MASS TRANSFER EXPERIMENT

Determination of Liquid Diffusion Coefficients

FRANCISCO RUIZ BEVIÁ, MARÍA DEL MAR OLAYA
University of Alicante • Alicante, Spain

Diffusion is the process by which matter is transported from one part of a system to another as a result of random molecular motions. The rate of many mass-transfer operations is determined by molecular diffusion, so finding it is important for predicting rates of mass transfer. Diffusion in liquids and solids is a slow process, with diffusivity in liquids about 8 x 10^{-6} m/s and in solids about 2 x 10^{-9} m/s.[1]

There are many accurate methods available to measure diffusion coefficients, explained in detail in the literature,[1-3] but when we are designing a laboratory experiment for students to measure diffusion, accuracy is not as important as is visual insight into the phenomena. This paper describes a simple experimental method to determine diffusion coefficients in liquids that works well for laboratory classes.

While the theoretical background of diffusion in liquids is described in detail in many textbooks,[1-3] an introductory treatment is given here as an immediate reference. For diffusion in unsteady state and without chemical reaction, Fick's first law of diffusion is

$$\frac{\partial C_A}{\partial t} = D_{AB} \nabla^2 C_A \tag{1}$$

where D_{AB} is the diffusion coefficient for A in a stationary liquid B, C_A is the concentration of A at time t and position (x,y,z), and ∇ is the gradient operator. Solutions of the diffusion equation can be obtained for a variety of initial and boundary conditions.[1] We are going to consider diffusion in one direction (z) in a system where the diffusing substance (A) and the stationary substance (B) occupy an infinite region, and the initial state is

$$t=0 \quad \text{for} \quad z<0 \rightarrow C_A = C_{Ao} \quad \text{and for} \quad z>0 \rightarrow C_A = 0$$

Francisco Ruiz Beviá *is Professor and Head of the Chemical Engineering Department at the Alicante University (Spain). He received his PhD from Valencia University (Spain). He conducts research in phase equilibria and in holographic interferometry applied to mass transfer.*
María del Mar Olaya López *received her BS in chemistry and her PhD in chemical engineering. She is currently Assistant Professor at the University of Alicante (Spain). Her research interests include phase equilibria and polymer structure, properties, and processing.*

This can be, for example, a column of clear water resting on a column of A solution at t=0 (see Figure 1). After a time t, those molecules of A close to the interface have diffused across the column of water. The concentration of A is dependent on the position and time and can be calculated by

$$C_A(z,t) = \frac{1}{2} C_{A_0} \operatorname{erfc} \frac{z}{2\sqrt{D_{AB} t}} \tag{2}$$

where erfc(x) is the complementary error function.

Considering that erfc(0) = 1, it is clear from Eq. (2) that

$$C_A = \frac{1}{2} C_{A_0}$$

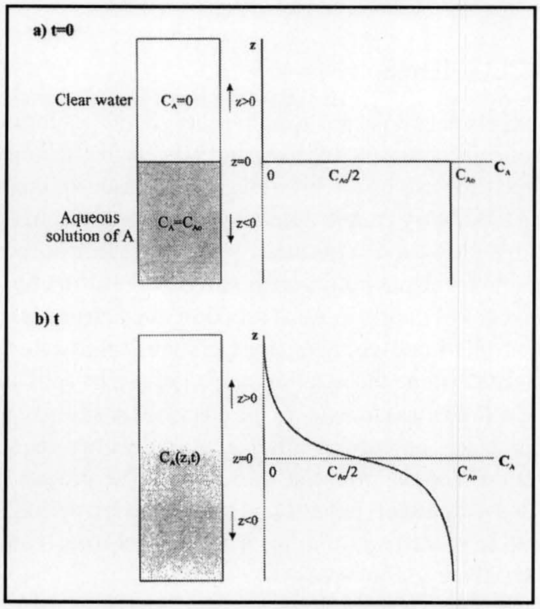

Figure 1. *Unsteady-state diffusion experiment in liquids:*
a) *at time t=0 and* ***b)*** *at time t=t.*

