A SIMPLE REFRACTION EXPERIMENT
for Probing Diffusion in Ternary Mixtures

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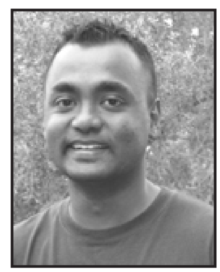
Diffusion in mixtures is one of the most important molecular transport processes in the understanding of mass transfer operations in chemical engineering,[1, 2] and it is the fundamental phenomenon underlying chemical processes ranging from mass transport in living cells and separations to corrosion. Consequently, reports in the literature on chemical education have frequently focused on simple experimental demonstrations for diffusion in liquids.[3-11] Here, we describe an experiment based on Wiener's method[12] for measuring one-dimensional diffusion in ternary aqueous solutions and incorporate several new features that provide an opportunity for students to practice computer calculations.

The method relies on using refraction of laser light from the concentration gradient near a solvent-solution interface. Past reports[7, 10, 11] have used this optical technique for undergraduate-level demonstrations of diffusion in a physical chemistry laboratory. In these past reports, diffusion of single solutes such as KCl or CsCl in liquids such as water or glycerol was examined experimentally to demonstrate one-dimensional diffusion in binary mixtures as well as the impact of solvent viscosity on the diffusion coefficient. We show that the optical technique described in literature can be also used to analyze diffusion in ternary mixtures of simple species, namely KCl and sucrose in water.

In the experiment described here, we chose mixtures of KCl and sucrose but the method can be extended to other solutes. In other work, we have explored the application of this method to solutions of linear and globular polymers.[13] KCl and sucrose, in addition to being inexpensive, have various other advantages. For example, well-established literature exists on diffusion studies of these chemicals in water.[14-17] The rapid diffusion (~90 minutes) of both species makes them conducive for a laboratory session, and the materials are nontoxic for students. Furthermore, transparent solutions with a stable solution-water interface can be easily prepared for both KCl and sucrose.

From an educational perspective, the laboratory experiment described in this paper has many useful features. It demonstrates to students how a molecular scale process manifests



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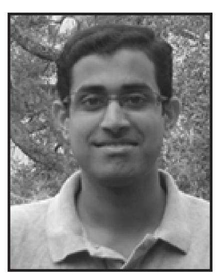

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itself into macroscopic observables and provides them a visual display of the time evolution of the concentration profile (Figure 1), which is governed by the diffusion equation in one dimension.

$$\frac{\partial c_A}{\partial t} = D_{AB} \frac{\partial^2 c_A}{\partial z^2} \qquad (1)$$

New elements are incorporated in the implementation of the experiment to give students' practice in skills such as digital capture and digitization of experimental data, plotting and baseline correction, familiarity with simple statistical concepts such as Gaussian distributions, and finally multivariable, nonlinear data fitting using common software such as Excel™. The experiment can also be extended to reinforce a variety of concepts ranging from simple statistical and error analysis to more advanced concepts of mass transfer such as the importance of cross-diffusional contributions in mixtures. Thus, the experiment is suitable for incorporation into the curriculum at various stages depending on the emphasis placed on the different aspects of the experiment. For example, it can be used as an introductory hands-on learning opportunity at a freshman or sophomore level in chemical engineering or related fields of environmental engineering, biochemical engineering, physics, and physical chemistry to emphasize the mathematical and computational aspects of the experiment with lesser emphasis on diffusion theory. Alternatively, it can be incorporated in a chemical engineering laboratory at a junior or senior level in coordination with the typical course on mass transfer theory that covers topics of diffusion in binary and ternary systems.

