Measurement of Diffusion Coefficient Using a Closed Capillary Technique

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A new technique to determine rapidly diffusion coefficients in liquids is described. Diffusion experiments are carried out in closed capillaries constructed from scintillation material. The rate of diffusion of radioactive tracers is detected in the capillaries using a standard liquid scintillation analyzer. Solution of the Fickian diffusion equation using Laplace transforms with bias to the initial data allows diffusion coefficients to be determined in a fraction of the time taken by the traditional equilibrium method. Results of tracer diffusion experiments for tritium in water show good agreement between short time and equilibrium analyses, with the short time method requiring an experiment time 1/8th of the time of the equilibrium method.

The use of radioactive tracers is described for the *in situ* measurement of diffusion in liquids by Passiniemi et al. (1977). The advantages of these techniques are that experiments required only very small concentration gradients due to the sensitivity of the scintillation technique for determining radioactive decay and small sample volume, around 50 μL. The difficulty with the method described by Passiniemi et al. (1977) is that the equipment used is specially designed. Further, the data analysis technique uses the first-term approximation of the separation of variables solution of the Fickian diffusion equation (Eq. 1), which is only valid once the diffusional behavior is predominately exponential with time, occurring after time t'. This time t' may be prohibitively long for viscous fluid experiments.

For example, following the method of Passiniemi et al. (1977), determination of the self diffusion of water (viscosity 1 m·Pa·s) in a closed capillary takes approximately eight days. Hiss and Cussler (1973) determined for viscous Newtonian fluids that D is proportional to $\mu^{-2/3}$ implying that the experiment time required to determine the diffusion coefficient in a moderately viscous fluid, say 1 Pa·s, would take around 760 days.

In this article, a solution of the Fickian diffusion equation via Laplace transforms is used which allows an estimate of the diffusion coefficient from an experiment which requires much less time to run. Included in this analysis is a method of accounting for partial mixing of the labeled and unlabeled solutions which occurs during filling of the capillary. In addition, the equipment is designed to make use of plastic or glass scintillators that fit into standard liquid scintillation counters.

Experimental

The experimental equipment is shown in Figure 1. The tubing is constructed from scintillating plastic (Nuclear Enterprises NE102a). Teflon stoppers support the capillary in an outer glass tube, while brass caps with silicone sealant are used to seal the capillaries. The size and shape of the apparatus is designed for use with the Liquid Scintillation Analyzer (LSA). The pin on the bottom brass cap has a length equal to the depth of the teflon stopper and the capillary is filled to the bottom of the top stopper, ensuring that the diffusion path is accurately known.

To test the proposed closed capillary technique, measurements have been performed on the diffusivity of tritiated water in water. Approximately 20 μL of distilled water labeled with 2.0% vol/vol 5-m Ci/mL tritium (Amersham, U.S.A.) is placed in the lower half of the capillary which is covered with stainless steel tubing to block the radiation. The top section of the capillary is filled with unlabeled distilled water. Care is taken to ensure that no air bubbles are present and the top cap is sealed onto the top stopper.

The vial is placed in a scintillation counter (Packard Tri-Carb Liquid Scintillation Analyzer 2000CA) which has been normalized, and is counted every three hours. In order to obtain sufficient accuracy, it is necessary to count the vial for a period, Δt. In the case of water experiments this is 60 min. The temperature is maintained at 15±0.5°C. As the tracer diffuses into the upper section, the number of counts per min (CPM) is monitored by the scintillation counter. In this arrangement, the scintillation cocktail embedded in the plastic capillary does not interfere with the diffusion in the capillary. β^- particles emitted from a radioactive decay interact with

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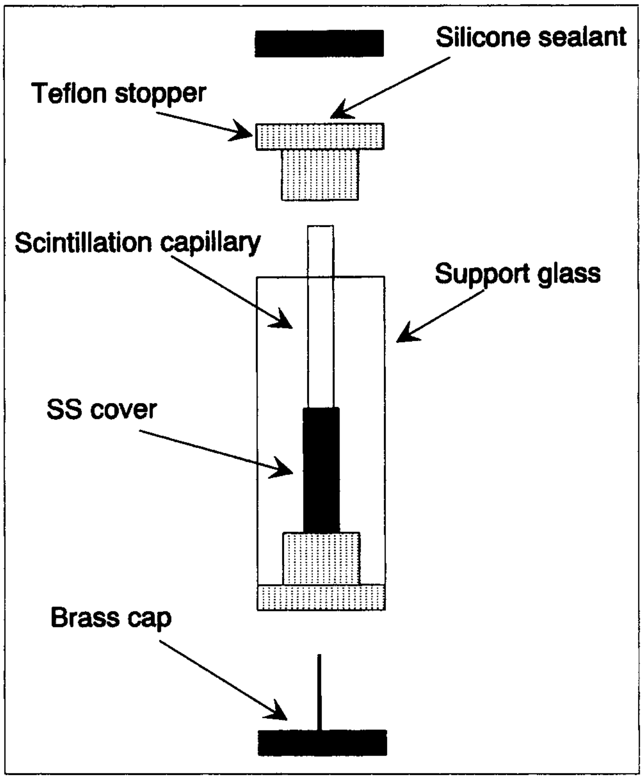