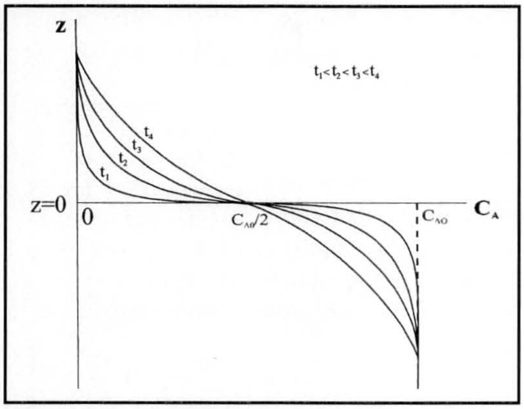

Figure 2. *Qualitative concentration profiles for different times for nonstationary diffusion experiments as predicted by Eq. (2).*

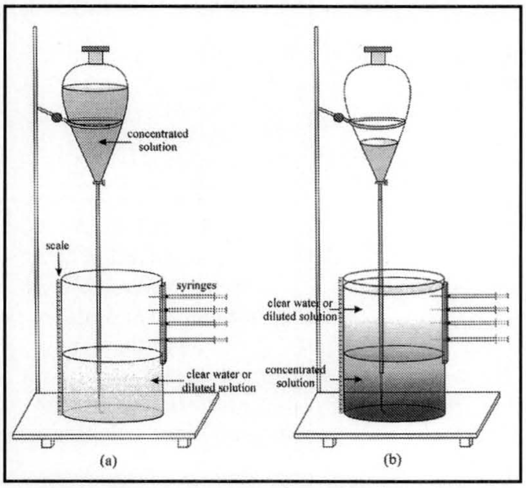

Figure 3. *Experimental method to obtain diffusion coefficients:* ***a)*** *before discharge, and* ***b)*** *after concentrated solution is discharged.*

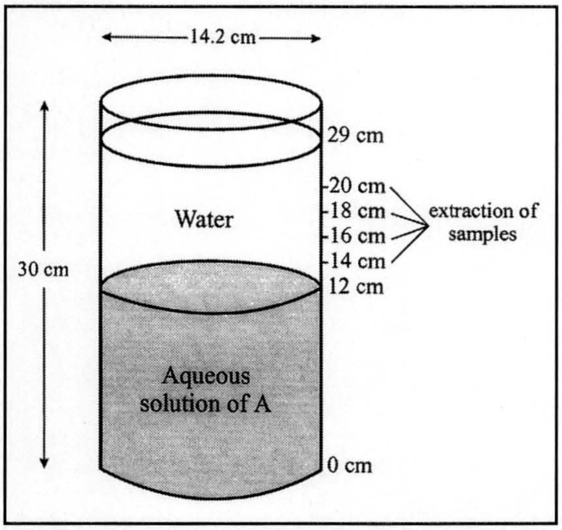

Figure 4. *Initial situation in the diffusion cell: dimensions of the cell, sample extraction points, and initial limits of the solutions.*

at z = 0 for all t > 0, even though the volumes of both solutions are not equal. This is because this model considers that both columns are infinite. Therefore, this model will be adequate only for short experiments where the concentrations at the top and the bottom of the diffusion cell do not change with time. Figure 2 shows a qualitative representation with concentration curves as a function of position and time that can be obtained using Eq. (2).

If the column of clear water is changed to a diluted solution of A, Eq. (2) becomes

$$C_A(z,t)=C_{A0,m}+\frac{1}{2}\left(C_{A0,M}-C_{A0,m}\right)\operatorname{erfc}\frac{z}{2\sqrt{D_{AB}t}} \qquad (3)$$

where $C_{A0,M}$ and $C_{A0,m}$ are the concentrations of the solute A in the more concentrated and diluted solutions, respectively.

