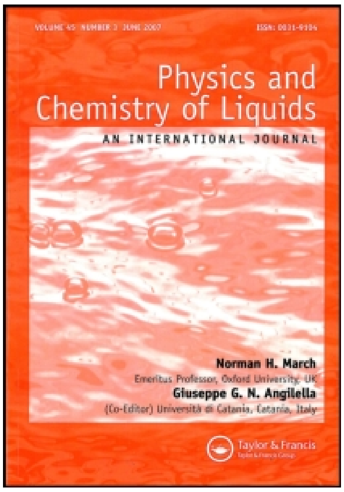

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Diaphragm Diffusion Cell: A Closed Form Solution to the Transport Equation and its Application to the Determination of the Concentration Dependence of the Hcl:H_2o Interdiffusion Coefficient

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DIAPHRAGM DIFFUSION CELL: A CLOSED FORM SOLUTION TO THE TRANSPORT EQUATION AND ITS APPLICATION TO THE DETERMINATION OF THE CONCENTRATION DEPENDENCE OF THE HCl:H_2O INTERDIFFUSION COEFFICIENT

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In a thermodynamically non-ideal solution, the interdiffusion coefficient $D(c)$ of a two-component system is a function of the concentration c. Since the mean concentration $\bar{c}$ in a diaphragm cell remains constant during interdiffusion, we have found it useful to expand $D(c)$ in a Taylor series about $\bar{c}$. After truncating the series and substituting the result into the diaphragm cell transport equation, we obtain a Bernoulli ordinary differential equation, which we solve in closed form. This solution is experimentally tested by determining $D(c)$ from diaphragm cell data which we accumulated on aqueous hydrochloric acid at 25°C. Our results are in qualitative agreement with those of R. H. Stokes, who obtained $D(c)$ from diaphragm cell data by using a graphical method [*J. Am. Chem. Soc.* **72**, 2243 (1950)].

KEY WORDS: Interdiffusion, aqueous hydrochloric acid.

1 INTRODUCTION

A diaphragm cell consists of two well stirred solution compartments on opposite sides of a membrane, which is usually a sintered glass disk. Once the geometric cell constant for the device has been determined by calibration, the interdiffusion coefficient of a two component liquid solution can be determined by following the relaxation of the concentration difference, $\Delta c(t)$, (of either solute or solvent) that exists across the frit. In the special case that solute and solvent form a thermodynamically ideal solution, the interdiffusion coefficient D is a constant, which may be determined using the equation

$$D = \frac{1}{\beta t} \ln\left(\frac{\Delta c(0)}{\Delta c(t)}\right). \tag{1.1}$$

In Eq. (1.1),

$$\Delta c(t) = c_1(t) - c_2(t), \tag{1.2}$$

where $c_1(t)$ and $c_2(t)$ are the concentrations below and above the frit, respectively, at time t, while $c_1(0)$ and $c_2(0)$ are the initial values of $c_1(t)$ and $c_2(t)$. The cell constant β is given by

$$\beta = \frac{A}{l}\left(\frac{1}{V_1} + \frac{1}{V_2}\right), \tag{1.3}$$

where V_1 and V_2 are the volumes of solution below and above the frit, while A and l are the effective cross sectional area and thickness of the frit[1-4].

In the general case where solute and solvent form a thermodynamically non-ideal solution, however, the diffusion coefficient is a function of concentration[5]. Eq. (1.1) still holds in this case, if D is replaced by an appropriate concentration-average $\bar{D}$.[1-4] The cell constant β is ordinarily determined from Eq. (1.1) using $\Delta c(t)$ *vs* t data for aqueous KCl at 25°C, where $c_1(0) = 0.5$ M, $c_2(0) = 0.0$ M, and $\bar{D} = 1.840 \times 10^{-5}$ cm^2/sec.[1] In the case, however, where the function $D(c)$ is required, it must be unfolded from determinations of $\bar{D}$. An empirical method for accomplishing this was developed by Stokes[6].

