An Isopiestic Method for Measurement of Electrolyte Activity Coefficients

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The need for greater efficiency and better water quality control in industrial plants has led to the development of process simulators for industrial water systems in recent years (Aronson et al., 1982; Musil and Nielsen, 1984; Tien, 1985). The simulation of chemical equilibria in aqueous electrolyte systems was made possible by the work of Meissner and Kusik (1972), Pitzer (1973), Bromley (1973), and others who have developed semiempirical equations to predict activity coefficients in these solutions. These equations use single-component data along with interaction parameters to predict the behavior of mixtures. The development of accurate predictive equations for mixtures has been hindered by the lack of data on multicomponent solutions and single-component solutions at temperatures other than 25°C. To obtain a desired accuracy in activity coefficient data from vapor pressure data, vapor pressure measurements must be obtained at a much higher degree of precision, as errors in vapor pressure measurement are amplified when converted to activity coefficients. One method capable of such accuracy for nonvolatile electrolytes is the isopiestic method.

A modified isopiestic apparatus described herein allows visual determination of steady state and reduces the possibility of temperature gradients between solutions. Potassium chloride solutions were studied using NaCl as the reference solution. Vapor pressures determined with this apparatus were compared to the data of Robinson and Stokes (1965), giving an average absolute error of 0.008%. Pitzer's equation was fitted to the osmotic coefficient data, giving an average absolute error of 0.21% and standard deviation of 0.0009. The activity coefficients that were calculated from the experimental data compare favorably with those reported by Robinson and Stokes. The accuracy of the results obtained using the apparatus described demonstrates the temperature uniformity possible with a water bath.

Theory

The isopiestic method is a simple but highly accurate method of measuring the vapor pressure of a solution of nonvolatile electrolyte by equilibration with a solution of known vapor pressure. An isopiestic apparatus contains two or more solutions in contact with each other through the vapor space and in thermal contact through some conducting medium. The vapor space is evacuated so that it will contain only water vapor. At equilibrium the temperature and pressure of all phases must be equal.

When equilibrium is established in the isopiestic apparatus all phases must have the same activity. Therefore, if the activity of water is known for one solution it is known for all solutions, and by measuring equilibrium concentrations the osmotic coefficient can be calculated for the unknown solutions. The ratio of osmotic coefficients of two solutions in equilibrium is:

$$R = \phi_B/\phi_A = \nu_A m_A/\nu_B m_B \qquad (1)$$

where R is known as the isopiestic ratio. Therefore when the osmotic coefficient of solution A in the apparatus is known, that of B can be calculated by the following equation

$$\phi_B = R\,\phi_A \qquad (2)$$

Pitzer and Mayorga (1973) have given a semiempirical equation for the osmotic coefficient of electrolyte mx as,

$$\phi - 1 = |z_m z_x| f^\phi + m(2\nu_m\nu_x/\nu) B^\phi_{mx} + m^2\, 2(\nu_m\nu_x)^{3/2}/\nu]\, C^\phi_{mx} \qquad (3)$$

where

$$f^\phi = -A^\phi[I^{1/2}/(1 + bI^{1/2})] \qquad (4)$$

$$B^\phi_{mx} = \beta^{(0)}_{mx} + \beta^{(1)}_{mx} \exp(-\alpha I^{1/2}) \qquad (5)$$

The term A^ϕ is the Debye-Huckel coefficient having a value of 0.392 at 25°C for water, and I is the ionic strength of the solution. By curve-fitting experimental data for a single electrolyte solution to this equation, the parameters $\beta^{(0)}_{mx}$, $\beta^{(1)}_{mx}$, and C^ϕ_{mx} can

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be determined. Equation 3 can then be integrated analytically to yield the activity coefficient expression.

Experimental Procedure

Apparatus

The isopiestic apparatus was designed to be relatively inexpensive, simple to use, and yet capable of producing accurate results (i.e., ±0.5% error in activity coefficient) in a reasonable amount of time.

The sample cell that was constructed consists of a glass manifold made of Pyrex tubing with three tapered joints for the attachment of solution flasks and a high-vacuum stopcock for isolation of the system after evacuation. The solution flasks consist of 10 mL boiling flasks with standard taper joints. A diagram of the complete apparatus is given in Figure 1. In order to provide constant temperature as well as improved heat transfer to and from the solutions, a recirculated water bath was constructed with an accurate temperature controller. In order to eliminate any temperature gradient in the bath containing the sample cells, the temperature controlled, cooling coil, and stirrer were placed in a separate bath. Water from the top of the sample-cell bath was pumped through the controlled bath in a large copper coil and then reinjected into the sample-cell bath through a distribution plate in the bottom. The controlled bath was held at 25.00 ± .01°C by the temperature controller. Both baths and the tubing between were insulated to prevent fluctuation of temperature due to room temperature variations. The temperature in the sample-cell bath was monitored with an ASTM standard thermometer marked to 0.1°C. The accuracy of this method was found to be highly sensitive to experimental technique, warranting a detailed outline of the procedure.