Figure 1. Experimental equipment.

scintillators in the plastic to give off light which is detected in the scintillation counter.

To allow for quenching and counting efficiencies less than one, it is standard practice in liquid scintillation counting to use a set of standards of known activity to relate CPM to decays per min (DPM) which is proportional to the quantity of the radioactive species in the exposed solution at time, t. However, in this case the concentration of the radioactive species is only varied over a small range, corresponding to a variation in activity in the measurement section of approximately 300 CPM. The amount of plastic scintillator is constant throughout the experiment. Therefore, it is assumed in this study that CPM is directly proportional to DPM and hence to the average concentration determined over the count time, Δt. Thus, by repeating this counting process many times, the progressive change in the solute CPM in the upper section of the capillary is measured, as shown in Figure 2.

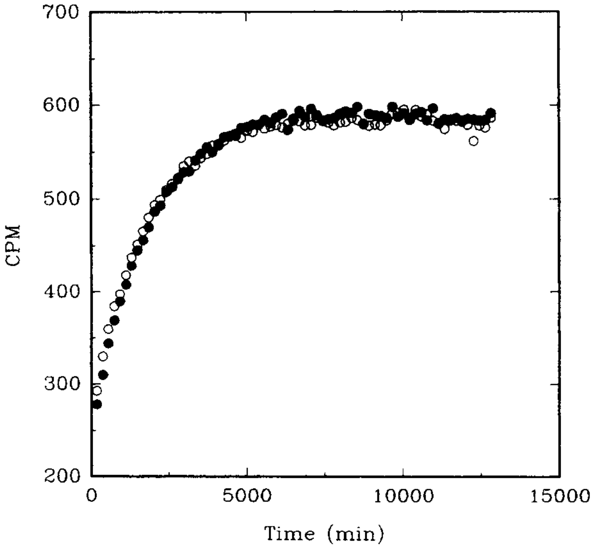

Figure 2. Typical data obtained from two repeat diffusion experiments.

Upon conclusion of the experiment CPM_0 is determined by noting counts in the top section of the capillary and then inverting the cell to allow the cover to slide to expose the "lower" region and determining the counts in that region. The total counts in the capillary are determined by relating the counts obtained in the exposed sections to the lengths exposed. This method is only suitable when $h_1 \approx h_2$ as the number of counts in the doubly exposed $(h_1 < h_2)$ or unexposed $(h_1 > h_2)$ regions should be small.

The diffusion coefficient is determined by solving the one-dimensional Fickian diffusion equation, Eq. 1, using two frames of reference and coupling the solutions of Eq. 1 at the common boundary condition:

$$\frac{\partial c(x,t)}{\partial t} = D\frac{\partial^2 c(x,t)}{\partial x^2} \tag{1}$$

Less viscous fluids, such as water, tend to mix at the interface, resulting in an intermediate region where the concentration is between 0 and C_0. Also, discrepancies between the actual interface and the boundary of the covered section can influence the diffusion coefficients calculated when using the short time solution. Accounting for these effects gives the following boundary conditions and an expression for the concentration profile in the "mixed" region (Figure 3):

Region 1: Active Section

$$\frac{\partial c(x,t)}{\partial x} = 0, \quad x = -h_1, \quad t \geq 0$$

$$c(x,t) = C_0, \quad -h_1 < x < -(\delta + \lambda), \quad t = 0 \tag{2}$$

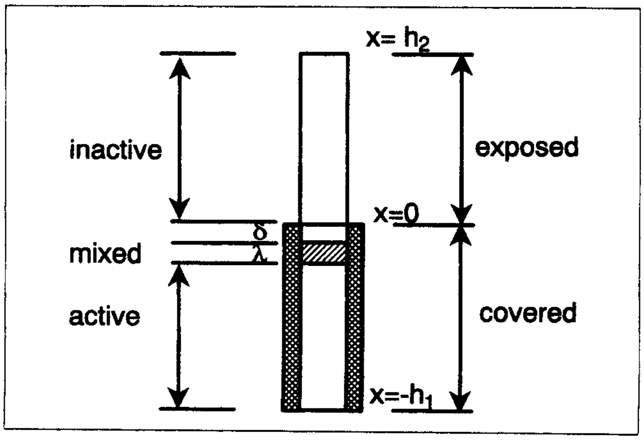

Figure 3. Boundary conditions allowing for interface shift and mixing.

