coefficient. Additionally, the parameters of the New Hydration Theory were fitted to reproduce the activity coefficients of the individual ions, and thus the results obtained, which are also presented in Figure 7, are comparable to those obtained with the Khoshkbarchi-Vera equation.

Table 7. Values of the Parameters of Eqs. 21 and 22

	HCl		NaOH		KOH	
	H^+	Cl^-	Na^+	OH^-	K^+	OH^-
Parameters of Eq. 21						
B	44.80	305.88	301.15	−165.74	99.00	183.51
C	−1.236	1.826	0.683	−0.384	−0.082	0.3146
rms*	0.026	0.072	0.077	0.015	0.014	0.010
Parameters of Eq. 22						
h	0.746	15.755	12.430	0.0	3.079	7.548
ρ	0.500	699.74	19.121	2.207	7.744	13.812
rms*	0.028	0.109	0.077	0.016	0.036	0.009

*Root-mean-square deviation.

Table 8. Parameters for Pitzer Equation,* Eq. 24

Species	b	c	Source**
H^+	1.67	5.525	$\gamma^2_{HCl}/\gamma_{KCl}$
Cl^-	1.265	0.014	γ_{KCl}
Na^+	1.541	0.126	$\gamma^2_{NaCl}/\gamma_{KCl}$
K^+	1.265	0.014	γ_{KCl}
OH^-	0.988	0.475	$\gamma^2_{KOH}/\gamma_{KCl}$

*Pitzer, 1991.

**Source indicates the assumption made to obtain the activity of the individual ion from a knowledge of mean ionic activity coefficients in addition to the assumption $\gamma_{Cl^-} = \gamma^{KCl}_{\pm}$.

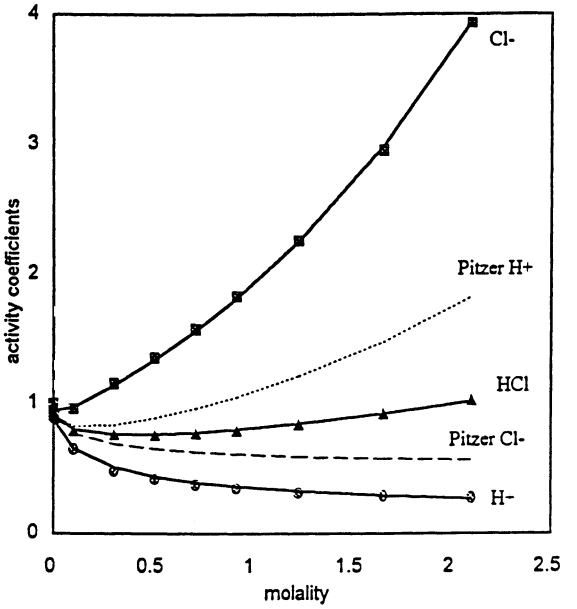

Figure 5. Experimental activity coefficients in the HCl system vs. predictions of Pitzer's model.

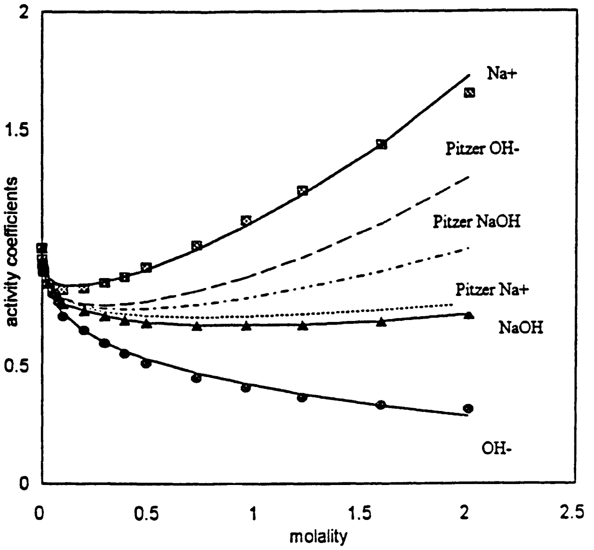

Figure 6. Experimental activity coefficients in the NaOH system vs. predictions of Pitzer's model.