EXPERIMENTAL PROCEDURE

The apparatus that we propose using to obtain diffusion coefficients in liquids is shown in Figure 3. It consists of

- *A poly methyl methacrylate (PMMA) diffusion cell where four syringes have been incorporated at positions where the samples will be taken out of the system.*
- *A funnel or tank with the A solution that will be discharged slowly to the bottom of the diffusion cell (which previously contains clear water or a diluted solution) through a pipe with a capillary tube in the extreme.*

The experimental method consists of the following steps:

1) Clear water or diluted solution is placed inside the diffusion cell.
2) The funnel is filled with the more-concentrated solution of A. The solution should reach the extreme of the capillary tube and no bubbles should be present.
3) This capillary tube is placed inside the diffusion cell, on the bottom of the vessel under the column of water (or the more-diluted solution).
4) The key of the funnel or tank is opened and the solution starts going out to the vessel, raising the column of water very slowly as a piston. The objective of the discharge process is to raise the water column (with a lower density) to have the system prepared in the initial conditions to begin the diffusion experiment. This process should be done carefully in order to avoid mixture of both solutions and to maintain a sharp interface between the solutions.
5) The previous process is finished when the two columns reach the desired volume. The key in the funnel is closed. In Figure 4 the initial situation in the diffusion cell is shown with dimensions and positions for sampling, in accordance with our laboratory experiment.
6) The system is maintained in this way (avoiding movement) until the experiment is finished (we consider two or three weeks).
7) Samples from each syringe are taken out every two or three days. The sample volume (5 ml) is negligible compared to the initial volume.
8) Samples are analyzed, using an adequate technique for the solute used, to obtain concentrations.
9) When a set of concentrations as a function of position and time is obtained, Eq. (2) or (3) is used to calculate the experimental diffusion coefficient D_{AB}. This calculation should be done by optimization. A spreadsheet can be prepared to perform nonlinear regression with D_{AB} as the parameter that should be optimized to minimize the objective function

$$\text{O.F.}=\sum_{n}\left(C_{A(\text{exp})}-C_{A(\text{cal})}\right)^{2} \tag{4}$$

where $C_{A(exp)}$ is the experimental concentration of A obtained in each position of the diffusion cell, and $C_{A(cal)}$ is the concentration calculated using Eq. (2) or (3).

Two experiments are proposed using the same apparatus:

- *Diffusion of the electrolyte $CuSO_4$*
- *Diffusion of ethylene glycol*

The first of these experiments was selected because students can see how the color, concentrated in the bottom of the bottle at t = 0 slowly spreads through the diffusion cell. Concentrations of $CuSO_4$ as a function of position and time are obtained using UV-spectroscopy (Jenway 6300 spectrophotometer). The wavelength selected was 800 nm. Due to the small volume of sample available, microcuvettes were used. Students prepare standards with known concentrations of $CuSO_4$ to obtain the calibration curve.

The experiment with ethylene glycol was chosen to introduce gas chromatography as an analytical method to obtain the concentration as a function of position and time. The apparatus is a Shimadzu GC-14A with an AOC-14 Auto Injector and an electronic integrator C-R64 Chromatopac. The column was a 2 m x 1/8" Chromosorb 102. The column temperature was 180°C, and detection was carried out by thermal conductivity (TCD) if water and ethylene glycol were to be analyzed to check mass balances or by flame ionization detector (FID) if only ethylene glycol was analyzed. The helium flow rate was 30 cm^3/min. The internal standard method was applied for the quantitative analysis, using ethanol as the standard.