Region 2: Mixed Section

$$c(x,t) = \frac{C_0}{\lambda}(-\lambda - x),\ -(\lambda+\delta) < x < -\delta,\ t=0 \qquad (3)$$

Region 3: Inactive and Exposed Section

$$\frac{\partial c(x,t)}{\partial x} = 0,\ x = h_2,\ t \geq 0$$

$$c(x,t) = 0,\ -\delta < x < h_2,\ t=0 \qquad (4)$$

Using standard techniques, (Crank, 1986) the solution of the Fickian diffusion, Eq. 1, is given by Eq. 5:

$$\int_0^{h_2} c_2(x,t)\,dx = \frac{C_0 h_2}{(h_1+h_2)}\left(h_1 - \delta - \frac{\lambda}{2}\right) + \frac{4C_0(h_1+h_2)^2}{\lambda\pi^3}\sum_{n=1}^{\infty}\frac{1}{n^3}(-1)^n e^{\frac{-n^2\pi^2 tD}{(h_1+h_2)^2}} \times \sin\frac{\left(h_1-\delta-\frac{\lambda}{2}\right)n\pi}{(h_1+h_2)}\sin\frac{\lambda n\pi}{2(h_1+h_2)}\sin\frac{-h_2 n\pi}{(h_1+h_2)} \qquad (5)$$

The integral of the concentration in the exposed section is determined, because in the scintillation counter only the total tracer population in the exposed section can be recorded.

This form of the solution is applicable at all times, but the first term approximation, (that is, truncation after $n=1$) commonly used is valid provided $t \gg h_1^2/D,\ h_2^2/D$. However, at small t, that is, $t \ll h_1^2/D,\ h_2^2/D$, Eq. 5 is not very useful, as many terms are required. It is straightforward to obtain a more useful expression at small t (Crank, 1986):

$$\int_0^{h_2} c_2(x,t)\,dx = C_0\sqrt{\frac{D}{\pi}}\,t^{1/2} - \frac{C_0}{2}\left(\delta + \frac{\lambda}{2}\right) + \ldots \qquad (6)$$

valid for

$$t \ll \frac{h_1^2}{D}, \frac{h_2^2}{D} \qquad (7)$$

Changing from the total tracer population over the exposed length to the average counts per min over the count time, CPM(t):

$$\mathrm{CPM}(t) = \frac{\alpha}{\Delta t}\int_t^{t+\Delta t} dt \int_0^{h_2} dx\, c(x,t) \qquad (8)$$

If the shielding is not present, a count rate, CPM_0, is measured. Thus, CPM_0 can be expressed in terms of the initial concentration of the tracer, C_0, as:

$$\mathrm{CPM}_0 = \alpha\left[h_1 - \left(\delta + \frac{\lambda}{2}\right)\right]C_0 \qquad (9)$$

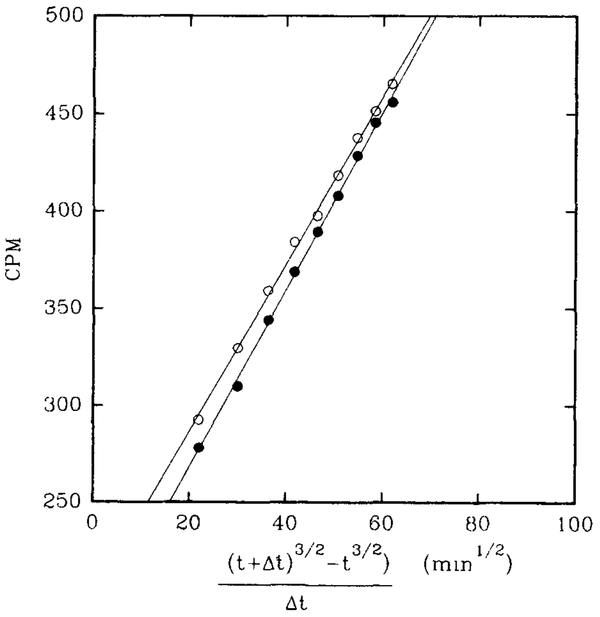

Figure 4. Plot of CPM vs. $[(t+\Delta t)^{3/2} - t^{3/2}]/\Delta t$ for two repeat runs.

