Measurement and Correlation of Ion Activity in Aqueous Single Electrolyte Solutions

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Ion-selective electrodes were used to measure the activity coefficients at 298.2 K of individual ions in aqueous solutions of NaCl and NaBr up to of 5 molal and of KCl up to 4 molal. The mean ionic activity coefficients of NaCl, NaBr, and KCl, obtained from the values of the activity coefficients of the individual ions, show good agreement with values reported in the literature. The experimental results show that the activity coefficients are different for the anion and the cation in an aqueous solution of a single electrolyte and that, as expected from the ion-ion and ion-solvent interactions, the activity coefficient of an ion depends on the nature of its counterion. A modified form of the Pitzer's model, which distinguishes between the activity coefficients of the anion and the cation, was used to correlate the experimental results.

Introduction

The experimental determination of the activity of individual ions in aqueous solutions of electrolytes has received considerable attention in the study of the biological systems (Eisenman, 1967). While the measuring of mean ionic activity coefficients of electrolytes in aqueous solutions has been the subject of many studies, no reliable data of activity coefficients of the individual ionic species are available in the literature. In fact, until now, there are no measurements reported for the activity coefficients of both the cation and the anion that properly reproduce the values of the mean ionic activity coefficient in aqueous solutions of single electrolytes. Single ion activity coefficients are well-defined quantities in statistical mechanics and are important in the modeling and design of processes that involve ion exchange (Ashrafizadeh et al., 1993). Most of the complexity in measuring activity coefficients of the individual ionic species in electrolyte solutions comes from the interrelationship between the liquid junction potential and the ionic activity coefficients. The liquid junction potential is a complicated function of the ionic activities, $m\gamma$, and the transference numbers, τ, of all the ionic species present in the liquid junction layer. This relation takes the form (Bates, 1965):

$$E_J = -\frac{RT}{F}\int_l^k \Sigma\left(\frac{\tau}{z}\, d\ln m\gamma\right)_i \tag{1}$$

where k and l represent the two end solutions of the liquid junction, z_i denotes the charge of ion i and the summation runs over all ions in the solution. From Eq. 1, it is evident that calculation of the liquid junction potential needs a knowledge of the ionic activity coefficients, which in turn requires a knowledge of the liquid junction potential. This circle, and probably the lack of proper measuring instrumentation, soon led researchers to accept the impossibility of these kinds of measurements with an acceptable accuracy. However, some of them remained with the hope that this problem may be resolved in the future (Bates, 1965; Shatkay and Lerman, 1969). It should be pointed out that measuring the activity coefficient of ions, as discussed by Taylor (1927) and Gibbs (1928), cannot be done on the basis of exact thermodynamics only and that some approximations need to be made. On the other hand, these approximations can be reduced to a minimum by using proper measuring techniques and the activity coefficient of ions can be obtained with good accuracy as shown below.

Taylor (1927), MacInnes et al. (1938), and Harned and Owen (1958) emphasized the fact that to find the liquid junction potential, it is necessary to go outside the domain of exact thermodynamics. Guggenheim (1929) discussed the physical aspects of the activity of ions and tried to establish a thermodynamic framework based on the electrochemical potential of the ions. Lewis and Randall (1961) mentioned the possibility of measuring the activity coefficient of individual ions in solutions of electrolytes and discussed the thermody-

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namic relations for such systems. MacInnes (1961) discussed the determination of the liquid junction potential, but his method required the use of a rigorous nonequilibrium thermodynamics treatment. Bates (1965) used a modified Henderson equation to calculate the liquid junction potential, and consequently the activity of the hydrogen ion. Shatkay and Lerman (1969) attempted to measure the activities of sodium and chloride ions in a NaCl solution using a sodium-ion-selective electrode and an AgCl/Ag electrode, each against a calomel reference electrode. They modified the Henderson equation to calculate the liquid junction potential. Their treatment assumed a Nernstian slope for the electrode potential, (RT/z_iF), and their measurements were limited by the lack of a chloride-ion-selective electrode to measure the activity of the chloride ion. Bates et al. (1970) used the data of Shatkay and Lerman with a modified hydration model to calculate ion activity coefficients. Komar and Kaftanov (1974) presented a method for estimation of the activity coefficient of chloride ions in potassium chloride solution based on an interpolation of the experimental values of the mean ionic activity coefficient. Milazzo et al. (1975) proposed a procedure to obtain the activity coefficient of ions and analyzed the effect of the mathematical approximations on the reliability of the data measured. They showed that, by using the appropriate experimental techniques and instruments, the effect of uncertainties arising from the approximations required can be reduced to an acceptable level and reliable data can be obtained. Mokhov et al. (1977) reported values of the activity coefficients of sodium and chloride ions in sodium chloride aqueous solutions at different temperatures. Their values, however, give a poor reproduction of the mean ionic activity coefficient of sodium chloride and fluctuate randomly at concentrations above one molal.

In this study the activity coefficients of sodium, potassium, chloride, and bromide ions are measured in aqueous solutions of NaCl, KCl, and NaBr. An electrochemical cell, with ion-selective electrodes (ISE) and an AgCl/Ag, KCl (4M, saturated with AgCl) single junction reference electrode (SJ), has been used. In the experiments, the potential difference values of the cells; (ISE) |salt| KCl, AgCl/Ag (SJ) were measured. These values were then used to obtain the activity coefficients of the single ions in solution, by means of a new technique. The new technique proposed here minimizes the error due to the liquid junction potential and does not require the assumption of a Nernstian slope of the electrode potential as a function of the logarithm of the activity of the ion.

Many parametric models have been developed to correlate the mean ionic activity coefficients of electrolytes (Cruz and Renon, 1978; Haghtalab and Vera, 1988), but few give expressions to calculate the activity coefficients of the ions in solutions. In this work we propose a two-parameter correlation based on Pitzer's model (Pitzer, 1980) for the activity coefficients of the individual ions.