Recently, we have shown that a mathematically rigorous method for determining $D(c)$ from $\Delta c(t)$ *vs* t data can be obtained by integration of the two first order, ordinary differential equations governing the time evolution of $c_1(t)$ and $c_2(t)$.[7,8] These equations are satisfied by two integrals. The first integral may be expressed as

$$\bar{c} = \frac{V_1 c_1(t) + V_2 c_2(t)}{V_1 + V_2} = \frac{V_1 c_1(0) + V_2 c_2(0)}{V_1 + V_2}, \tag{1.4}$$

where the volume- averaged mean concentration $\bar{c}$ is a constant of motion determined by the initial values $c_1(0)$ and $c_2(0)$. The second integral is found by solving the differential equation

$$\frac{d\Delta c(t)}{dt} = -\beta \int_{c_2(t)}^{c_1(t)} D(c)dc, \tag{1.5}$$

where $D(c)$ is an arbitrary function of the concentration c. To specify $D(c)$, it may be expanded in a Taylor series about $\bar{c}$ as

$$D(c) = D(\bar{c}) + \sum_{n=1}^{\infty} \frac{D^{(n)}(\bar{c})}{n!} (c - \bar{c})^n, \tag{1.6}$$

where $D^{(n)}(\bar{c})$ is the nth concentration derivative of $D(c)$ evaluated at $c = \bar{c}$. After substitution of Eq. (1.6) into Eq. (1.5) and evaluation of the indicated integral, the variables t and Δc may be separated and the resulting equation integrated to obtain the infinite series

$$t = B_0 + B_L \ln(\Delta c) + B_1(\Delta c) + B_2(\Delta c)^2 + B_3(\Delta c)^3 + \cdots, \tag{1.7}$$

which constitutes the solution to Eq. (1.5). In Eq. (1.7), the coefficients B_k, $k = 0, L, 1, 2, \ldots$, are determined as follows: B_0 is evaluated in terms of the other B_k by substituting into Eq. (1.7) $t = 0$ and $\Delta c(0) = c_1(0) - c_2(0)$; B_L is given by

$$B_L = -\frac{1}{\beta D(\bar{c})}, \tag{1.8}$$

while the remaining B_k, $k = 1, 2, 3, \ldots$, depend upon β, V_1, V_2 and various of the concentration derivatives, $D^{(n)}(\bar{c})$. In the special case that $V_1 = V_2$, the odd indexed coefficients, B_{2k+1}, $k = 0, 1, 2, \ldots$, are identically zero.

The procedure described in reference 8 for determining the form of $D(c)$ is based upon Eqs. (1.6) and (1.7). For a fixed value of $\bar{c}$ and with $V_1 \neq V_2$, $\Delta c(t)$ *vs* t data were fitted to Eq. (1.7) with B_0, B_L, B_1, B_2, B_3, etc., treated as least squares adjustable parameters. The values for $D(\bar{c})$ and $D^{(n)}(c)$, $n = 1, 2, \ldots$, were extracted from the least squares parameters by using Eq. (1.8) and the similar formulae given in Reference 8.

Since any $\Delta c(t)$ *vs* t data set is necessarily finite in extent, the infinite series represented by Eq. (1.7) must be truncated if it is to be employed with the least squares method. For example, after truncating Eq. (1.7) at $(\Delta c)^3$ (i.e. dropping all terms of order $(\Delta c)^3$ and higher), we analyzed $\Delta c(t)$ *vs* t data for aqueous HCl at 25°C and $\bar{c} = 1$ M and determined values for B_L, B_1, and B_2. The precision of the data prevented any of the higher order coefficients from being evaluated. From B_L, B_1, and B_2, the values of $D(\bar{c})$, $D^{(1)}(\bar{c})$, and $D^{(2)}(\bar{c})$ were computed[8].

In a subsequent study using a cell with $V_1 = V_2$ (which causes B_1, B_3, B_5, etc., to vanish), we truncated Eq. (1.7) at $(\Delta c)^2$ and fitted the result to $\Delta c(t)$ *vs* t data obtained from solutions of $CuSO_4 + H_2O$, $CoSO_4 + H_2O$, and $Ni(SO_3NH_2)_2 + H_2O$ at 25°C.[9] In the case of $CuSO_4 + H_2O$, both Rayleigh interferometric[10] and Harned conductimetric[11] measurements were available for comparison. Our diaphragm cell results for $D(c)$ were in satisfactory agreement at high concentration with the Rayleigh and Harned results but differed from them by as much as 10% at low concentration[9]. We have analyzed some of the possible causes behind these differences[9].