RESULTS AND DISCUSSION

Diffusion of $CuSO_4$ • In Table 1 the concentrations of $CuSO_4$ as a function of position and time obtained in the diffusion experiment for $CuSO_4$ are presented. Initial conditions were a column of clear water resting on a column of an aqueous solution of $CuSO_4$ (see Figure 4). These experimental results are used to obtain the diffusion coefficient for $CuSO_4$

$$D_{CuSO_4}=4.9\times10^{-6}\,\text{cm}^2/\text{s} \tag{5}$$

Figure 5 shows experimental points and calculated curves with this diffusion coefficient. Diffusion coefficients are strongly concentration-dependent; therefore, comparisons should be done for similar values of initial concentration. In the literature we found a paper[4] where aqueous diffusion coefficients for $CuSO_4$ are determined for different concentrations using a diaphragm cell technique (see Table 2). The initial concentration that we have used in the experiment is 60 g/L. Therefore, according to these authors, a value between 4.86 x 10^{-6} cm^2/s and 4.95 x 10^{-6} cm^2/s should be obtained for the concentration that has been used in the laboratory, which is consistent with our result.

Diffusion of ethylene glycol • The concentrations obtained for the ethylene glycol experiment are shown in Table 3. Initial conditions for the diffusion experiment with ethylene glycol are two aqueous solutions of ethylene glycol, 5 and 20% mass. For this experiment, the initial interface (z=0) was placed at 13.5 cm high in the diffusion cell. These experimental results are used to obtain the diffusion coefficient for ethylene glycol by optimization using Eq. (3). The diffusion

TABLE 2
Diffusion coefficients at 25°C for copper sulfate in water obtained by the diaphragm cell technique.[4]

Conc. $CuSO_4$ (g/L)	*10^6 D_{AB} (cm^2/s)*
0	8.50
16	5.64
32	5.37
48	5.23
56	4.95
64	4.86
96	4.45
128	4.24
159	4.07
191	3.95
224 (saturation)	3.83

TABLE 1
Concentration of $CuSO_4$ as a Function of Position and Time (z=0 at the initial interface between the two liquid columns).

Initial concentrations: Concentrated solution is 60 g/L and diluted solution is clear water

time (h)	*z (cm)*	*Conc. $CuSO_4$ (g/L)*
46	8	0.00
	6	0.00
	4	0.00
	2	1.96
70	8	0.00
	6	0.00
	4	0.00
	2	3.86
95	8	0.00
	6	0.00
	4	1.02
	2	8.13
120	8	0.00
	6	0.03
	4	1.58
	2	9.33
143	8	0.06
	6	0.22
	4	2.15
	2	10.2
174	8	0.15
	6	0.24
	4	2.78
	2	11.2
193	8	0.48
	6	0.52
	4	3.25
	2	12.0
215	8	0.50
	6	1.04
	4	4.65
	2	13.5

TABLE 3
Concentration of ethylene glycol (EG) as a function of position and time (z=0 at the initial interface between the two liquid columns).

Initial concentrations: concentrated solution is 20% mass and diluted solution is 5% mass

time (h)	*z (cm)*	*Conc. EG (% mass)*
21	6.5	5.00
	4.5	5.01
	2.5	5.21
	0.5	9.83
40	6.5	5.06
	4.5	5.09
	2.5	5.94
	0.5	10.52
71	6.5	5.12
	4.5	5.35
	2.5	6.95
	0.5	10.93
158	6.5	5.33
	4.5	6.14
	2.5	8.16
	0.5	11.29
192	6.5	5.51
	4.5	6.59
	2.5	8.47
	0.5	11.61

coefficient obtained is

$$D_{\text{ethylene glycol}} = 11 \times 10^{-6}\,\text{cm}^2/\text{s} \qquad (6)$$

Figure 6 shows the experimental points and calculated curves with this diffusion coefficient. Fernández-Sempere, *et al.*,[5] determined the diffusion coefficient for aqueous solutions of ethylene glycol at different initial concentrations and 25°C using the holographic interferometric technique. Table 4 shows the results published by these authors. The result that our students obtained in the laboratory using a much more rudimentary or basic technique is consistent with the literature data.