Method

The salts used in this research were reagent grade and were used without further purification. Distilled, deionized water was used as the solvent. The NaCl and KCl salts were dried in a convection oven overnight at above 100°C. The dry salt was weighed into the solution flasks using an analytical balance accurate to 0.1 mg. The third flask was charged with approximately 5.0 mL of distilled, deionized water and attached to the center arm of the manifold while the flasks containing the dry salt were attached to the outer arms of the manifold with carefully greased tapered joints. This technique allowed a visual indication of equilibrium when the center flask was dry, and prevented loss of salt from the flasks by splashing on evacuation. Each flask also contained two 4 mm glass beads to aid in the stirring of the salt solutions as the flasks were shaken periodically and to prevent serious splashing of the water on evacuation of the system. The system was evacuated until all the dissolved gases were removed from the distilled water in the center flask, then the cell was isolated with the stopcock. After waiting a few minutes the cell was reevacuated and again isolated. This was repeated several times to assure that all air was removed from the system. The cell was then suspended in the recirculated bath and allowed to equilibrate at 25°C for three days for most solutions, equilibrium being indicated by the disappearance of water from the center flask. For very dilute solutions the amount of time required for distillation of all the pure water onto the salts was found to be impractically long. Therefore the water was added directly to the dry salts, making them approximately the equilibrium concentration while placing only two or three drops of water in the center flask. In this manner only a small amount of water needed to distill in order to achieve equilibrium. Two weeks were allowed for equilibration of the most dilute solutions.

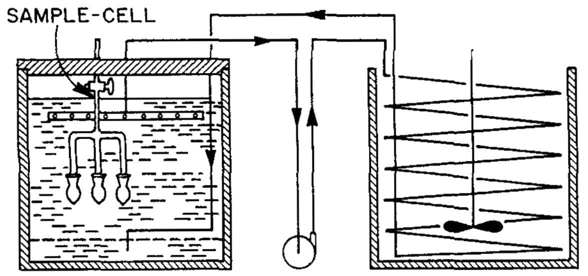

Figure 1. Isopiestic apparatus, showing sample cell and circulating bath details.

When equilibration was complete, dry air preheated to 25°C to prevent condensation on the flask wall was readmitted to the cell. The two flasks containing the salt solutions were removed and stoppered immediately with lightly greased glass stoppers. The flasks were then placed in a dessicator for several hours to assure complete dryness on the outside. The stoppers were then removed and the flask and solution weighed immediately. A thin pipet connected to a vacuum line was used to remove the salt and rinse solutions from the flasks so that the vacuum grease in the neck of the flask is undisturbed. The open flasks were placed in the dessicator again, generally overnight, to assure complete dryness, after which the dry, empty flasks were weighed and the weights of solutions determined. All weighings were corrected to vacuum. From the weight of solution and the initial weight of salt, the molality of each solution was calculated. Finally the osmotic coefficient of the KCl solution was calculated from Eq. 2 using the data of Robinson and Stokes for the osmotic coefficient of the NaCl reference solution.

Analysis of Errors

Several potential sources of error in the method described were identified and their magnitudes estimated. The primary source of error would be the existence of a temperature gradient in the water bath between the two solutions. This becomes especially critical at low concentrations. The vapor pressure, P_{H_2O}, of a salt solution is a function of both concentration and temperature. The change in vapor pressure due to small changes in concentration or temperature can be estimated by the total derivative:

$$\delta P_{H_2O} = (\partial P_{H_2O}/\partial m)_T \, \delta m + (\partial P_{H_2O}/\partial T)_m \, \delta T \qquad (6)$$

Because the two solutions in equilibrium must have equal vapor pressures, δP_{H_2O} must be the same for each solution. By equating the total derivatives for the two solutions and using the conservation of mass, the error in concentration due to temperature deviation from 25°C can be calculated. The error caused when the temperature of both solutions deviates in the same direction by the same amount is small compared to the error of a gradient between the solutions. The partial derivatives in Eq. 6 were estimated from vapor pressure data for NaCl and KCl solutions. Figure 2 is a plot of the percent error in the osmotic coefficient