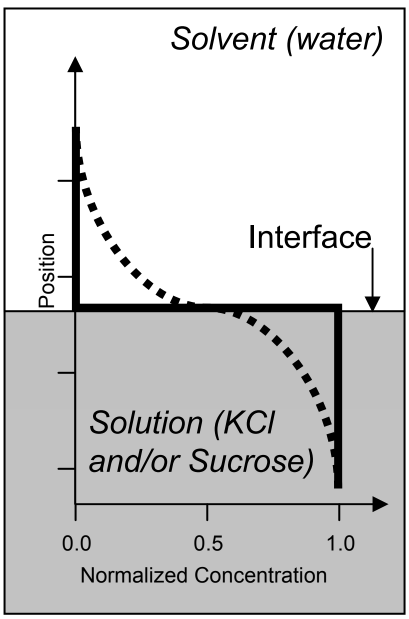


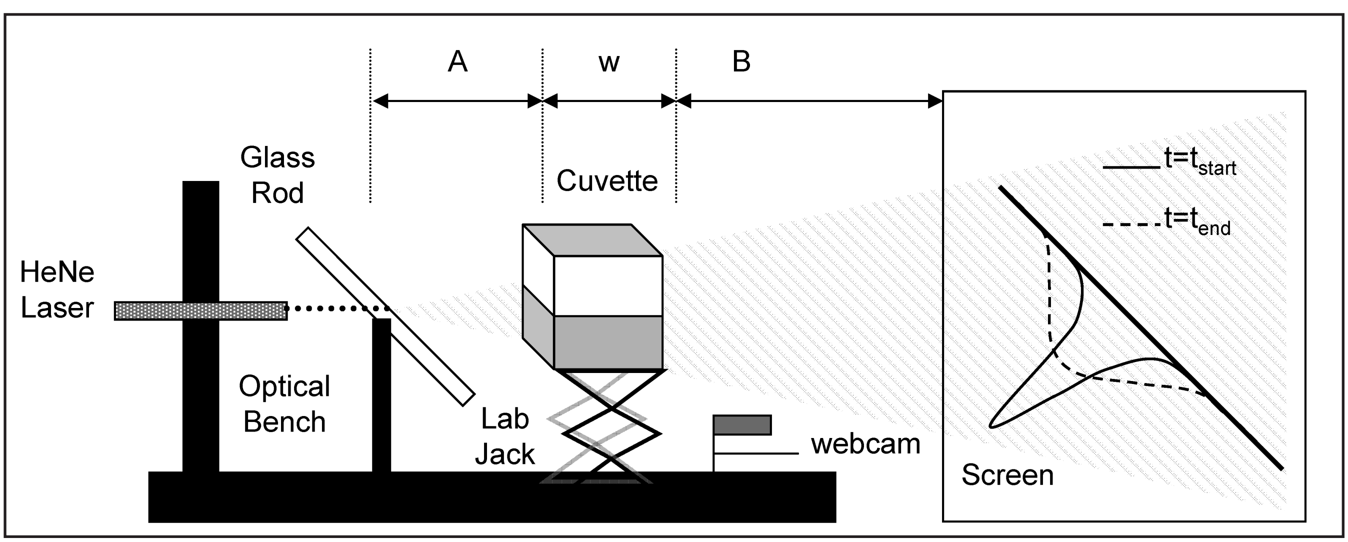
Figure 1. (right) *Schematic representation of initial step concentration gradient (solid line) and concentration profile as diffusion of solute occurs across the interface (dashed line).*

LABORATORY DESCRIPTION

Experimental Plan

A schematic of the experimental setup is shown in Figure 2. A 12"×18" aluminum breadboard (MB1218 from Thorlabs, Newton, NJ: cost~$200) was used as the platform. The various components shown in Figure 2 could be fixed to the breadboard using the threaded holes, which is convenient as it makes the whole assembly portable. An inexpensive alternative is to use any flat surface such as a table or countertop. A 5 mW laser diode module (31-0508 from Coherent Inc., Wilsonville, OR: cost~$180) was held using a laboratory stand and clamp. It was fanned through a commonly available laboratory glass rod (OD=3mm) to create a thin diagonal band of laser light at 45 degrees to the horizontal to scan several depths in the cuvette simultaneously. We found that a laser leveler readily available from home improvement stores can be a reasonable inexpensive substitute to the laser diode. As a safety measure, students were explicitly warned to avoid direct eye contact with the laser beam. The distances A and B shown in Figure 2 were adjustable and could be used to manipulate the magnification of the projected optical curve on the screen.

Figure 2. (below) *Schematic representation of experimental arrangement and the optical deflection curve.*



In our setup, the distances A and B were approximately 13 cm and 50 cm, respectively. A rectangular refraction cuvette (09417107 from Cynmar, Carlinville, IL: cost ~$5) measuring 60×30×62mm was initially half-filled with a solution of KCl and/or sucrose purchased from Fisher Scientific. De-ionized water used in experiments was obtained from an EasyPure UV system (Barnstead, IA). A 0.2μm filter in this system removed particulate matter. The ternary solutions studied contained a total of 10wt% solute in the following ratios: (A) 25% KCl, 75% sucrose; (B) 50% KCl, 50% sucrose; (C) 75% KCL, 25% sucrose. In addition, experiments were also performed with binary mixtures containing 10wt% of either KCl or sucrose.