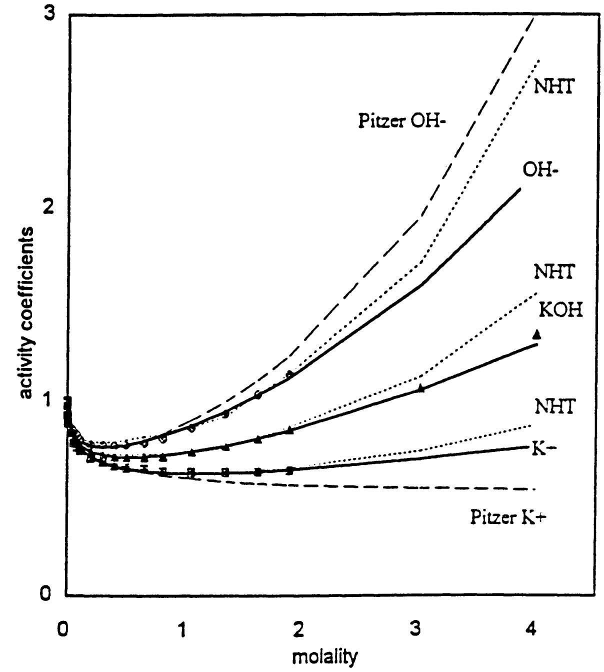

Figure 7. KOH system.

Predictions of Pitzer's model (– – – –) vs. experimental activity coefficients (symbols) and their correlation with Eqs. 21 (—) and 22 (· · · ·).

Conclusions

In some sense, the most interesting result obtained in this study is the relative magnitude of the activity coefficients of the cation and the anion in the KOH and HCl systems. As observed by Rabie et al. (1999), the Hydration Theory of Bates et al. (1970) predicts that in MeCl aqueous electrolyte systems the activity coefficients of the cation Me^+ are always larger than the activity coefficients of the chloride anions. The experimental measurements of Khoshkbarchi and Vera (1996a) showed that potassium ions are an exception to this rule. This experimental result was confirmed by Rabie et al. (1999). Recent measurements for other 1:1 electrolyte systems (Taghikhani et al., 1999, 2000) have found that in different systems, the potassium ion has activity coefficients smaller than its counterion, while other cations show the opposite trend. The present study shows that the behavior of potassium in the KOH system is consistent with the results of all previous studies and adds the behavior of the hydrogen ion in the HCl system to the list of exceptions.

At this point, it is interesting to obtain a general view of the behavior of the activity coefficient of individual ions in aqueous solutions of 1:1 electrolytes. Figure 8 compares the individual activity coefficients of all the cations having OH^- and Cl^- as counterion. The activity coefficients of sodium are always higher than potassium, and the activity coefficients of cations in bases are larger than in the corresponding chlorides. The activity coefficient of the hydrogen ion shows the highest negative deviations from unity due to its strong affinity to water. Figure 9 presents the comparison of the activity coefficients of Cl^- and OH^- anions in the presence of univalent cations. The activity coefficients of the hydroxyl ion

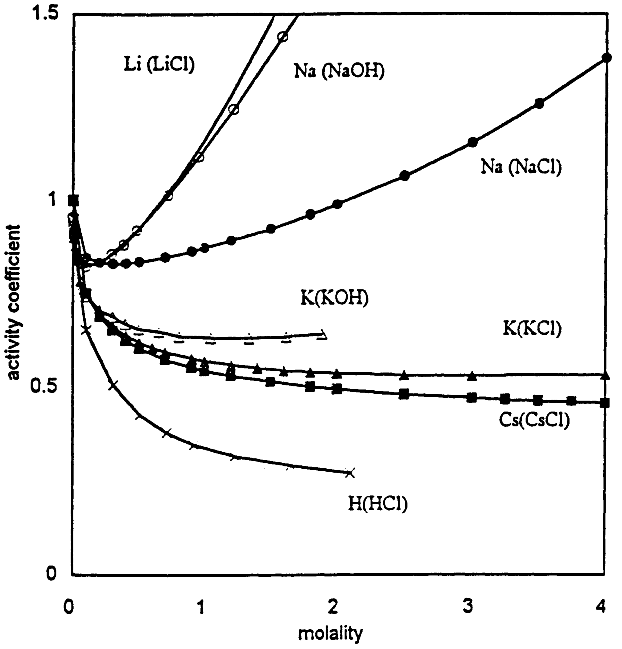

Figure 8. Activity coefficients of cations in chlorides and hydroxides.

