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A Simple Method for Determining Differential Diffusion Coefficients from Aqueous Electrolyte Diaphragm Cell Data at Temperatures Below 0°C

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A method is introduced to allow the calculation of differential diffusion coefficients from integral diffusion coefficient data collected with diaphragm cells below 0°C. The method is demonstrated with concentrated potassium hydroxide diaphragm cell data at -15°C and with published data from Stokes. Differential diffusion coefficients, calculated using Stokes' method and the proposed method, are compared for the HCl-water system at 25°C.
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First introduced in 1928 by Northrop and Anson,[1] the diaphragm cell method for determining diffusion coefficients is still commonly used due to its simplicity and low cost. The method has a number of limitations, but remains an excellent choice for aggressive solutions that cannot be easily tested with interferometric methods. Stokes[2] introduced a graphical method for extracting differential diffusion coefficients from integral diffusion data, but for aqueous solutions, this method is limited to temperatures at or above 0°C. In this paper, a new method is proposed that can be used at lower temperatures and that reduces the number of solution steps to a single linear regression procedure.

Background Information

Various forms of the diaphragm cell have been described in great detail elsewhere,[3-9] but in summary, a diaphragm cell consists of two well-stirred compartments of known volume separated by a membrane. Frequently, the membrane is composed of fine porosity glass frit, but it may also be made of porous Teflon, platinum, or other substances. To measure diffusion coefficients, solutions of different composition are placed on either side of the membrane and stirring commences. After a measured period of time has passed, the solutions are withdrawn from both compartments and the concentrations are measured. Figure 1 shows a simple schematic diagram of a diaphragm cell.

The diaphragm cell method of measuring diffusion coefficients is a relative method which requires calibration against a known system, typically 0.1 M KCl–water at 25°C. The fundamental equation for the integral diffusion coefficient for a binary system is

$$\overline{D}_{t,c} = \frac{1}{\beta t} \ln\left[\frac{(c_1 - c_2)}{(c_3 - c_4)}\right] \qquad [1]$$

in which $\overline{D}_{t,c}$ is an integral diffusion coefficient averaged over time and concentration, β is the cell calibration constant, t is the time of the experiment, c_1 is the initial concentration of the solution in the bottom compartment of the cell, c_2 is the initial concentration of the solution in the top compartment of the cell, c_3 is the final concentration of the solution in the bottom compartment of the cell, and c_4 is the final concentration of the solution in the top compartment of the cell. It should be noted that the diaphragm cell can only directly measure integral diffusion coefficients. However, differential diffusion coefficients are often needed and, in 1950, Stokes introduced a reliable graphical technique which allows differential diffusion coefficients to be extracted from integral diffusion coefficient data for electrolytes.

Stokes' method.—Stokes' derivation began with an equation derived by Gordon[10] relating the differential diffusion coefficient to the integral diffusion coefficient

$$\overline{D}_{t,c} = \frac{1}{\overline{c}_B - \overline{c}_T} \int_{\overline{c}_T}^{\overline{c}_B} D\,dc \qquad [2]$$

in which $\overline{c}_B$ and $\overline{c}_T$ are the arithmetic means of the initial and final concentrations in the bottom and top compartments of the diaphragm cell, respectively, and D is the differential diffusion coefficient. Stokes defined a new integral diffusion coefficient, $\overline{D}_c$, which is the integral diffusion coefficient for a "vanishingly short duration" between a solution of concentration c in the bottom compartment and pure water in the top compartment. Now, for an experiment of vanishingly short duration, the concentrations of the compartments do not change. In this limit, Eq. 2 may be rewritten as

$$\overline{D}_c = \frac{1}{c} \int_0^c D\,dc \qquad [3]$$

By combining Eq. 2 and 3 for a hypothetical experiment of vanishingly short duration, the following expression results

$$\overline{D}_c[\overline{c}_B] = \overline{D}_{t,c} - \left(\frac{\overline{c}_T}{\overline{c}_B}\right)\left\{\overline{D}_{t,c} - \overline{D}_c[\overline{c}_T]\right\} \qquad [4]$$
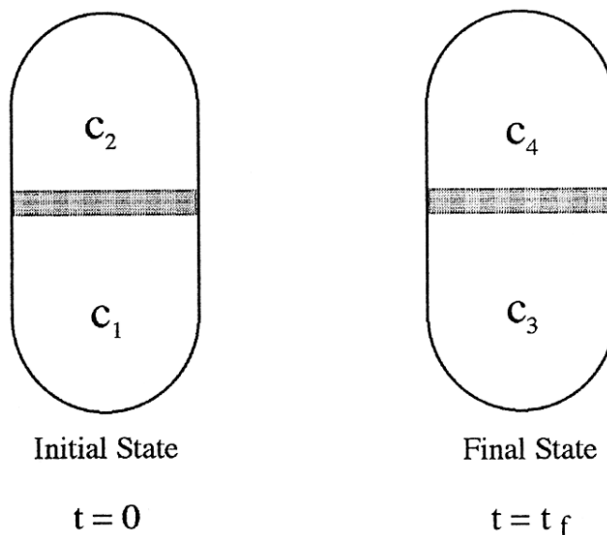
Figure 1. Schematic of diaphragm cell.