TABLE 4
Diffusion coefficients at 25°C for ethylene glycol (EG) in water obtained using holographic interferometry.[5]

W_{EG} (% mass)	$10^6 D_{AB}$ (cm²/s)
5.0	11.35
22.5	9.33
40.0	7.82
62.7	5.59
99.2	2.70

The reproducibility of the obtained diffusion coefficients is difficult to evaluate, but we can give an approximate value of 10% when results obtained using a good laboratory practice are considered.

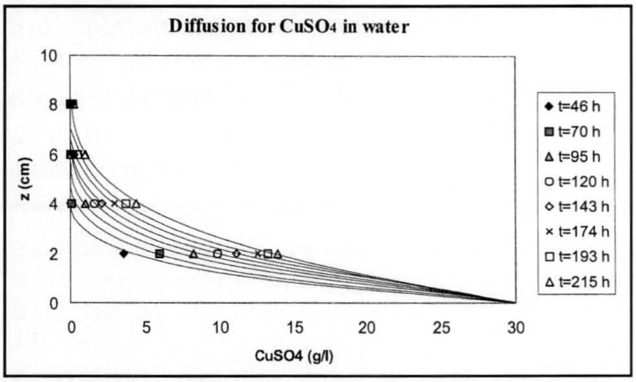

Figure 5. *Experimental and calculated (—) concentrations profiles at different times obtained for the experiment with Copper Sulfate (curves calculated for the experimental value D=4.9 x 10⁻⁶ cm²/s and Eq. (2).*

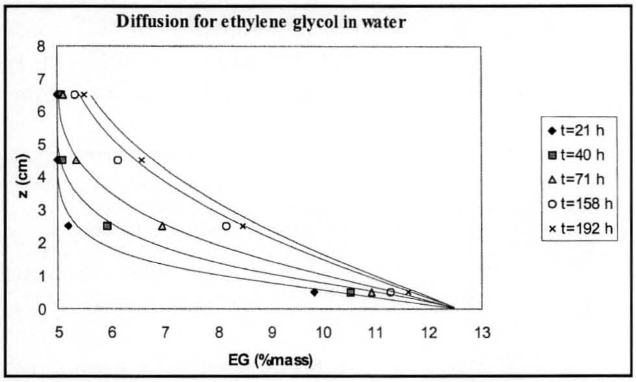

Figure 6. *Experimental and calculated (—) concentrations profiles at different times obtained for the experiment with ethylene glycol (curves calculated for the experimental value D=11 x 10⁻⁶ cm²/s and Eq. (3).*

CONCLUSIONS

We have described a simple laboratory experiment to introduce diffusion in liquids to students. We designed a diffusion cell (made of poly methyl methacrylate) to obtain diffusion coefficients in liquids; Equations (2) and (3) can be used to obtain the experimental diffusion coefficients for $CuSO_4$ and ethylene glycol, respectively, when the concentration as a function of position and time is previously obtained in diffusion experiments using the diffusion cell and the methodology proposed; and to validate the diffusion coefficients obtained in this study, comparisons with the values previously determined by other authors using high accuracy techniques have been made. The results show that it is possible to obtain good results for the diffusion coefficients using the methodology proposed in this paper.

GENERAL REMARKS

The experiments described in this paper are integrated in a group of transport phenomena laboratory classes for second-year students. The objective is to provide students with clear insight to the phenomena explained in the classroom by using simple experiments. One drawback is that several weeks are required, but most of the students feel that this laboratory helps them understand diffusion phenomena and how a diffusion coefficient can be evaluated from data and by using a model. The experiments on unsteady-state diffusion in liquids are completed with another in steady state (vapor diffusion), described by Nirdosh, *et al.*[6]

NOMENCLATURE

C_A	concentration of A as a function of position and time
D_{AB}	diffusion coefficient for A in a stationary liquid B
erfc(x)	complementary error function
O.F.	objective function
t	time
z	direction for diffusion

Subscripts

o	initial
M	concentrated solution
m	diluted solution
exp	experimental
cal	calculated

Superscripts

∞	infinite dilution

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