Although Eq. (1.7) constitutes an exact solution to Eq. (1.5), we have continued, nonetheless, to look for related, closed form approximate solutions which may prove to be more satisfactory for the purposes of data analysis. In this paper, we report such a solution obtained by truncating the Taylor series in Eq. (1.6) *before* substitution into the right hand side of Eq. (1.5). In Section 2, we show how this truncation causes Eq. (1.5) to assume the form of a Bernoulli equation, which can be solved in closed form. Using some measurements carried out on $\bar{c} = 2M$ aqueous HCl with judiciously selected values of V_1 and V_2, we demonstrate in Section 3 how our solution to Eq. (1.5) may be employed to cast various $\Delta c(t)$ *vs* t data sets into the form of straight lines, whose least squares parameters yield values for $D(\bar{c})$, $D^{(1)}(\bar{c})$, and $D^{(2)}(\bar{c})$. In Section 4, we compute $D(c)$ in the case of aqueous HCl for values of c lying between 1.5 M and 3.5 M using these coefficients and a three-term truncation of Eq. (1.6) and compare our results with values reported by Stokes[12] for the same concentration range.

2 THEORY

A Approximate solution to Eq. (1.5) for the case $V_1 \neq V_2$

After truncating Eq. (1.6) at the term in $(c - \bar{c})^2$, substituting the result into Eq. (1.5), changing the variable of integration from c to $y = c - \bar{c}$, where $dc = dy$, and integrating with respect to y, we obtain the transport equation

$$\frac{d\Delta c}{dt} = -\beta\left[D(\bar{c}) + \frac{D^{(1)}(\bar{c})}{2}(1 - 2\alpha)(\Delta c)^2\right], \tag{2.1}$$

where

$$\alpha = \frac{V_1}{V_1 + V_2}. \tag{2.2}$$

Eq. (2.1) is a Bernoulli differential equation, which may be solved by standard methods.[13] These methods yield

$$\frac{\Delta c(0)}{\Delta c(t)} - 1 = \left[1 + \frac{(1 - 2\alpha)D^{(1)}(\bar{c})\Delta c(0)}{D(\bar{c})}\right][\exp(2\beta D(\bar{c})t) - 1]. \tag{2.3}$$

Using Eqs. (1.4) and (2.2), the value of $\bar{c}$ appearing in Eq. (2.3) can be written as

$$\bar{c} = \alpha c_1(0) + (1 - \alpha)c_2(0). \tag{2.4}$$

Eq. (2.3) contains the two parameters $D(\bar{c})$ and $D^{(1)}(\bar{c})$, which need to be evaluated using experimental data. In this regard, a single set of $\Delta c(t)$ *vs* t data is insufficient. There remains, however, flexibility in Eq. (2.3), which we next exploit.

While maintaining the value of $\bar{c}$ invariant, we suppose that the cell is operated in a *conjugate* manner such that the new and old compartment volumes are related as $V_1^* = V_2$ and $V_2^* = V_1$. The condition preserving the value of $\bar{c}$ specifies that the new initial concentrations $c_1^*(0)$ and $c_2^*(0)$ must satisfy

$$c_1^*(0) = (1/\alpha^*)[\bar{c} - (1 - \alpha^*)c_2^*(0)], \tag{2.5}$$

where

$$\alpha^* = \frac{V_1^*}{V_1^* + V_2^*} = 1 - \alpha. \tag{2.6}$$

The values of the initial concentrations $c_1^*(0)$ and $c_2^*(0)$ specify the initial concentration difference

$$\Delta c^*(0) = c_1^*(0) - c_2^*(0) \tag{2.7}$$

for the conjugate case. Note that because Eq. (1.3) is symmetric in V_1 and V_2, the value of β is unchanged when $V_1^* = V_2$ and $V_2^* = V$. In order to suppress gravity driven mixing, in the conjugate experiment the cell must be positioned such that the denser solution is again on the bottom. After adding star (*) superscripts to $\Delta c(t)$ and $\Delta c(0)$ in Eq. (2.3) and substituting Eq. (2.6), we obtain

$$\frac{\Delta c^*(0)}{\Delta c^*(t)} - 1 = \left[1 - \frac{(1 - 2\alpha)D^{(1)}(\bar{c})\Delta c^*(0)}{2D(\bar{c})}\right][\exp(2\beta D(\bar{c})t) - 1], \tag{2.8}$$

which governs the time dependence of concentration differences, $\Delta c^*(t)$, in the conjugate case.