Initially, the cuvette was raised or lowered using a laboratory jack until the air-solution interface (marked by a discontinuity) could be located on the screen. The experiment was carried out by carefully pouring the solvent (water) upon the aqueous mixture (KCl and/or sucrose) in the cuvette to create a sharp boundary (solid line in Figure 1). The diffusion of the solute molecules from concentrated solution into the water phase with time leads to a decrease in the sharpness of the interface (dashed line in Figure 1). As a consequence, the refractive index gradient at the boundary changed with time and a skewed Gaussian curve developed on the screen as the beam traversed the mixture-water interface. Over time, diffusion of the solute caused the optical curve to become broader and smaller in peak height. The optical trace was projected on a screen (a box covered with blank paper or graph paper) and was photographed using a digital Web camera (Rosewill RCM-32301 from Newegg, Whittier, CA: cost ~ $30) at regular intervals of time. A free software (Automouseclicker18, Version 2.10) allowed automatic image capture with the Web camera at pre-determined intervals by clicking the capture button for the camera.

THEORY

At any particular time during the diffusion process, the gradient in the concentration ($\partial c/\partial x$) near the interface results in a gradient in the refractive index ($\partial n/\partial x$). For binary mixtures of a single solute species in a solvent this gradient is best described by the Gaussian function[7]:

$$\frac{\partial n}{\partial x} = \frac{\Delta n_o}{\sqrt{4\pi D\left(t - t_0\right)}} \exp\left(-\frac{\left(x - x_0\right)^2}{4D\left(t - t_0\right)}\right) \qquad (2)$$

Here Δn_o represents the difference in the refractive index contrast between the aqueous solution of the solute (KCl or