in which $\overline{D}_c[\overline{c}_B]$ and $\overline{D}_c[\overline{c}_T]$ are the time-independent integral diffusion coefficient values for hypothetical experiments with initial concentrations of $\overline{c}_T$ and $\overline{c}_B$, respectively. Stokes' method makes use of an iterative graphical procedure to find the time-independent integral diffusion coefficients. To apply the method, experimental values for c_1, $\overline{D}_{t,c}$, $\overline{c}_B$, $\overline{c}_T$ must be available over a concentration range. The procedure is as follows. Step 1: plot the actual experimental data $\overline{D}_{t,c}$ vs. $\sqrt{c_1}$. Draw a smooth line between the experimental data points, extrapolating to the Nernst limiting value. (Although this fitting was originally done manually, it may, of course, be done with any convenient regression package.) Step 2: from the fitted line in the above plot, read the values of the predicted diffusion coefficient at $\overline{c}_T$ for each experimental run. (This is the first approximation of $\overline{D}_c[\overline{c}_T]$). Step 3: calculate values for $\overline{D}[\overline{c}_B]$ using Eq. 4. Step 4: plot the diffusion coefficients from Step 3 ($\overline{D}_c[\overline{c}_B]$) vs. $\sqrt{\overline{c}_B}$ experimental data. Fit a smooth curve as before and, from this curve, read the values of $\overline{D}_c[\overline{c}_T]$ at each $\overline{c}_T$ experimental value. (This is the second approximation of $\overline{D}_t[\overline{c}_T]$). Step 5: Calculate values for $\overline{D}_c[\overline{c}_B]$ using Eq. 4. Steps 4 and 5 may be repeated, but Stokes' method typically converges after the second iteration.

Equation 3 may be differentiated to yield

$$D = \overline{D}_c + c \frac{d\overline{D}_c}{dc} \qquad [5]$$

Using the values of $\overline{D}_c$ determined in the step-wise regression, the differential diffusion coefficients may be directly calculated. The differential terms in Eq. 5 may be determined numerically or graphically.

Stokes' method is relatively easy to implement and widely accepted, but is limited to the case of where $c_2 = 0$. For aqueous solutions, this necessarily limits the lowest experimental temperature to values equal or greater than 0°C. We would now like to propose a simpler method for aqueous electrolyte solutions which may also be used at temperatures below 0°C.

Proposed method.—Returning to Eq. 2, assume that the differential diffusion coefficient is a function of concentration in the form

$$D = K_1 + K_2\sqrt{c} + K_3c + K_4c^{3/2} + K_5c^2 \qquad [6]$$

where K_1-K_5 are constants. It should be noted that this expression has no theoretical basis, but has been found to accurately describe the shape of the differential diffusion coefficient over a wide range of concentration for a number of binary electrolyte systems. Substituting Eq. 6 into Eq. 2 yields the following integral

$$\overline{D}_{t,c} = \frac{1}{\overline{c}_B - \overline{c}_T} \int_{\overline{c}_T}^{\overline{c}_B} \left(K_1 + K_2\sqrt{c} + K_3c + K_4c^{3/2} + K_5c^2\right)dc \qquad [7]$$

Integrating the left side of Eq. 7 results in the expression

$$\overline{D}_{t,c} = \frac{1}{\overline{c}_B - \overline{c}_T}\left(K_1c + \frac{2}{3}K_2c^{3/2} + \frac{1}{2}K_3c^2 \right.$$

$$\left. + \frac{2}{5}K_4c^{5/2} + \frac{1}{3}K_5c^3\right)\Bigg|_{\overline{c}_T}^{\overline{c}_B} \qquad [8]$$

which, when evaluated over the limits of integration and simplified, gives

$$\overline{D}_{t,c} = K_1 + \frac{K_2}{1.5}X_1 + \frac{K_3}{2}X_2 + \frac{K_4}{2.5}X_3 + \frac{K_5}{3}X_4 \qquad [9]$$

where

$$X_1 = \left(\frac{\overline{c}_B^{1.5} - \overline{c}_T^{1.5}}{\overline{c}_B - \overline{c}_T}\right) \qquad [10]$$

$$X_2 = \left(\frac{\overline{c}_B^2 - \overline{c}_T^2}{\overline{c}_B - \overline{c}_T}\right) \qquad [11]$$

$$X_3 = \left(\frac{\overline{c}_B^{2.5} - \overline{c}_T^{2.5}}{\overline{c}_B - \overline{c}_T}\right) \qquad [12]$$

$$X_4 = \left(\frac{\overline{c}_B^3 - \overline{c}_T^3}{\overline{c}_B - \overline{c}_T}\right) \qquad [13]$$