We now suppose that the $\Delta c^*(t)$ data are taken at precisely the same times, t, as the $\Delta c(t)$ *vs* t set. Equations (2.3) and (2.8) may then be added together to obtain

$$\ln\left[\frac{\Delta c(0)\Delta c^*(0)}{\Delta c(0) + \Delta c^*(0)}\left(\frac{1}{\Delta c(t)} + \frac{1}{\Delta c^*(t)}\right)\right] = \beta D(\bar{c})t. \tag{2.9}$$

If data are combined according to Eq. (2.9) and the left hand side is plotted on the ordinate with t on the abscissa, a straight line passing through the origin with slope $\beta D(\bar{c})$ should result.

Once $D(\bar{c})$ has been obtained from the slope of the line predicted by Eq. (2.9), $D^{(1)}(\bar{c})$ may be evaluated either by fitting the $\Delta c(t)$ *vs* t data to Eq. (2.3) or $\Delta c^*(t)$ *vs* t data to Eq. (2.8). If, however, Eqs. (2.3) and (2.8) are subtracted, we obtain

$$\left(\frac{1}{\Delta c(t)} - \frac{1}{\Delta c(0)}\right) - \left(\frac{1}{\Delta c^*(t)} - \frac{1}{\Delta c(*(0)}\right) = \left[\left(\frac{1}{\Delta c(0)} - \frac{1}{\Delta c(*(0)}\right) + \frac{(1 - 2\alpha)D^{(1)}(\bar{c})}{D(\bar{c})}\right] \times [\exp(\beta D(\bar{c})t) - 1] \tag{2.10}$$

where both data sets are combined in one equation. When the combined data sets are plotted according to Eq. (2.10) with the left hand side on the ordinate and $\exp(\beta D(\bar{c})t) - 1$ on the abscissa, a straight line through the origin having a slope given by the quantity within the first square bracket on the right side should result. From the numerical value of the slope, the value of $D^{(1)}(\bar{c})$ may be computed.

B Approximate solution of Eq. (1.5) for the case $V_1 = V_2$

We truncate Eq. (1.6) at the term in $(c - \bar{c})^4$ and substitute the result into Eq. (1.5), setting $\alpha = \frac{1}{2}$ as required by Eq. (2.2) with $V_1 = V_2$; after changing the variable of integration from c to $y = c - \bar{c}$ and integrating, we obtain the Bernoulli equation

$$\frac{d\Delta c}{dt} = -\beta\left[D(\bar{c})\Delta c + \frac{1}{24}D^{(2)}(\bar{c})(\Delta c)^3\right]. \tag{2.11}$$

In the case $V_1 = V_2$, the integral on the right hand side of Eq. (1.5) is insensitive to all $D^{(2k+1)}(\bar{c})$, $k = 0, 1, 2, \ldots,$[7,8] hence, the right hand side of Eq. (2.11) is correct up to fifth order in (Δc). The solution to Eq. (2.11) is

$$\left(\frac{\Delta c(0)}{\Delta c(t)}\right)^2 - 1 = \left[1 + \frac{D^{(2)}(\bar{c})(\Delta c(0))^2}{24D(\bar{c})}\right][\exp(2\beta D(\bar{c})t) - 1]. \tag{2.12}$$

Given that $D(\bar{c})$ is known and that the value of $\bar{c}$ remains fixed by choosing $c_1(0)$ and $c_2(0)$ such that

$$\bar{c} = \tfrac{1}{2}(c_1(0) + c_2(0)), \tag{2.13}$$

then Eq. (2.12) may be applied to determine the value of $D^{(2)}(\bar{c})$ without any reference to the data sets described in Section 2(A). If the left hand side of Eq. (2.12) is plotted on the ordinate with $\exp(2\beta D(\bar{c})t) - 1$ plotted on the abscissa, then $\Delta c(t)$ *vs* t data taken in a cell with $V_1 = V_2$ should form a straight line through the origin. From the slope of the line given by the quantity within the first square bracket on the right hand side of Eq. (2.13), the value of $D^{(2)}(\bar{c})$ may be evaluated.