New Method to Reduce the Experimental Data

For a particular ionic species i at a molality m_k in an aqueous solution, the potential E_k of the corresponding ISE with respect to a reference electrode, is related to the activity coefficient γ_k by

$$E_k = E^\circ_{i,k} + S\ln(m_k\gamma_k) \tag{2}$$

where for generality we have designated by S the slope of E_k vs. $\ln(m_k\gamma_k)$ instead of using (RT/z_iF) which assumes an ideal Nernstian behavior. It should be noted that the slope S in Eq. 2 is a positive number for cations and a negative number for anions. As discussed by Skoog and Leary (1992), the term $E^\circ_{i,k}$ is a combination of the standard potential, the junction potential and the asymmetry potential of the ISE $E^\circ_{\rm ISE}$, in addition to the reference electrode electrochemical potential, E_{RE} and the junction potential $E_{J,k}$. Thus we write

$$E^\circ_{i,k} = (E^\circ_{ISE} - E_{RE}) + E_{J,k} = E^\circ + E_{J,k} \tag{3}$$

As mentioned before, previous research has shown that it is not possible to measure experimentally the values of S and $E^\circ_{i,k}$. The potential $E^\circ_{i,k}$ is a function of the molality m_k of the solution through the term $E_{J,k}$, therefore, combining Eqs. 2 and 3 we write

$$(E_k - E_{J,k}) = E^\circ + S\ln(m_k\gamma_k) \tag{4}$$

We propose here a method that eliminates the need to evaluate S and E° and uses instead a dimensionless ISE potential ξ_k defined by

$$\xi_k = \frac{(E_k - E_{J,k}) - (E_1 - E_{J,1})}{(E_2 - E_{J,2}) - (E_1 - E_{J,1})} \tag{5}$$

where the points 1 and 2 represent two arbitrary fixed salt concentrations. Thus, combining Eqs. 4 and 5 we obtain:

$$\xi_k = \alpha + \beta\ln(m_k\gamma_k) \tag{6}$$

with

$$\alpha = \frac{-\ln(m_1\gamma_1)}{\ln(m_1\gamma_1/m_2\gamma_2)} \tag{7}$$

and

$$\beta = \frac{1}{\ln(m_1\gamma_1/m_2\gamma_2)} \tag{8}$$

Note that the derivation of Eq. 6 relies on the assumptions that both S and E° in Eq. 4 are constant over the concentration range studied. The validity of these assumptions is discussed at the end of this section. Before discussing the method for the evaluation of α and β from experimental data, we digress briefly to explain in detail how to obtain the numerical value of the dimensionless ion selective electrode potential, ξ_k.

The evaluation of ξ_k requires the knowledge of the experimentally measured values of E_1, E_2, and E_k at molalities m_1, m_2, and m_k, respectively. In addition, it is necessary to evaluate the junction potentials $E_{J,1}$, $E_{J,2}$, and $E_{J,k}$. In general, the value of the junction potential $E_{J,k}$ at a fixed composition can be estimated by the Henderson equation as modified by Bates (1965). In this equation the ionic mobilities in the two end solutions are considered to be equal to the limiting equivalent conductivities of the ions in the original Henderson equation. The modified Henderson equation with limiting conductivities is written as (Bates, 1965):

$$E_{J,k}=\frac{RT}{F}\frac{\left[\sum c_{+}\lambda_{+}^{\circ}-\sum c_{-}\lambda_{-}^{\circ}\right]_{k}-\left[\sum c_{+}\lambda_{+}^{\circ}-\sum c_{-}\lambda_{-}^{\circ}\right]_{l}}{\left[\sum c_{+}\lambda_{+}^{\circ}|z_{-}|+\sum c_{-}\lambda_{-}^{\circ}|z_{-}|\right]_{k}-\left[\sum c_{+}\lambda_{+}^{\circ}|z_{+}|-\sum c_{-}\lambda_{-}^{\circ}|z_{-}|\right]_{l}}\times\ln\frac{\left[\sum c_{+}\lambda_{+}^{\circ}|z_{-}|+\sum c_{-}\lambda_{-}^{\circ}|z_{-}|\right]_{k}}{\left[\sum c_{+}\lambda_{+}^{\circ}|z_{-}|+\sum c_{-}\lambda_{-}^{\circ}|z_{-}|\right]_{l}} \tag{9}$$

where λ° is the limiting equivalent ionic conductance and c is the concentration of ions in equivalent per liter. In this equation the end solutions are represented by the subscripts k and l and the cation and anion by plus and minus signs. For a system in which k is the solution of molality m_k and the solution l is a saturated solution of KCl (such as the case of SJ electrodes), Eq. 9, at 298.2 K, can be simplified to

$$E_{J,k}=59.155\frac{\left[\sum c_{+}\lambda_{+}^{\circ}-\sum c_{-}\lambda_{-}^{\circ}\right]_{k}+11.6}{\left[\sum c_{+}\lambda_{+}^{\circ}|z_{-}|+\sum c_{-}\lambda_{-}^{\circ}|z_{-}|\right]_{k}-623}\times\log\frac{\left[\sum c_{+}\lambda_{+}^{\circ}|z_{-}|+\sum c_{-}\lambda_{-}^{\circ}|z_{-}|\right]_{k}}{623} \tag{10}$$

The values of the limiting equivalent ionic conductances used in this article are those given by Robinson and Stokes (1959). Shatkay and Lerman (1969) used the same idea of Bates (1965) to modify the Henderson equation, but they used the equivalent conductivity at the concentration of the solution instead of the limiting equivalent ionic conductance. The approach of Shatkay and Lerman (1969) needs the values of the transport number and conductivity of the ions at the solution concentration. This, in turn, introduces new approximations and uncertainties in the results. As shown by the same authors, the final results of both models are quite similar over a wide range of concentration. Therefore, in this work we have eliminated the effect of the transfer numbers of the ions by using the Henderson equation as modified by Bates (1965) to express the junction potential. A method that can help to further reduce the error introduced by the junction potential approximation is to divide the total range of concentration of ions into small intervals and use the treatment just discussed for each interval. In this way, for each subrange of concentration, we would have approximately, $E_{J,1}\approx E_{J,2}$.