Values for K_1-K_5 can be determined by using any statistical regression package on a body of experimental data which includes more than five sets of values of $\overline{D}_{t,c}$, c_1, c_2, c_3, and c_4. If exactly five sets of data are available, than the coefficients K_1-K_5 can be found using linear algebra.

After the coefficients are determined, the differential diffusion coefficient may be easily calculated for any concentration in the experimental range by using Eq. 6. It should be noted that for aqueous electrolytes at temperatures of 0°C or greater, K_1 must be set equal to the Nernst limiting value at infinite dilution. This condition does not apply at temperatures below 0°C, because the Onsager-Fuoss theory is limited to liquids.[11]

Demonstration of the Proposed Method

Diaphragm cell experiments were conducted for concentrated solutions of potassium hydroxide and water at −15°C. The experiments were duplicated for each set of concentrations. Table I lists the values of $\overline{D}_{t,c}$, $\overline{c}_B$, $\overline{c}_T$, and calculated values of X_1-X_4 for the experiments. Using a statistical regression software package, these values were linearly regressed to Eq. 9 and the regression coefficients K_1-K_5 were determined. The regression coefficients are shown in Table II. The square of the correlation coefficient (R^2, the "proportion of variance explained") is 0.920 and the standard error of the prediction is 9.16×10^{-8}. The maximum variation of a predicted value from an experimental value was 9.50×10^{-8}. This variation occurred for the second diffusion experiment at the c_1 concentration of 6 M.

Figure 2 shows the experimental integral diffusion coefficients and the regressed integral diffusion coefficient predictions vs. the square root of the initial concentration in the bottom compartment

Table I. Experimental diaphragm cell data for KOH-water system at −15°C (concentrations in mol/L and diffusivities in cm²/s).

| $\overline{D}_{t,c}$	c_1	c_2	c_3	c_4	$\overline{c}_B$	$\overline{c}_T$	X_1	X_2	X_3	X_4
1.301×10^{-5}	4	3.5	3.916	3.583	3.958	3.542	2.904	7.500	18.160	42.225
1.298×10^{-5}	6	4	5.669	4.330	5.835	4.165	3.350	10.000	28.046	75.689
1.336×10^{-5}	8	4	7.317	4.681	7.659	4.341	3.662	11.999	37.090	110.734
1.343×10^{-5}	10	4	8.971	4.999	9.486	4.499	3.945	13.985	46.964	152.897
1.341×10^{-5}	11	4	9.840	5.215	10.420	4.608	4.085	15.028	52.459	177.816
1.307×10^{-5}	4	3.5	3.917	3.583	3.959	3.542	2.904	7.500	18.162	42.231
1.284×10^{-5}	6	4	5.667	4.323	5.834	4.162	3.349	9.995	28.028	75.624
1.345×10^{-5}	8	4	7.312	4.684	7.656	4.342	3.662	11.998	37.084	110.710
1.344×10^{-5}	10	4	8.973	5.030	9.487	4.515	3.947	14.002	47.041	153.210
1.347×10^{-5}	11	4	9.820	5.218	10.410	4.609	4.084	15.019	52.412	177.591

Table II. Regression constants for the proposed method using data from Table I.

| Regression constant	Value	Units
K_1	$2.56628614 \times 10^{-4}$	cm^2/s
K_2	$-3.67808158 \times 10^{-4}$	$cm^2\,L^{1/2}/(s\,mol^{1/2})$
K_3	$2.02788366 \times 10^{-4}$	$cm^2\,L/(s\,mol)$
K_4	$-4.82810122 \times 10^{-5}$	$cm^2\,L^{3/2}/(s\,mol^{3/2})$
K_5	$4.18234884 \times 10^{-6}$	$cm^2\,L^2/(s\,mol^2)$