3 EXPERIMENT

A Equipment and procedures

Two standard Stokes diaphragm cells were constructed from 10–16 μm porosity sintered glass disks fused into 40 mm i.d. glass tubing. The data listed in Table 1 were taken with the cylindrical axis of cell #1 parallel to gravity and the 130 cm^3 volume compartment on the bottom and the 65.8 cm^3 volume compartment on the top. The data listed in Table 2 were taken with cell #1 in the inverted configuration with the 65.8 cm^3 volume on the bottom and the 130 cm^3 volume on the top. The data

Table 1 HCl data from cell #1 in the standard configuration. $V_1 = 130$ cm^3, $V_2 = 65.8$ cm^3, $\alpha = 0.664$, $\beta = 0.162$ cm^{-2}, $\bar{c} = 2.00$ M, temperature = 25 ± 0.01°C

t(sec)	$c_1(t)(M)$	$c_2(t)(M)$	$\Delta c(t)(M)$
0	2.253	1.500	0.753
14,400	2.199	1.519	0.680
25,200	2.171	1.532	0.639
43,200	2.132	1.551	0.581
64,380	2.084	1.581	0.503
83,400	2.034	1.592	0.442
118,800	1.981	1.619	0.362
158,400	1.925	1.652	0.273

Table 2 HCl data from cell #1 in the conjugate configuration $V_1^* = 65.8$ cm^3, $V_2^* = 130$ cm^3, $\alpha^* = 0.336$, $\beta = 0.162$ cm^{-2}, $\bar{c} = 2.00$ M, temperature = 25 ± 0.01°C

t(sec)	$c_1^*(t)(M)$	$c_2^*(t)(M)$	$\Delta c^*(t)(M)$
0	2.988	1.500	1.488
14,400	2.926	1.584	1.342
25,200	2.889	1.646	1.243
43,200	2.850	1.742	1.108
63,380	2.799	1.842	0.957
86,400	2.754	1.931	0.823
118,800	2.703	2.042	0.661
158,400	2.643	2.146	0.497

Table 3 HCl data from cell #2. $V_1 = V_2 = 67.2$ cm^3, $\beta = 0.186$ cm^{-2}, $\bar{c} = 2.00$ M, temperature = 25 ± 0.01°C

t(sec)	$c_1(t)M$	$c_2(t)M$	$\Delta c(t)(M)$
0	3.500	0.500	3.000
14,400	3.331	0.659	2.672
25,200	3.228	0.758	2.470
43,200	3.054	0.921	2.133
64,800	2.892	1.084	1.808
86,160	2.753	1.224	1.529
99,600	2.700	1.278	1.422
118,800	2.589	1.390	1.199
158,400	2.432	1.540	0.892

listed in Table 3 were taken with cell #2 having $V_1 = V_2 = 67.2$ cm^3. The values of the relevant cell and solution parameters for each experiment are listed in the headings of Tables 1–3, respectively.

Both cells included ground glass joints through which the solution compartments could be filled reproducibly to the exclusion of any air bubbles. In ordinary use, an air space above the solution in the top compartment of a Stokes cell is immaterial, but in the case of cell #1, which had to be operated in two orientations differing by 180°, no air could be tolerated in either compartment.

Prior to the start of each run, a concentration gradient was established within the frit following the standard "prediffusion" procedure.[1,2,8] All concentrations were determined by conductivity measurements using a calibrated Radiometer (Copenhagen) model CDM 83 conductivity meter capable of reading conductivities ranging from 1.3 μS/cm to 1300 μS/cm. The diaphragm cell constants β listed in the captions to Tables 1–3, were determined using aqueous KCl with $c_1(0) = 0.5$ M, $c_2(0) = 0.0$ M, and $\bar{D} = 1.840 \times 10^{-5}$ cm^2/sec as recommended by Woolf and Tilley[14].

B Materials

Potassium chloride was Mallinckrodt AR Grade Lot 6858 KBCX, while the hydrochloric acid was Mallinckrodt AR Grade Lot 3560 KCMS. Both were used without further purification. Water once distilled from a glass system and deaerated by aspiration to a residual conductivity of 1.5 μS/cm was used as the solvent for all solutions.