For the calculation of the parameters α and β of Eq. 6, we now proceed as follows. Since at low salt concentrations (lower than 0.01 m) the activity coefficient of an ion can be expressed by the Debye–Hückel equation and at higher concentrations the activity coefficient can be considered to be the product of a contribution of a Debye–Hückel activity coefficient term and a residual term, Eq. 6 at any molality k can be written as

$$\xi_k=\alpha+\beta[\ln(m_k)+\ln(\gamma_k^{D\text{-}H})+\ln(\gamma_k^{R})] \tag{11}$$

For the Debye–Hückel contribution we use the form:

$$\ln\gamma^{D\text{-}H}=\frac{-Az_i^2\sqrt{I}}{1+\sqrt{I}} \tag{12}$$

where the Debye–Hückel constant A, at 298.2 K, is equal to 1.1762 $\mathrm{kg}^{1/2}\mathrm{mol}^{1/2}$ and z_i is charge of the ionic species i in the solution. In Eq. 12 the ionic strength I is defined as

$$I=\frac{1}{2}\sum(mz^2)_i \tag{13}$$

At low salt concentrations the residual activity coefficient of any ion can be considered to be unity and the ion activity coefficient is solely due to the contribution of the Debye–Hückel term. Therefore, for low salt concentrations Eq. 11 can be written as

$$\xi_k^{LC}=\alpha+\beta[\ln(m_k)+\ln(\gamma_k^{D\text{-}H})] \tag{14}$$

where superscript LC denotes that Eq. 14 is restricted to data at low salt concentrations for which the activity coefficient of the ions in the solution is given by the Debye–Hückel equation. The constants α and β of the Eq. 14 can be evaluated by a linear fitting of a series of electromotive force (emf) measurements at various salt concentrations lower than 0.01 m. By extending Eq. 11 to higher salt concentrations and subtracting the value of ξ_i^{LC} obtained from Eq. 14, the residual activity coefficient of the ionic species in the solution can be calculated as

$$\ln(\gamma_k^{R})=\frac{\xi_k-\xi_k^{LC}}{\beta} \tag{15}$$

Once the residual activity coefficient of an ion i is known at a molality m_k, its activity coefficient can be calculated from

$$\ln(\gamma_i)=\ln(\gamma_i^{D\text{-}H})+\ln(\gamma_i^{R}) \tag{16}$$

The activity coefficient calculated in this way is based on the assumption that $(E_k-E_{J,k})$ in Eq. 4 is a linear function of $\ln(m\gamma)$, with a constant slope S over the whole range of salt concentration. The question arises whether, when this function is nonlinear, false values for activity coefficients may be calculated with the method proposed here. To show the effect of nonlinearity in the electrode behavior we consider the slope of the electrode, S, at any arbitrary concentration of salt k, to deviate from the linear behavior by ΔS_k. As a result of this change in the electrode slope, the experiments would provide a pseudo-activity coefficient, γ_k', instead of actual activity coefficient, γ_k. After some algebra, the pseudo-activity coefficient can be related to the real activity coefficient by the following relation:

$$\gamma_k'=m_k^{\Delta S_k/S}\gamma_k^{[(\Delta S_k/S)+1]}. \tag{17}$$

Since all the previous equations (Eqs. 2 to 14) for γ_k' would also hold for γ_k', the error due to the nonlinearity of Eq. 4

seems to be undetectable. However, combination of the values of γ'_k obtained in such a case for both the cation and the anion would fail to reproduce the values of mean ionic activity coefficient of the electrolyte measured by independent means for the single salt solution. Thus, if the activity coefficients of the ions can regenerate the values of the mean ionic activity coefficients of the electrolyte reported in the literature, then this is a convincing proof that the values obtained are good approximations to the true values of the activity coefficients of the ions in solution. A similar argument can be put forward to show that if E° changes considerably over the composition range studied, the values of the activity coefficients of the individual ions obtained would have a vanishingly small possibility of reproducing the known values of the mean ionic activity coefficients of the electrolyte.

Materials and Methods

Sodium chloride of 99.99% purity was obtained from Aldrich (Milwaukee, WI), potassium chloride 99.9% and sodium bromide 99.9% were obtained from A&C American Chemicals LTD. (Montreal). All the salts were oven-dried for 72 hours prior to use. During the drying period, the salts were taken out of the oven after 48 hours, 56 hours, and 72 hours and after cooling them in a vacuum desiccator, they were weighed. After 48 hours, no change in their weights was observed. A sodium-ion-selective electrode glass body model 13-620-500, a chloride-ion-selective electrode polymer body model 13-620-518 and the single-junction reference electrode model 13-620-46 were obtained from Fisher Scientific (Montreal). The single-junction electrode was preferred over a double-junction electrode due to the need to minimize junction potentials. The bromide-ion-selective electrode model 94-35 was obtained from Orion (MA) and the potassium-ion-selective electrode model F2312K was obtained from Radiometer (Copenhagen, Denmark). An Orion pH/ISE meter (MA) model EA 920 with a resolution of ±0.1 mV, was used to monitor the emf measurements with two BNC (Bayonet Neil-Concelman) connectors for ion-selective electrodes and two pin-tip connectors for the reference electrode. During the experiments the solutions were stirred continuously in a thermostatic bath at 298.2±0.1 K.

To condition the electrodes, according to the manufacturer procedure, the sodium-ion-selective electrode was immersed in 0.1 M solution of the NaCl 24 hours prior to the measurement, and the potassium-ion-selective electrode was immersed in a 0.01-m solution of KCl 4 hours prior to the experiments. The experiments were done by measuring the emf of both the cation and the anion ion selective electrodes against a single-junction reference electrode in a glass beaker containing 500 mL of solution. All the instruments were grounded prior to and during the experiments. The experiments were started with the lowest concentration of salt and the concentration was increased by addition of solid salt. The error on the molality of the chloride and of the potassium caused by the outgoing flow of the internal solution of the reference electrode was minimized by choosing a large volume of solution, 500 mL, and by performing the experiments at lower concentrations first. The rate of the outgoing flow of the solution from the reference electrode is less than 0.07 mL/hr and, since the low concentration experiments were performed first, the maximum error in molality of the dilute solutions is estimated to be less than 1%. For more concentrated solutions the maximum error in molality is estimated to be less than 0.1%. For ions other than chloride and potassium, the interference caused by these two ions coming from the reference electrode is totally negligible. Due to the large volume of the beaker used in this study, the presence of concentration gradients, which would produce erroneous experimental readings, was a distinct possibility. In order to minimize this risk, a vigorous stirring was maintained during the experiments. All the solutions were prepared based on molality and the water was also weighed. The compositions of the initial solutions were accurate within ±0.01 wt. %. The readings of the potentiometer were made only when the drift was less than 0.1 mV. All the experiments were replicated four times and the data reported are the average of the replicas. Sample variances were obtained from the replicas for each point and a pooled standard deviation was calculated using these values. The 95% confidence interval in γ_i was calculated as ±0.008, and ±0.003 for sodium and chloride ions in NaCl solution, ±0.012, and ±0.003 for potassium and chloride ions in KCl solution and ±0.008, and ±0.003 for sodium and bromide ions in NaBr solution, respectively. In all experiments deionized water with the conductivity of less than 0.8 μS/cm was used. Before using it to prepare samples, the distilled water was passed through ion-exchange columns-type Easy pure RF, Compact Ultrapure Water System, Barnstead Thermoline.