Additional data from Rabie et al. (1999) and from Taghikhani et al. (1999).

in KOH are larger than in NaOH. The same is true for the activity coefficient of the chloride ion in KCl and NaCl. The activity coefficient of chloride ion in HCl shows the largest positive deviations from unity.

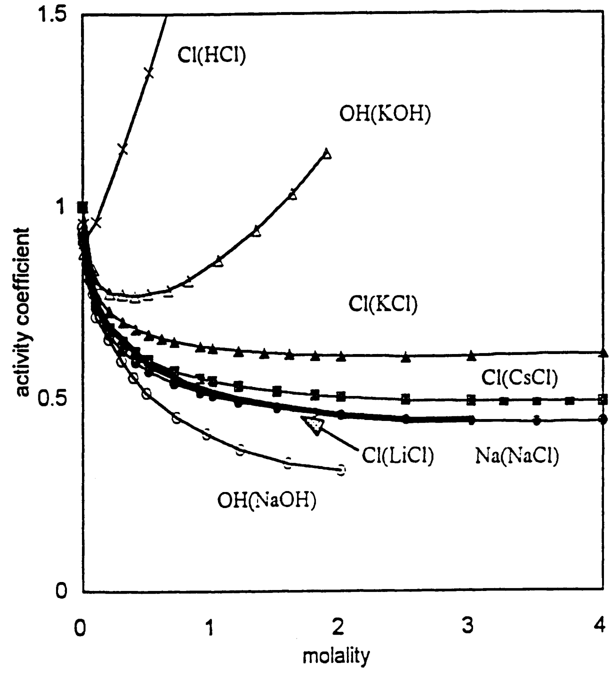

Figure 9. Activity coefficients of anions in chlorides and hydroxides.

Additional data from Rabie et al. (1999) and from Taghikhani et al. (1999).

From a more general point of view, the present study confirms that the experimental method based on the use of ion-selective electrodes produces reliable values of the activity coefficients of individual ions. In all previous studies (Khoshkbarchi and Vera, 1996a,b; Marcos-Arroyo et al., 1996; Taghikhani et al., 1999), where this method was used to measure independently the activity coefficients of the cation and the anion against a common single junction reference electrode, the possibility of a compensation of errors arising from the uncertainty in the estimate of the junction potential was always open for discussion. The effect of this uncertainty, however, was demonstrated to be small (Rabie et al., 1999), and this fact justified the evaluation of the activity coefficient of an ion from measurements of the activity of its counterion (Marcos-Arroyo et al., 1996; Rabie et al., 1999; Taghikhani et al., 1999; Rodil and Vera, 2001). The agreement between the values of pH obtained with the pH probe and the values obtained from measurements of the activities of the chloride ion in HCl solutions, or from the activities of the cations in basic solutions, provides additional support for this extension of the method. In fact, the activity coefficients of the individual ions Cl^-, K^+, and Na^+, were independently measured against a single-junction reference electrode, while the pH probe had its own internal reference electrode. Thus, there is no possible compensation of any error introduced by a poor estimate of the junction potential of the reference electrode. Since the pH electrode has its own internal reference, the operational pH values measured are totally independent of the system used to measure the activity of the ions using an ion-selective electrode and a single-junction reference electrode. While the preceding agreement suggests that the experimental results produced by the ion-selective electrodes technique are reliable, it also speaks highly of the scientific clarity of those who constructed the operational scale pH with limited experimental support.

Acknowledgments

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