Standard stock solutions of KCl were prepared volumetrically from weighed, dried potassium chloride. Stock solutions of HCl were standardized by titration against weighed tris(hydroxymethyl)aminomethane.

4 RESULTS AND CONCLUSIONS

Our experimental results are summarized in Tables 1–4.

In Table 1, we list data taken with aqueous HCl at 25 ± 0.01°C in cell #1, which had unequal compartment volumes. The value for α given in the caption to the table was computed from V_1 and V_2 using Eq. (2.2). The $t = 0$ values of $c_1(t)$ and $c_2(t)$ are given in the first line of the table and were combined according to Eq. (1.4) to evaluate $\bar{c}$.

Data taken with aqueous HCl in cell #1 in the conjugate configuration are listed in Table 2. The value of α^* was computed using Eq. (2.6), while the value of β was unchanged by virtue of the symmetry of Eq. (1.3). The initial value, $c_2^*(0) = 1.500$ M, was selected for the sake of convenience to be identical with the value of $c_2(0)$ in Table 1. When combined with $\bar{c} = 2.00$ M according to Eq. (2.5), $c_2^*(0) = 1.500$ M served to specify the value $c_1^*(0) = 2.988$ M of the concentration in lower compartment listed in Table 2.

Table 4 Interdiffusion coefficient and its concentration derivatives for aqueous HCl at $\bar{c} = 2.00$ M and 25 ± 0.01°C

$D(\bar{c})(10^{-5}\ cm^2\ sec^{-1})$	$D^{(1)}(\bar{c})(10^{-5}\ cm^2\ sec^{-1}\ M^{-1})$	$D^{(2)}(\bar{c})(10^{-5}\ cm^2\ sec^{-1}\ M^{-2})$
4.01	1.43	0.745

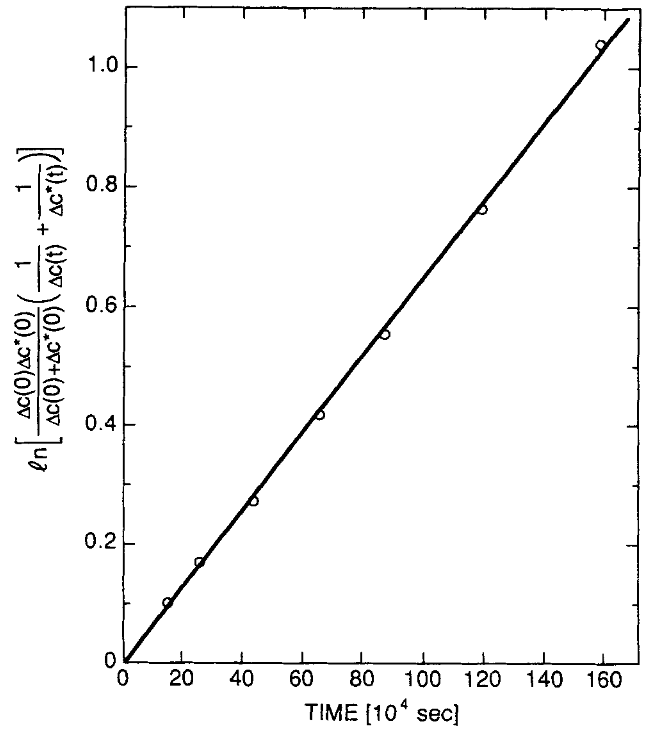

Figure 1 Data in Tables 1 and 2 plotted according to Eq. (2.9).

The data sets from Tables 1 and 2 were combined according to Eq. (2.9) and plotted in Figure 1. Giving each data point equal weight in a linear, zero intercept, least squares fit[15] resulted in an excellent straight line, the slope of which, when combined with $\beta = 0.162\ \text{cm}^{-2}$, gave the value of $D(\bar{c})$ listed in Table 4.