(c_1). The predicted integral diffusion coefficients were calculated from Eq. 9 by using the experimental values of c_1-c_4 from Table I and are shown as symbols on Fig. 2. For clarity, a line has been interpolated between the predicted values of $\overline{D}_{t,c}$. It is important to realize that the interpolated line does not represent Eq. 9, since experimental values of c_1-c_4 are necessary to calculate the predicted $\overline{D}_{t,c}$ values. Figure 3 shows the differential diffusion function (Eq. 6), which also uses the regression coefficients K_1-K_5 and which is valid over the entire tested concentration range.
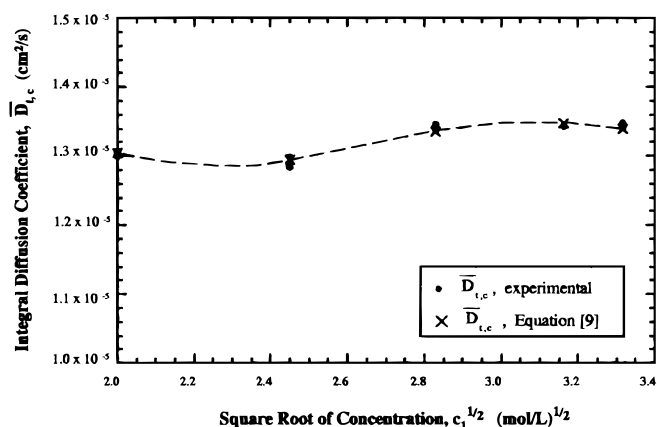
Figure 2. Comparison of experimental integral diffusion coefficients (Table I) to predicted integral diffusion coefficients (Eq. 9) for the system KOH-water at $-15°C$.
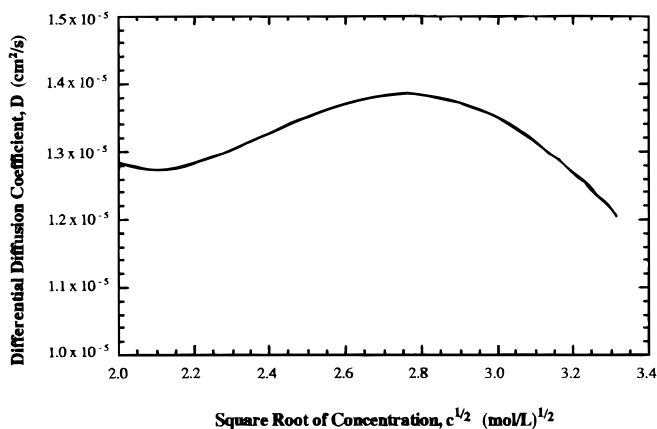
Figure 3. Predicted differential diffusion coefficients using the proposed method (Eq. 6) for the system KOH-water at $-15°C$.
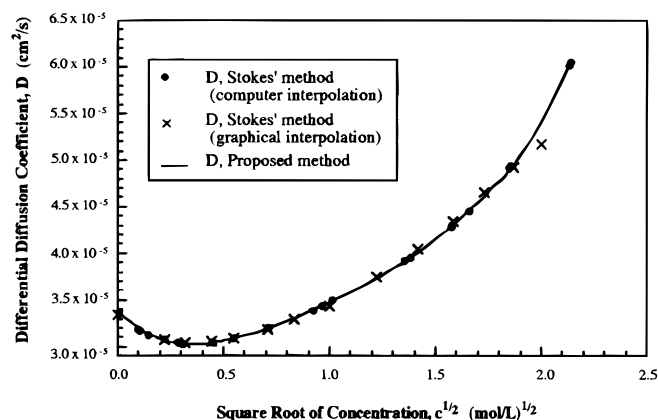
Figure 4. Comparison of the predictions of Stokes' method and the proposed method for the system HCl-water at 25°C. (Data from Stokes.[2])

Comparison with the Stokes Method

Using experimental data from Stokes;[2] the differential diffusion coefficients for the HCl-water system at 25°C were calculated using Stokes' method (regressing parabolic time-independent diffusion coefficient curves with a regression package) and with the proposed method. The Nernst limiting value at infinite dilution was calculated using the Onsager-Fuoss theory with limiting equivalent ion conductivities from Prentice.[12] The results of the two methods are compared in Fig. 4 to tabular differential diffusion coefficients published by Stokes,[2] who used graphical interpolation to determine the differential diffusion coefficients. There is substantial agreement between Stokes' method (as fitted with a regression package) and the proposed method. The average percent difference between values predicted by the two methods is 0.0123%. There is a slight deviation at higher concentrations for Stokes' method using graphical interpolation. This deviation may be due to the inherent lack of precision in graphical methods.

Conclusions

A simple method has been proposed that will permit differential diffusion coefficients to be calculated from diaphragm cell experiments below 0°C. The method eliminates the stepwise approximations required by Stokes' method and generates a set of linear equations which can easily be regressed with any statistical package. The proposed method yields values in good agreement with previous work by Stokes.

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