Results and Discussion

Figures 1 and 2 show the dimensionless potentials ξ of

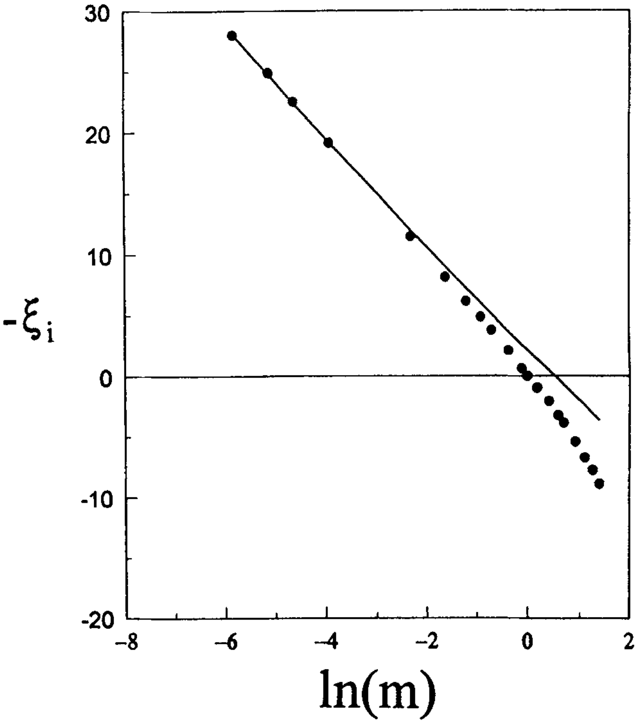

Figure 1. Effect of concentration on the deviation from linear behavior of the dimensionless potential of sodium ion in a sodium chloride solution.

●: Dimensionless potential of sodium ion; ——: linear behavior at low concentrations, Eq. 14.

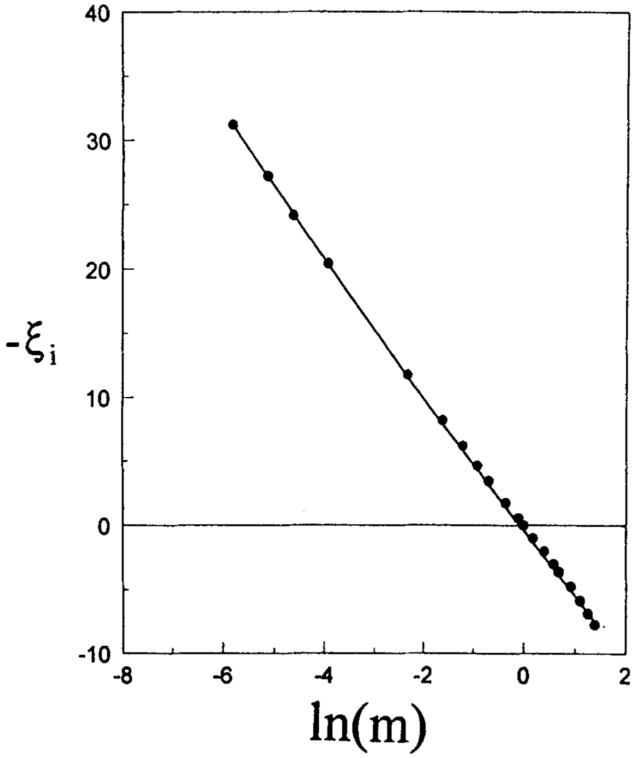

Figure 2. Effect of concentration on the deviation from linear behavior of the dimensionless potential of chloride ion in a sodium chloride solution.

●: Dimensionless potential of sodium ion; ——: linear behavior at low concentrations, Eq. 14.

sodium and chloride ions, obtained with the ion-selective electrodes, as a function of $\ln(m)$. In all cases, the values of ξ were calculated using molality 1 and 1.2 as reference points for Eq. 5. The straight lines drawn over the experimental points at low concentrations in Figures 1 and 2 correspond to Eq. 14, which is only valid in the dilute region of the electrolyte. These lines are tangent to the ξ vs. $\ln(m)$ curves at low concentrations and deviate from the experimental values at higher concentrations. The deviation of the experimental points from the straight line given by Eq. 14 is due to the term $\ln(\gamma^R)$ in Eq. 11. Thus, the difference between the linear behavior of ξ^{LC}, from Eq. 14, and the experimental points gives the value of $\ln(\gamma^R)$.

Figures 3 to 5 show the activity coefficients of the sodium, potassium, bromide and chloride ions at various molalities in the solutions of sodium chloride, potassium chloride, and sodium bromide, respectively. As shown in Figures 3 to 5 the activity coefficients of the cation and the anion are different from each other. These results are in agreement with the study of Bates et al. (1970) and Cruz and Renon (1978) and show the shortcomings of models that consider the activity coefficients of the cation and the anion to be equal to each other at each molality. Figures 3 to 5 also show that the curves of the activity coefficients of the cation and the anion vs. $\ln(m)$ pass through a minimum.