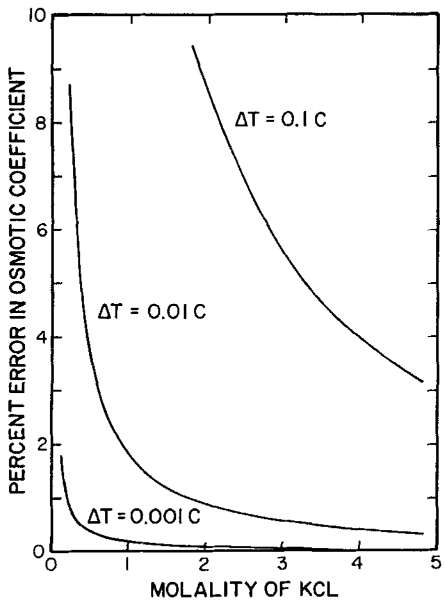

Figure 2. Effect of sample cell temperature gradients on osmotic coefficient accuracy as a function of salt concentration for KCl.

Table 1. Experimental Results

Isopiestic Molalities		Osmotic Coefficients
m_{KCl}	m_{NaCl}	ϕ_{KCl}
0.09872	0.09873	0.9325
0.09893	0.09828	0.9265
0.5274	0.5122	0.8946
0.8168	0.7709	0.8757*
0.9634	0.9237	0.8944
1.043	1.001	0.8981
1.157	1.109	0.9009
1.929	1.808	0.9120
2.919	2.667	0.9351
4.129	3.648	0.9633**
4.148	3.675	0.9675
4.509	3.926	0.9668**
Saturation	4.185	—

*This result excluded from data treatment due to vacuum grease contamination of solution.

**These results excluded from data treatment because of apparent concentration gradients due to lack of mixing.

vs. concentration of KCl for several temperature gradients. The figure illustrates the importance of uniform temperatures in the dilute region and gives a practical lower limit to isopiestic measurements.

The weighing method was tested to determine the magnitude of error involved. It is believed that the largest error in the osmotic coefficient due to error in weighing would be on the order of ±0.1% using a balance sensitive to ±0.1 mg.

Errors in the osmotic coefficient due to inert impurities should be approximately proportional to the percent impurity. For the salts used in this research this error should be less than ±0.3%.

The actual range of experimental error cannot be stated conclusively at this time due to our inability to detect temperature gradients less than 0.02°C. However, the accuracy of our data seems to indicate uniformity of temperature greater than our ability to measure.

Results and Discussion

The results obtained are given in Table 1, including the observed molalities, which have been corrected to vacuum, and the osmotic coefficients, which are calculated according to Eq. 2. Three of the data points were excluded from the curve-fitting procedure because they were obviously in error. The data point at 0.8168 m KCl is excluded because during the equilibration, vacuum grease was observed to have run down into the solutions. The two data points at 4.129 and 4.509 m KCl are also excluded. Although no visual indication suggested that anything was wrong with these runs, their proximity to saturation may have caused concentration gradients due to lack of mixing. To test this hypothesis a run was subsequently made at 4.148 m KCl and the cells were shaken lightly several times a day during equilibration, resulting in much closer agreement with literature data. The experimentally determined osmotic coefficients are compared with the data of Robinson and Stokes in Table 2 and Figure 3. The accepted data points were curve-fitted with Pitzer's equation for the osmotic coefficient, using a least-squares program, giving an average absolute percent error of 0.21% and standard deviation of 0.00093. The coefficients of Pitzer's equation obtained by curve fit were as follows:

$$\beta^{(0)}_{mx} = 0.05041176$$

$$b^{(1)}_{mx} = 0.195522$$

$$C^{\phi}_{mx} = 0.001355442$$

The curve generated by curve-fitting Pitzer's equation is also given in Figure 3. The experimentally determined vapor pressures are compared to those of Robinson and Stokes in Table 3 and show much closer agreement than the osmotic coefficients.