When the data sets in Tables 1 and 2 were combined by least squares according to Eq. (2.10), the straight line shown in Figure 2 resulted. From the least squares slope and values of α and $\Delta c(0)$ obtained from Table 1 and the values of $\Delta c^*(0)$ and $D(\bar{c})$ obtained from Tables 2 and 4, respectively, the value of the instantaneous first derivative, $D^{(1)}(\bar{c})$, shown in Table 4, was computed. By contrast, when the data in Table 1 were combined according to Eq. (2.3), we obtained $D^{(1)}(\bar{c}) = 1.29 \times 10^{-5}\ \text{cm}^2\ \text{sec}^{-1}\ \text{M}^{-1}$, whereas when the data in Table 2 were combined according to Eq. (2.8), we obtained $D^{(1)}(\bar{c}) = 1.57 \times 10^{-5}\ \text{cm}^2\ \text{sec}^{-1}\ \text{M}^{-1}$. The value of $D^{(1)}(\bar{c})$ listed in Table 4 coincidently represents the arithmetic mean of the latter two; the differences among them may be caused by experimental error.

Data taken with aqueous HCl in cell #2 are summarized in Table 3. These data were fitted by least squares to Eq. (2.12) to produce the straight line shown in Figure 3. When the values of $\Delta c(0)$ and $D(\bar{c})$ listed in Tables 3 and 4, respectively, were combined with the least squares slope, the value of the instantaneous second derivative, $D^{(2)}(\bar{c})$, shown in Table 4 resulted.

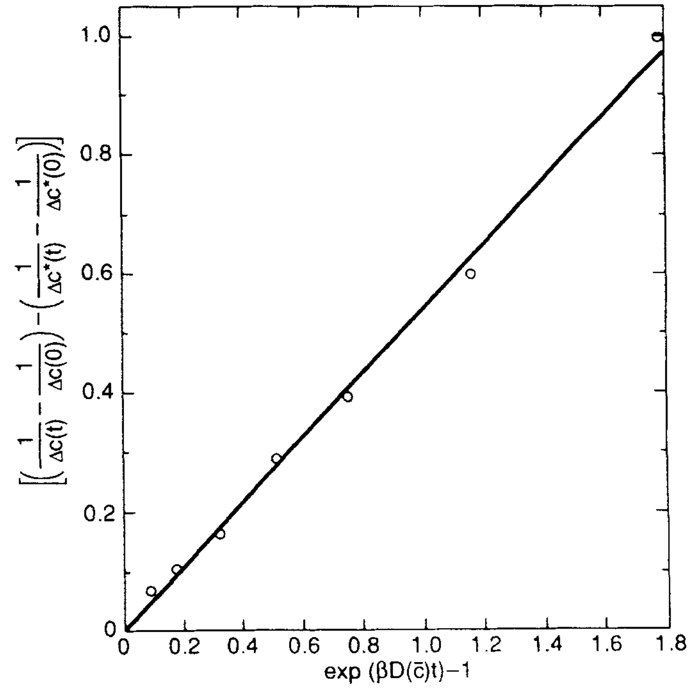

Figure 2 Data in Tables 1 and 2 plotted according to Eq. (2.10).

Note that all numerical procedures outlined above are simple enough that they can be performed with a good hand-held calculator, which is a great advantage over earlier, graphical methods.

Truncating the Taylor series in Eq. (1.6) at the term in $(c-\bar{c})^3$ and substituting $\bar{c}=2.00$ M and the values of $D(\bar{c})$, $D^{(1)}(\bar{c})$, and $D^{(2)}(\bar{c})$ from Table 4 into the resulting quadratic produced the following polynomial representation for $D(c)$

$$D(c)=4.01+1.43(c-2)+0.745(c-2)^2. \tag{4.1}$$

In Eq. (4.1), the units of c are M, while $D(c)$ is expressed as a multiple of 10^{-5} cm^2/sec.

In Table 5, values of $D(c)$ computed from Eq. (4.1) are compared with the results of the Stokes graphical method[6] for the concentration interval, $1.5\text{ M}\leq c\leq 2.5\text{ M}$, which brackets the origin, $\bar{c}=2.0$ M, of the Taylor series. Although the Stokes method has no rigorous mathematical basis[6,8], it nonetheless produces a result in excellent agreement with ours at $\bar{c}=2$ M. Away from this one point, however, our value for the local slope, $D^{(1)}(\bar{c})$, is too large to represent the Stokes data. We can only speculate on the cause of this difference. First, in the case of our data, the second term within the first square bracket on the right hand side of Eq. (2.10) amounts to only 16% of the value of the entire bracket and, as such, may be too small to determine $D^{(1)}(\bar{c})$ accurately. Second, the values we chose for $\Delta c(0)$ and $\Delta c^*(0)$ may have been too large for us to safely ignore the term in $(\Delta c)^2$ when we derived Eqs. (2.3) and (2.8).