The numerical values of the activity coefficients of the corresponding cation and anion in solution of sodium chloride, potassium chloride, and sodium bromide, together with the comparison of experimental and reported values of the mean ionic activity coefficients, are presented in Tables 1 to 3. The experimental values of the mean ionic activity coefficients of the salt were obtained from its constituent ion activity coefficients, point to point, using the exact relation:

$$\gamma_{\pm} = (\gamma_+^{\nu+} \gamma_-^{\nu-})^{1/(\nu^+ + \nu^-)} \tag{18}$$

As it is shown in Tables 1 to 3 the values of the mean ionic activity coefficients of the salts obtained from the measurement of the single-ion activity coefficients are in good agreement with the reported values (Robinson and Stokes, 1959) up to 4 m for NaCl, 3 m for KCl, and 4 m for NaBr. It is important to note that the activity coefficients of the individual ions reported in Tables 1 to 3 were actually measured at the molalities indicated in the tables and that the values of the mean ionic activity coefficients reported as measured were obtained from the experimental values using Eq. 18. The literature values of the mean ionic activity coefficients, on the other hand, were obtained at regular composition intervals by smoothing experimental data obtained from isopiestic measurements. Smoothed values were also obtained in this work by a method described below.

The correction introduced by the Bates–Henderson method to account for the liquid junction potential gives a major improvement in the reproduction of the mean ionic

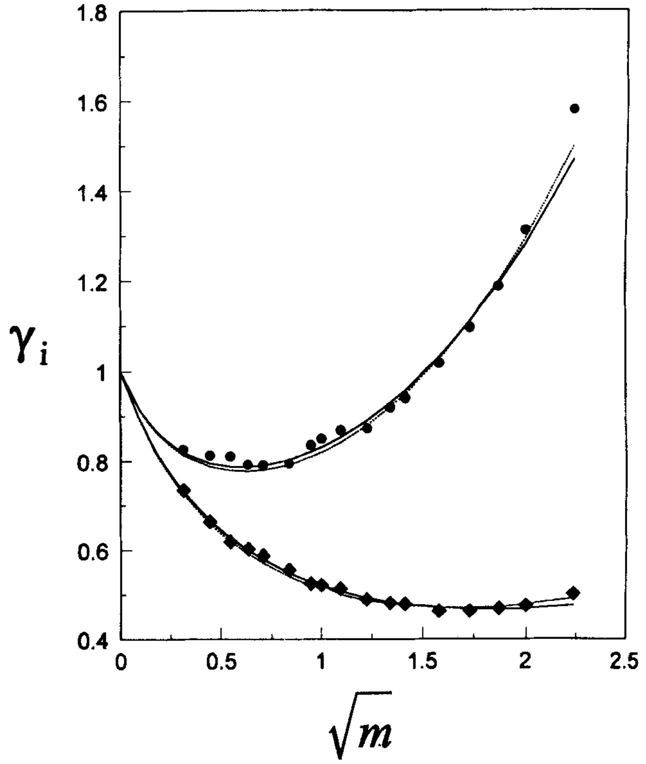

Figure 3. Activity coefficients of the sodium and chloride ions in solutions of NaCl at various concentrations.

●: Activity coefficient of the sodium ion; ◆: activity coefficient of the chloride ion. Correlation of experimental data using Eq. 19: —— parameters from Table 4a; - - - parameters from Table 4b.

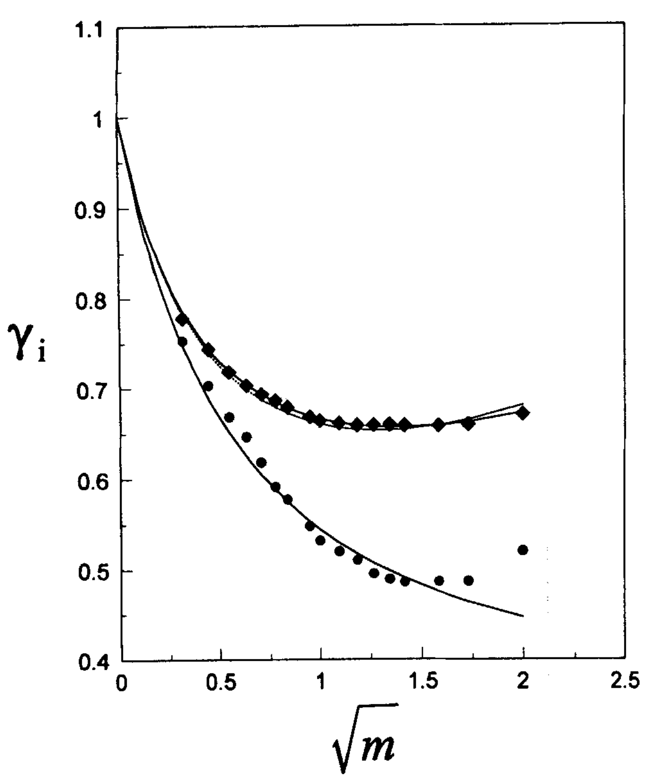

Figure 4. Activity coefficients of the potassium and chloride ions in solutions of KCl at various concentrations.

●: Activity coefficient of the potassium ion; ◆: activity coefficient of the chloride ion. Correlation of experimental data using Eq. 19: —— parameters from Table 4a; - - - parameters from Table 4b.

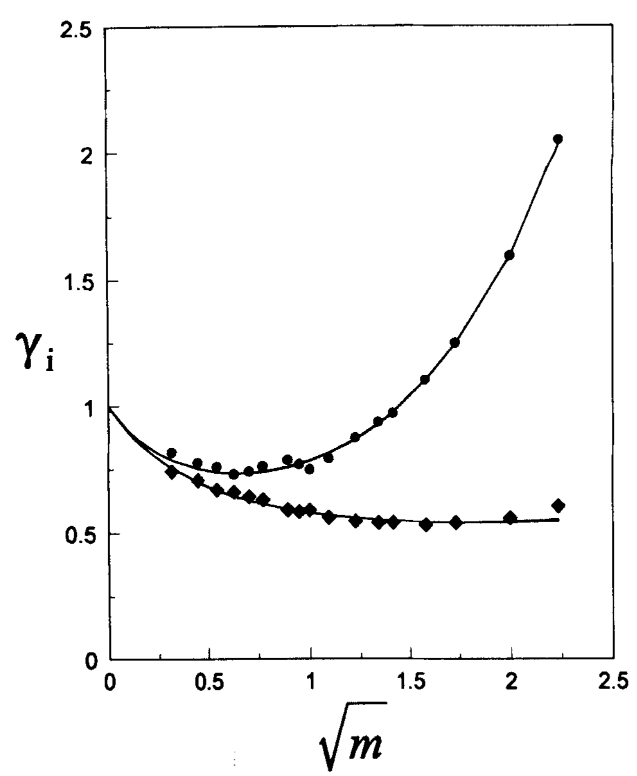

Figure 5. Activity coefficients of the sodium and bromide ions in solutions of NaBr at various concentrations.