Conclusions

The results obtained in this research are quite good considering the simplicity of the modified isopiestic apparatus. The method allows for visual observation of steady state. Also, the

Table 2. Comparison of Experimental Results with Literature Data

	ϕ_{KCl}		
m_{KCl}	Present Work	Robinson & Stokes (1965)	Difference %
0.09872	0.9325	0.9268	+0.62
0.09893	0.9265	0.9267	−0.02
0.5274	0.8946	0.8985	−0.43
0.8168	0.8757	0.8970	−2.4
0.9634	0.8944	0.8973	−0.32
1.043	0.8981	0.8977	+0.045
1.157	0.9009	0.8983	+0.29
1.929	0.9120	0.9109	+0.12
2.919	0.9351	0.9346	+0.05
4.129	0.9633	0.9686	−0.55
4.148	0.9675	0.9691	−0.17
4.509	0.9668	0.9798	−1.33

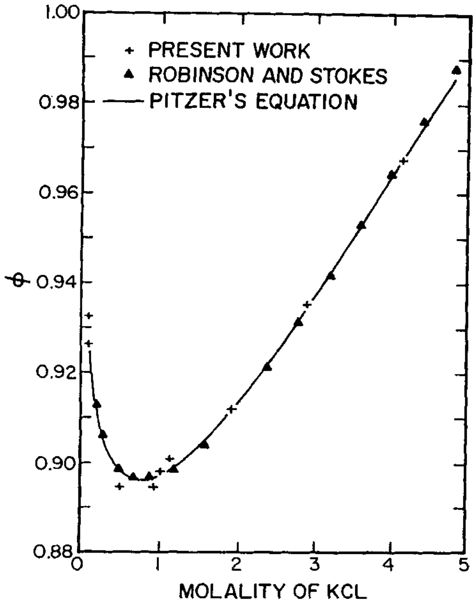

Figure 3. Comparison of osmotic coefficients of KCl in water as a function of concentration at 25°C.

time required for equilibration of solutions is comparable to that reported in the literature for a conventional apparatus. The results indicate that a water bath can provide sufficient temperature uniformity to obtain accurate results.

Single-component data at 25°C seem to be available on most of the major constituents of industrial water streams. Exceptions to this are the compounds $CaCO_3$, $MgCO_3$, $Ca(OH)_2$, and $Mg(OH)_2$. The sample cell material (glass) would be unsuitable for systems containing these constituents; to apply this approach would require the use of a more suitable material. Although some work has been done on measuring activity coefficients of single-component solutions at temperatures other than 25°C, there are still many gaps that need to be filled. The apparatus described in this work can be used to measure vapor pressures up to one atmosphere. Vapor pressure measurements need to be made on some typical industrial water solutions at various temperatures and compared with the vapor pressures predicted by a semiempirical equation. In some mixtures, certain components have a solubility higher than that in their pure solutions. In these mixtures, single-component data must be extrapolated in order to use the semiempirical equations. Vapor pressure measurements need to be made on these solutions to see if this is justified.

Table 3. Comparison of Experimental Vapor Pressure with Literature Data

	P_{H_2O}, mm Hg		
m_{KCl}	Present Work	Robinson & Stokes (1965)	Difference %
0.09872	23.674	23.675	0.004
0.09893	23.675	23.675	0.000
0.5274	23.353	23.351	−0.009
0.8168	23.149	23.134	−0.06
0.9634	23.027	23.024	−0.01
1.043	22.965	22.965	0.000
1.157	22.877	22.880	0.013
1.929	22.294	22.296	0.009
2.919	21.528	21.529	0.005
4.129	20.582	20.566	−0.08
4.148	20.555	20.551	−0.02
4.509	20.300	20.259	−0.2

SI conversion: Pa = mm Hg × 133

Notation

A^{ϕ} = Debye-Huckel coefficient
a_i = Activity of ith component
b = Pitzer equation parameter, $b = 1.2$ for 1:1 electrolyte
C^{ϕ} = Pitzer equation parameter
I = Ionic strength of solution, $I = \frac{1}{2} \Sigma m_i z_i^2$
m_i = Molality of ith species in solution
P_{H_2O} = Vapor pressure of H_2O
R = Isopiestic ratio
z_i = Charge of ith species

Greek letters

α = Pitzer equation parameter, $\alpha = 2.0$ for 1:1 electrolytes
$\beta^{(0)}$ = Pitzer equation parameter
$\beta^{(1)}$ = Pitzer equation parameter
γ_i = Activity coefficient of ith species
$\gamma^{\pm}$ = Mean activity coefficient of dissociated electrolyte
ν_i = Stoichiometric coefficient of ith species in a reaction
$\nu+, \nu-$ = Stoichiometric coefficient of cation and anion on dissociation of electrolyte
$\nu = \nu = \nu+ + \nu-$Osmotic coefficient of ith species
ϕ_i = Osmotic coefficient of ith species

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