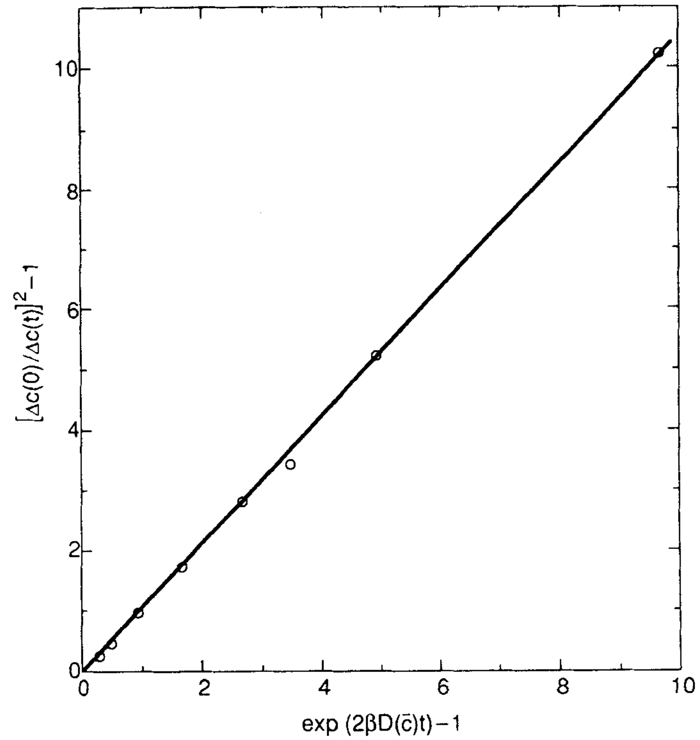

Figure 3 Data in Table 3 plotted according to Eq. (2.12).

A large value of $\Delta c(0)$ (or $\Delta c^*(0)$) is desirable from an experimental point of view in order to produce a sensible change in $\Delta c(t)$ (or $\Delta c^*(t)$) with t. A large concentration difference poses a greater threat, however, to the accuracy of Eqs. (2.3) and (2.8), which are derived from a Taylor series correct to order $(\Delta c)^1$ than it does to Eq. (2.12), which was derived from a series accurate to order $(\Delta c)^3$.

We have pointed out previously that since Eq. (1.6) contains no terms in $(c)^{1/2}$, it cannot represent $D(c)$ for aqueous, strong electrolytes in the limit of infinite dilution[8,9]. To protect the results reported in this paper from being affected by such an error, we selected the minimum concentrations in each experiment ($c_2(0)$ or $c_2^*(0)$)

Table 5 Comparison of Eq. (4.1) with the results obtained from the Stokes graphical method

c(M)	*D(c)(Eq. (4.1))*[a]	*D(c)(Stokes)*[a,b]
1.5	3.37	3.74
2.0	4.01	4.04
2.5	4.81	4.33

[a] Units are 10^{-5} cm^2 sec^{-1}.
[b] Reference 2, Appendix 11.2, p. 515.

such that they greatly exceeded the concentration (approximately 0.1 M for 1–1 electrolytes) where $(c)^{1/2}$ terms are expected to come into play.

Finally, if $V_1 \neq V_2$, Eq. (1.7) may be truncated at the term in $(\Delta c)^3$ to produce a representation of t *vs* Δc data, which is correct to order $(\Delta c)^2$. We have previously used this truncated series to determine the coefficients B_0, B_L, B_1, and B_2 by least squares fit to aqueous HCl data[8]. From these least squares coefficient, $D(\bar{c})$, $D^{(1)}(\bar{c})$, and $D^{(2)}(\bar{c})$ were computed. The relative value of the method of reference 8, as compared to the method presented herein, however, as well as the proper size for concentration differences, can be settled only by further experiment.

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