●: Activity coefficient of the sodium ion; ◆: activity coefficient of the bromide ion. Correlation of experimental data using Eq. 19: —— parameters from Table 4a; - - - parameters from Table 4b.

activity coefficients of electrolytes. It should be mentioned that to eliminate the error introduced by the junction potential, besides using the Bates–Henderson method, we also tried the method of dividing the concentration range into smaller intervals. The final results of both methods, up to 4 m for NaCl, 3 m for KCl, and 4 m for NaBr were different by about ±2.5%, and the additional complexity of using small concentration ranges did not diminish the deviation between the reported and experimentally measured mean ionic activity coefficients at higher concentrations. These deviations can be interpreted as an indication of either a failure of the electrodes to provide enough sensitivity at high concentrations or to a change in either E° or S, or both, in Eq. 4. Since the measurements of the single-ion activity coefficients were done independently for each ion, the agreement between the experimentally measured and reported values of mean ionic activity coefficients of the salt is considered to be a proof of the reliability of the single ion activity coefficients measured in this study.

Figures 6 to 7 show a comparison between the activity coefficients of sodium ions generated from NaCl and from NaBr and of chloride ions generated from NaCl and from KCl, respectively. As shown in these figures, since the sodium ion in a NaCl solution experiences a different environment and has different interaction with its counterion than the sodium ion in a NaBr solution, the activity coefficient of the sodium ion in a solution of NaCl is different from that of the NaBr solution at the same molality. The same effect is found for the chloride ions in KCl and in NaCl solutions. At high dilution, however, the effect of the counterion tends to disappear as suggested by Eqs. 15 and 16.

Table 1. Activity Coefficients of Sodium and Chloride Ions in NaCl Solutions at Various Concentrations

Conc. of NaCl (m)	γ_{Na^+} Meas.	γ_{Cl^-} Meas.	$\gamma_\pm$ Meas.	$\gamma_\pm$ Lit.*
0.1	0.841	0.734	0.785	0.778
0.2	0.827	0.663	0.740	0.735
0.3	0.825	0.618	0.714	0.710
0.4	0.805	0.602	0.696	0.693
0.5	0.804	0.587	0.687	0.681
0.7	0.808	0.555	0.669	0.667
0.9	0.851	0.524	0.668	0.659
1.0	0.865	0.521	0.671	0.657
1.2	0.884	0.513	0.673	0.654
1.5	0.888	0.489	0.659	0.656
1.8	0.939	0.481	0.672	0.662
2.0	0.956	0.479	0.677	0.668
2.5	1.048	0.462	0.696	0.688
3.0	1.143	0.463	0.727	0.714
3.5	1.210	0.469	0.753	0.746
4.0	1.336	0.475	0.796	0.783
5.0	1.580	0.501	0.890	0.874

*Robinson and Stokes (1959).

Table 2. Activity Coefficients of Potassium and Chloride Ions in KCl Solutions at Various Concentrations

Conc. of KCl (m)	γ_{K^+} Meas.	γ_{Cl^-} Meas.	$\gamma_\pm$ Meas.	$\gamma_\pm$ Lit.*
0.1	0.750	0.778	0.764	0.770
0.2	0.703	0.744	0.723	0.718
0.3	0.668	0.718	0.692	0.688
0.4	0.646	0.703	0.674	0.666
0.5	0.618	0.692	0.654	0.649
0.6	0.591	0.686	0.637	0.637
0.7	0.577	0.679	0.626	0.626
0.9	0.548	0.668	0.605	0.610
1.0	0.532	0.664	0.594	0.604
1.2	0.505	0.661	0.578	0.593
1.4	0.499	0.658	0.573	0.586
1.6	0.495	0.659	0.571	0.580
1.8	0.489	0.659	0.568	0.576
2.0	0.486	0.658	0.565	0.573
2.5	0.486	0.658	0.565	0.569
3.0	0.487	0.660	0.567	0.569
4.0	0.520	0.670	0.590	0.577

*Robinson and Stokes (1959).

Modeling

For the correlation of the experimental values of the activity coefficients of the individual ions we have used a modified form of an equation for ions proposed by Pitzer (1980). The equation used here has the form:

$$\ln \gamma_i = \frac{-A_x z_i^2 \sqrt{I_x}}{1+\rho\sqrt{I_x}} + B_i \frac{I_x^{3/2}}{1+\rho\sqrt{I_x}} + C_i \ln(1+\rho I_x^{2/3}), \qquad (19)$$

where A_x is the usual Debye–Hückel constant, which in mole fraction basis, at 298.2 K, is equal to 8.766. Since the form proposed by Pitzer (1980) does not distinguish between anions and cations of the same charge, we have introduced the adjustable parameters B_i and C_i. In Eq. 19, we have used $\rho = 9$ and I_x is defined as

$$I_x = \frac{1}{2}\sum x_i z_i^2, \qquad (20)$$

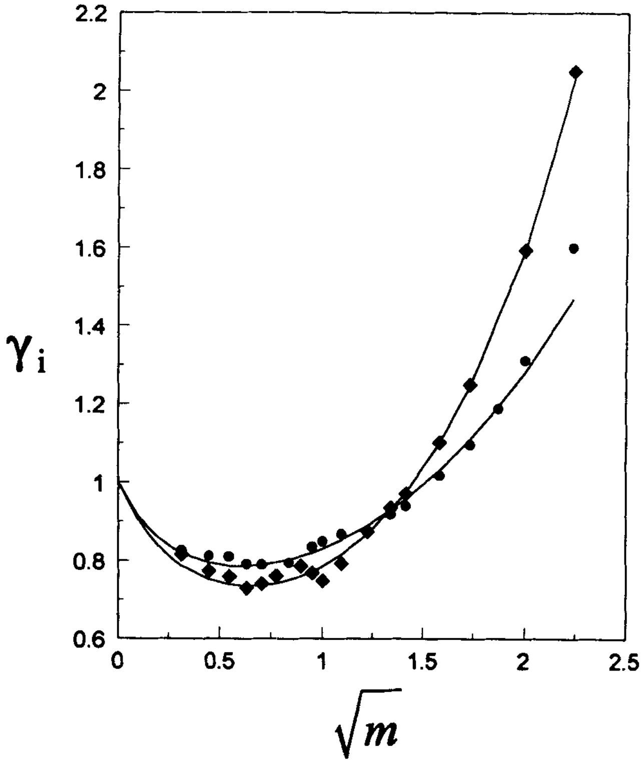

Figure 6. Comparison of the activity coefficients of the sodium ions in NaCl and NaBr solutions at various concentrations.