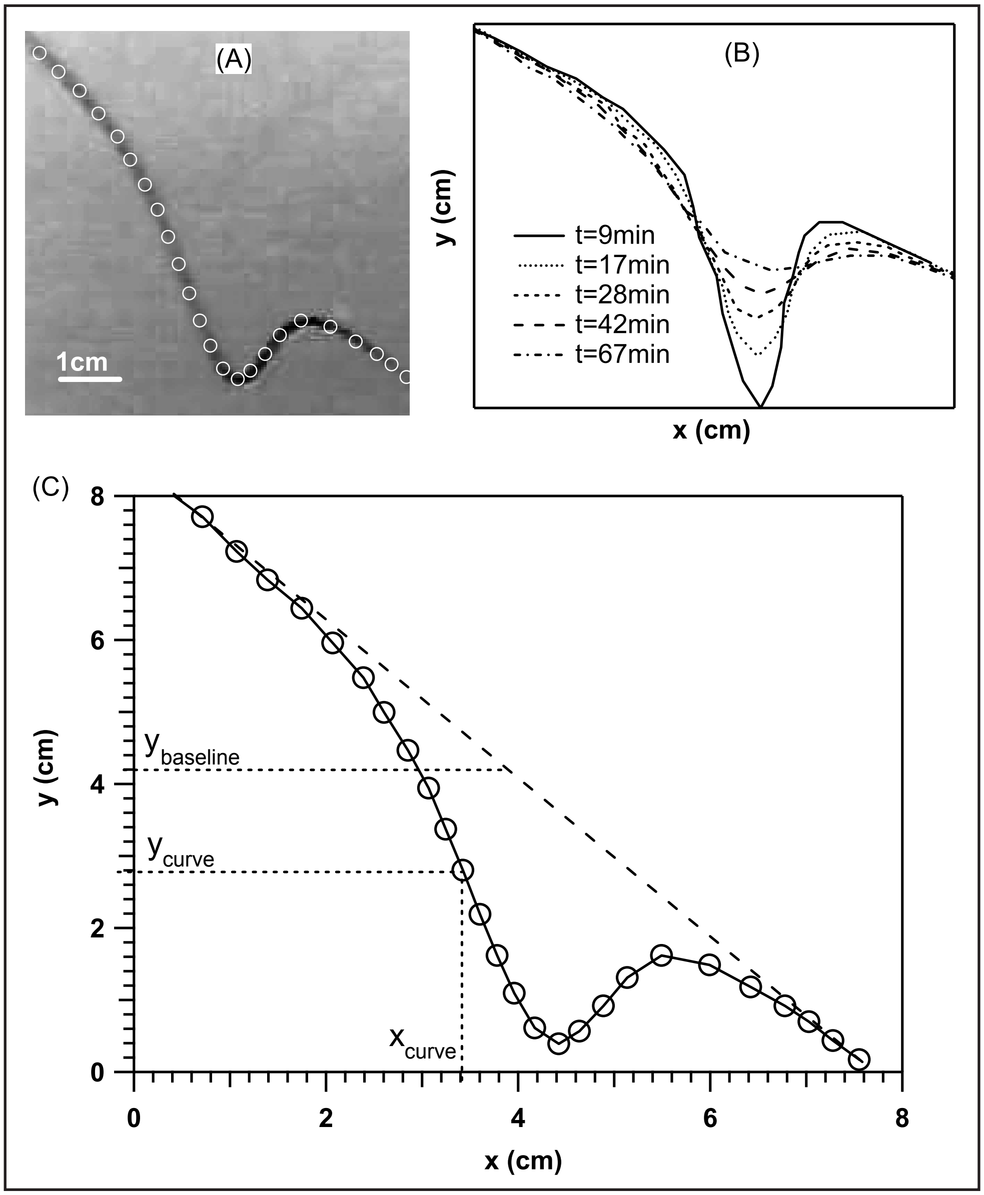


Figure 3. *(A) Image of the optical deflection curve illustrating the digitization procedure. (B) Digitized curves at different times. (C) Plot illustrating the baseline correction procedure.*

sucrose) and water at the initial time (t_0). The value of Δn_o depends on the initial weight fraction of the solute and is typically available in literature[19] or can be measured using a refractometer. D is the diffusion coefficient of the solute species.

In the case of ternary mixtures of two species α and β, we used a simplified extension of Eq. (2) for the overall gradient in refractive index.

$$\frac{\partial n}{\partial x}=\frac{\Delta n_{o\alpha}z_\alpha}{\sqrt{4\pi D_\alpha\left(t-t_0\right)}}\exp\left(-\frac{\left(x-x_0\right)^2}{4D_\alpha\left(t-t_0\right)}\right)+\frac{\Delta n_{o\beta}z_\beta}{\sqrt{4\pi D_\beta\left(t-t_0\right)}}\exp\left(-\frac{\left(x-x_0\right)^2}{4D_\beta\left(t-t_0\right)}\right)\qquad(3)$$

where the initial refractive index gradients ($\Delta n_{o\alpha}$, $\Delta n_{o\beta}$) for each species are scaled by the relative composition in solution using fractions (z_α, z_β). It should be noted that the implicit assumption in Eq. (3) is that the individual species in the mixture diffuse independently of each other. The non-zero contribution of cross-diffusional terms in multi-component mixtures is well known in research literature.[15-17, 20-22] Neglecting cross-term diffusion coefficients is reasonable within the context of an undergraduate laboratory experiment, however. This simplifying assumption keeps the data analysis simple and introduces relatively small error for the case of 10wt% total solute concentration.

DATA ANALYSIS AND RESULTS

Figure 3A shows a typical optical deflection projected on the screen. As indicated in the figure, by selecting points along the deflection curve, the experimental data can be digitized with respect to an arbitrary origin. Use of digitizing software provides an opportunity for students to become proficient at extracting data from scientific charts and plots, which is a skill that can also be useful in other contexts when students need to perform data analysis using published literature. Digitizing software widely available from the World Wide Web can be used (*e.g.*, shareware license products such as Datathief™, Grab It! Graph Digitizer™, Graph Digitizer Scout™ or open source products such as Engauge Digitizer). The use of this software typically requires importing the image file obtained from the Web camera, defining the origin and maximum values for x- and y- axes using the software interface, and finally obtaining the coordinates via mouse-click at different points along the deflection curve. The software captures the location of each mouse-click and provides a table of coordinates that can be imported and analyzed in spreadsheet or data-fitting software. As an alternative to digitization with software, coordinates can be read from an image of the deflection curve superimposed on a graph paper and recorded into a spreadsheet. This approach rapidly becomes laborious, however, when several curves have to be analyzed and also does not promote the use of computational tools.

Figure 3B shows a collection of the digitized curves at various times during the diffusion process demonstrating the broadening of the optical deflection curve with decreasing peak height. The skewed nature of the curve is corrected by subtracting the linear baseline from each point (Figure 3C) and plotting $y(=|y_{curve}-y_{baseline}|)$ vs. x ($=x_{curve}$). Since the y-coordinate is directly proportional to the refractive index gradient, Eq. (2) modified with scaling constants K_1 and K_2 describes the dependence of y on position and time as

$$y\left(x,t\right)=K_1\frac{\partial n}{\partial x}=\frac{K_1\Delta n_o}{\sqrt{4\pi D\left(t-t_0\right)}}\exp\left(-\frac{K_2\left(x-x_0\right)^2}{4D\left(t-t_0\right)}\right)\qquad(4)$$

K_1 and K_2 are experimental constants and incorporate the magnification of the optical deflection via distances A and B (Figure 2) and the refraction of the laser light by the acrylate cuvette wall.