and finally:

$$\mathrm{CPM} = \frac{2}{3}\frac{\mathrm{CPM}_0}{\left[h_1 - \left(\delta + \frac{\lambda}{2}\right)\right]}\sqrt{\frac{D}{\pi}}\left[\frac{(t+\Delta t)^{3/2} - t^{3/2}}{\Delta t}\right] - \frac{1}{2}\frac{\mathrm{CPM}_0\left(\delta + \frac{\lambda}{2}\right)}{\left[h_1 - \left(\delta + \frac{\lambda}{2}\right)\right]} \qquad (10)$$

From the intercept of the plot of $[(t+\Delta t)^{3/2} - t^{3/2}]/\Delta t$ vs. CPM(t) (Figure 4), $(\delta + \lambda/2)$ is obtained and is used to calculate D from the slope.

Results and Discussion

Data was analyzed using both equilibrium and short time techniques; the results are shown in Table 1.

Using the first-term approximation to the equilibrium solution of the Fickian diffusion equation (Eq. 1), the diffusion coefficient was determined using a Marquardt-Levenberg algorithm. The initial data point was neglected to avoid any error due to mixing at the interface and data was taken over a period of 200 h and used to produce the results shown in column 1 of Table 1. A typical plot is shown in Figure 2. The short time solution was found by plotting $[(t+\Delta t)^{3/2} - t^{3/2})/\Delta t]$ vs. CPM; a typical plot is shown in Figure 4 using data over the first 24 h of the experiment. The intercept (from Eq. 10) allowed the extent of mixing to be determined, and the slope gave the diffusion coefficient, which is presented in Table 1.

Only data that satisfied the criterion of "short time," (Eq. 7) were used. It was found that reliable data could be obtained in 24 h, which is a significant reduction compared to the 200 h required for the long time solution.

Table 1. Self Diffusion Coefficients of Tritiated Water at 15°C

Experiment	Equilibrium	Short Time	
	$D_T \times 10^9$ m^2/s	$D_T \times 10^9$ m^2/s	$(\delta + \lambda/2)$ cm
1	-	2.024	−0.973
2	-	2.070	−1.284
3	1.637	1.780	−0.904
4	1.706	1.742	−1.274
5	1.803	1.949	−3.059
6	-	1.809	−0.915
7	-	1.888	−1.038
8	1.689	1.803	−1.544
9	1.758	1.942	−0.952
10	-	1.945	−1.433
11	1.663	1.638	−1.099
12	1.592	1.634	−0.887
Avg.	1.693	1.852	−1.280
Error	±8.5%	±8.3%	

The results from long and short time analysis are in good agreement, despite the extent of mixing being significant. From the literature, D_T has been determined using a number of techniques and a review of these was presented by Weingärtner (1982). Using a diaphragm cell Mills (1973) found $D_T = 1.724 \pm 0.003 \times 10^9$ m^2/s, Wang et al. (1953) used the open ended capillary technique to determine $D_T = 1.83 \pm 0.055 \times 10^9$ m^2/s, and Pruppacher (1972) used a modified capillary method with an error of 1% and found $D_T = 1.953 \times 10^9$ m^2/s. Considering the errors of both the literature values and those reported here the agreement is good.

Conclusions

A new measurement technique has been developed to determine diffusion coefficients in liquids using standard liquid scintillation analyzers and extremely small volumes of liquid. Rapid experiments are possible using a solution to the diffusion equation for which the first-term approximation can be made at short time.

Acknowledgment

Support from the Australian Research Council and the Advanced Mineral Products Center is gratefully acknowledged.

Notation

$c(x,t)$ = concentration, kg/m^3
C_0 = concentration in active section at $t=0$, kg/cm^3
$c_2(x,t)$ = concentration in exposed section, $0<x<h_2$, kg/m^3
CPM = counts per min, counts/min
CPM$_0$ = counts per min in active section of capillary at $t=0$, counts/min
D = diffusion coefficient, m^2/s
h_1 = length of covered section of capillary, m
h_2 = length of exposed section of capillary, m
t = time, s
x = distance from center of capillary, m

Greek letters

α = efficiency factor for scintillation counter
δ = length of inactive liquid in covered section, m
Δt = count time, s
λ = length of mixed region in covered section, m

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Manuscript received March 16, 1993, and revision received June 3, 1993.