●: Activity coefficient of the sodium ion in a NaCl solution; ◆: activity coefficient of the sodium ion in a NaBr solution. —— : Correlation of experimental data using Eq. 19 with parameters from Table 4a.

Table 3. Activity Coefficients of Sodium and Bromide Ions in NaBr Solutions at Various Concentrations

Conc. of NaBr (m)	γ_{Na^+} Meas.	γ_{Br^-} Meas.	$\gamma_\pm$ Meas.	$\gamma_\pm$ Lit.*
0.1	0.816	0.741	0.777	0.783
0.2	0.774	0.706	0.739	0.742
0.3	0.759	0.669	0.712	0.720
0.4	0.730	0.660	0.694	0.706
0.5	0.741	0.642	0.690	0.697
0.6	0.761	0.630	0.692	0.692
0.8	0.786	0.590	0.681	0.687
0.9	0.769	0.583	0.669	0.686
1.0	0.749	0.589	0.664	0.687
1.2	0.793	0.560	0.666	0.691
1.5	0.874	0.546	0.691	0.709
1.8	0.935	0.540	0.710	0.718
2.0	0.970	0.541	0.724	0.731
2.5	1.101	0.531	0.764	0.768
3.0	1.249	0.539	0.820	0.816
4.0	1.564	0.558	0.934	0.934
5.0	2.049	0.604	1.112	1.083

*Robinson and Stokes (1959).

where x_i is the mole fraction of ion i in the mixture. The relation for the mean ionic activity coefficient of the electrolyte obtained by combining Eqs. 18 and 19 takes the form:

$$\ln \gamma_\pm = \frac{-A_x |z_+ z_-| \sqrt{I_x}}{1+\rho\sqrt{I_x}} + B_\pm \frac{I_x^{3/2}}{1+\rho\sqrt{I_x}} + C_\pm \ln(1+\rho I_x^{2/3}) \qquad (21)$$

with

$$B_\pm = (\nu_+ B_+ + \nu_- \cdot B_-)/(\nu_+ + \nu_-) \qquad (22)$$

and

$$C_\pm = (\nu_+ C_+ + \nu_- C_-)/(\nu_+ + \nu_-), \qquad (23)$$

where the subscripts plus and minus denote the parameter for the cation and anion. The parameters obtained for the

Table 4.

(a) Unconstrained Parameters of Eq. 21 for Sodium and Chloride Ions in NaCl Solutions, for Potassium and Chloride Ions in KCl Solutions, and for Sodium and Bromide Ions in NaBr Solutions

	NaCl		KCl		NaBr	
	Na^+	Cl^-	K^+	Cl^-	Na^+	Br^-
B	90.582	52.541	6.224	17.067	209.145	31.473
C	0.5705	−0.3815	−0.1808	0.2200	0.1430	−0.1035
rms*	0.068	0.021	0.054	0.011	0.077	0.043
Mean ionic rms*	0.041		0.021		0.049	

(b) Constrained Parameters of Eq. 21 for Sodium and Chloride Ions in NaCl Solutions, for Potassium and Chloride Ions in KCl Solutions, and for Sodium and Bromide Ions in NaBr Solutions

	NaCl		KCl		NaBr	
	Na^+	Cl^-	K^+	Cl^-	Na^+	Br^-
B	110.419	52.541	6.224	26.607	212.787	36.408
C	0.4800	−0.4800	−0.1808	0.1808	0.1230	−0.1230
rms*	0.090	0.034	0.054	0.020	0.077	0.043
Mean ionic rms*	0.042		0.025		0.059	

*rms = root mean square deviation.

ions studied in this work are tabulated in Table 4. Table 4a gives the parameters obtained from an unconstrained fit of the data. Notably for each salt, the value of C_+ is similar to the negative value of C_- . Table 4b gives the parameters obtained with the constraint $C_+ = C_-$. With this constraint, the term $C_\pm$ cancels in Eq. 21 and the mean ionic activity coefficient can be represented with a single parameter model that is similar to the Bromley's model (1973). The root-mean-square deviations of the fit of the mean ionic activity

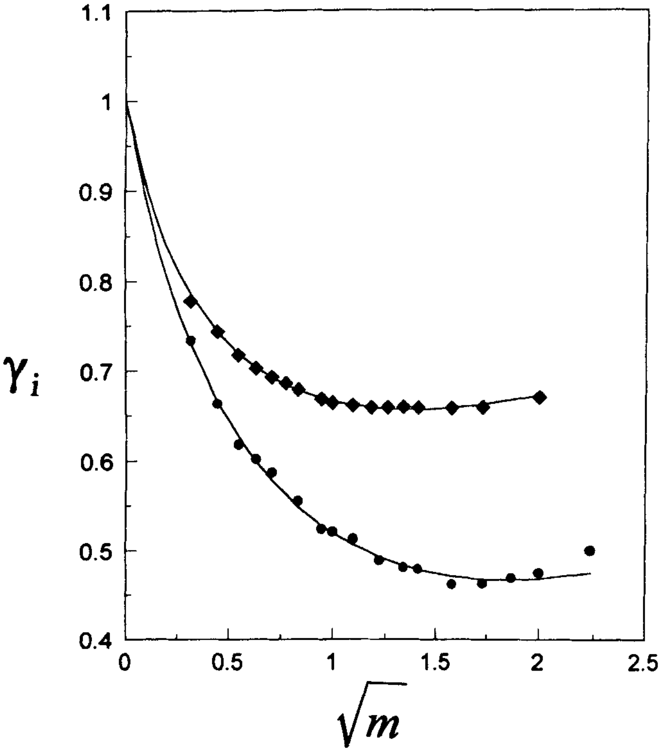

Figure 7. Comparison of the activity coefficients of the chloride ions in NaCl and KCl solutions at various concentrations.

●: Activity coefficient of the chloride ion in a NaCl solution; ◆: activity coefficient of the chloride ion in a KCl solution. ——: Correlation of experimental data using Eq. 19 with parameters from Table 4a.

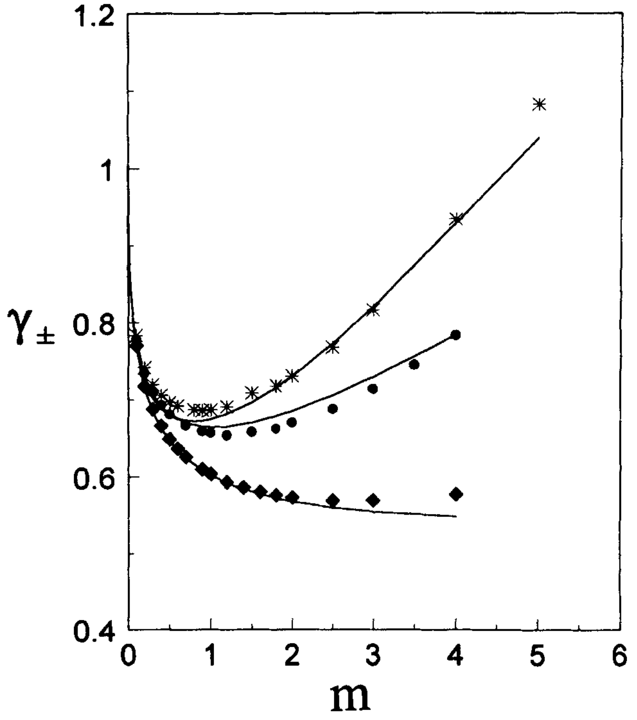

Figure 8. Mean ionic activity coefficients of NaCl, KCl, and NaBr at various concentrations.

Reported values (Robinson and Stockes, 1959) ●: NaCl; ◆: KCl; *: NaBr. ——: Results from Eq. 21 with parameters from Table 4a.

coefficients for each salt with each set of the parameters are also presented in Table 4. The solid lines in Figures 3 to 5 show the results obtained with Eq. 19 and the parameters reported in Table 4a. The values of the mean ionic activity coefficients calculated with the same set of parameters and Eq. 21 are compared in Figure 8 with the values reported by Robinson and Stokes (1959). It should be noted that the experimental points at the higher concentration for the activity coefficients of the ions were not included in the evaluation of the adjustable parameters for Eq. 19 nor in the calculation of the root-mean-square deviations. Equation 19 gives good estimates up to concentrations of 4 m for NaCl and NaBr and up to 3 m for KCl.

In this work we have also tested several other existing models for mean ionic activity coefficients that had explicit forms for the activity coefficients of the ions. The model of Chen et al. (1982) does not distinguish between ions. The models of Cruz and Renon (1978) and Haghtalab and Vera (1988, 1991) distinguish between ions, but they failed to reproduce the mean ionic and the anionic and cationic activity coefficients with a single set of parameters. On the other hand, they are not simple to handle when different parameters are required to fit the activity coefficients of anions and of cations. The correlation of Bromley (1973), which in some sense is similar to the one proposed here, had the potential for using different parameters for anions and cations and still retain a simple form for the mean ionic activity coefficient of the electrolyte. Bromley's equation, however, failed to produce a good fit of the activity coefficients of the individual ions.

Conclusions

The values of the mean ionic activity coefficients of single salts obtained using the method proposed in this work, compare well with values obtained with isopiestic measurements. This fact indicates that the activity coefficients of single ions can be obtained with good accuracy from ion-selective electrode measurements.

Bates et al. (1970) used data reported by Shatkay and Lerman (1969) to calculate the activity coefficients of the sodium ion and, using these values, together with the values of the mean ionic activity coefficient of the sodium chloride, they predicted the activity coefficients of the chloride ion. For any given set of values of activity coefficients of the sodium ion, however, it is possible to generate a set of values of the activity coefficients of the chloride ion that satisfies the values of the mean ionic activity coefficient of sodium chloride. Thus the work of Bates et al. (1970), even when reported values of the activity coefficients of ions that are in reasonable agreement with our results, failed to present a conclusive proof that these measurements were possible. The fact that we have measured the activity coefficients of both ions independently and obtained values that reproduce the mean ionic activity coefficients of the salts, eliminates any question regarding their physical meaning.

The method for the reduction of the experimental data proposed here has three essential features. First, by using the dimensionless electrode potential it minimizes the effect of the junction potential of the reference electrode. Second, it eliminates the need to evaluate E° and S, thus avoiding the assumption of the Nernstian behavior of the electrode. Third, by evaluating the constants α and β from data in the dilute region, it eliminates any further assumption on the concentration dependence of the activity coefficients.

The results obtained indicate that the activity coefficients of the cation and the anion of an electrolyte in aqueous solution are different one from the other. The activity coefficient of an ion in a solution of a 1:1 electrolyte clearly depends on the nature of its counterion. The preceding results indicate that a theoretically correct model should distinguish between the activity coefficients of anion and cation and should be able to correlate, with the same set of parameters, the mean ionic activity coefficients and the activity coefficients of the single ions. We have used here a simple correlation, based on the theoretical form proposed by Pitzer (1980), which satisfies conditions just discussed. The parameters used in the correlation for each ion are specific for the ion–counterion interaction in the system. As more experimental information on the activity coefficients of single ions becomes available, it is expected that better correlations can be proposed.

Acknowledgments

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Notation

A = Debye–Hückel constant molality base
A_x = Debye–Hückel constant mole fraction base
B = adjustable parameter
C = adjustable parameter
F = Faraday number
I_x = ionic strength on a mole fraction basis
R = universal gas constant
T = absolute temperature
x = mole fraction

Greek letter

ν_i = stoichiometric number of ions i

Superscripts

° = reference state
R = contribution of residual activity coefficient

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Correction

The first paragraph in the text of the R&D note titled "Excluded Volume Contribution to the Osmotic Second Virial Coefficient for Proteins" by Brian L. Neal and Abraham M. Lenhoff (April 1995, p. 1010) was intended as an abstract, but it was printed incorrectly due to an editorial/production error after the galley proofs had been corrected by the authors.