Use of digitizing software provides an opportunity for students to become proficient at extracting data from scientific charts and plots, which is a skill that can also be useful in other contexts.

Prior to characterizing the ternary systems, the scaling factors K_1 and K_2 were determined experimentally using only KCl in water (in an undergraduate laboratory, this step may be completed beforehand by a teaching assistant). Data was collected using 10%, 15%, and 23% solutions of KCl. For each solution, the value of Δn_o was taken from literature and Eq. (4) was used to fit the y(x,t) data as a function of both variables for a common set of parameters K_1, K_2, x_0, t_0, and D_{KCl} using least squares fitting in Excel™ using the Solver add-in. The average K_1 and K_2 values of these runs were used as constants in all further experimental studies. As a check, the binary diffusivity of sucrose in 10% solution in water was also measured. Table 1 shows that there is a good agreement between the measured binary diffusivity values for KCl and sucrose with those found in literature.

In the case of ternary mixtures of KCl-sucrose-water, the total solute concentration was held constant at 10wt% and relative ratio of KCl and sucrose (z_α:z_β) in the solution was

TABLE 1

Substance	D(cm^2/s) (from fit)	D(cm^2/s) (from literature[17])
KCl[a]	1.81×10^{-5}	1.87×10^{-5}
Sucrose[b]	4.45×10^{-6}	4.77×10^{-6}

[a] $n_o(KCl) = 1.215\times10^{-4}c_o(g/L)+1.3334$
[b] $n_o(sucrose) = 1.601\times10^{-4}c_o(g/L)+1.3318$
using literature data[19]

varied (0.25:0.75, 0.5:0.5, 0.75:0.25). From the deflection curves obtained (Figure 4) for each solution, the relative fractions (y_α,y_β) of the individual solutes were obtained using a fit to Eq. (5).

$$y(x,t) = K_1 \frac{\partial n}{\partial x} = \frac{K_1 \Delta n_{o\alpha} z_\alpha}{\sqrt{4\pi D_\alpha (t-t_0)}} \exp\left(-\frac{K_2 (x-x_0)^2}{4D_\alpha (t-t_0)}\right) + \frac{K_1 \Delta n_{o\beta} z_\beta}{\sqrt{4\pi D_\beta (t-t_0)}} \exp\left(-\frac{K_2 (x-x_0)^2}{4D_\beta (t-t_0)}\right) \quad (5)$$

During this regression of the experimental data, the diffusivity and the refractive index increment (Δn_o,D) were held constant for both species while the parameters (z_α, z_β, x_0, and t_0) were changed. The optical curve at several different times was regressed using least-squares fitting in Microsoft Excel™ using the Solver add-in (illustrative worksheets are available at <http://www.eng.usf.edu/~vkgupta/diffusion.html>). From Table 2, we can see that the predicted values of relative ratios of the individual solutes agree quite well with the known solution concentration.

SUMMARY

The experimental method outlined above offers a rapid, visually instructive, and easy method for studying diffusion. It also functions as a pedagogical tool for practicing skills such as data acquisition, graphing, and regression using common software such as Excel™. The laboratory experiment reinforces concepts in chemical sciences such as molecular basis of macroscopic properties and diffusional mass transfer alongside mathematical concepts of partial differential diffusion equation, the Gaussian form of the concentration gradient, and multivariable functions. Aspects such as error analysis of the data can be incorporated by having the students consider consequences of not choosing sufficient points or sufficient care during digitization or using only a few time intervals. Although we assumed that the cross-term diffusivities were not significant, the experiment outlined above can be extended to higher (>10%) weight fractions of KCl/sucrose mixtures where the cross-term diffusivities do become important and predicted relative compositions for the solutes begin to deviate significantly from solution conditions. An investigation in this direction could then easily form the basis of mini-projects for student teams.

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TABLE 2

Composition ratio in a 10% solution of KCl and Sucrose	Composition ratio from fit	
KCl:Sucrose	z_{KCl}	$z_{sucrose}$
0.75:0.25	0.72	0.28
0.50:0.50	0.52	0.48
0.25:0.75	0.23	0.77

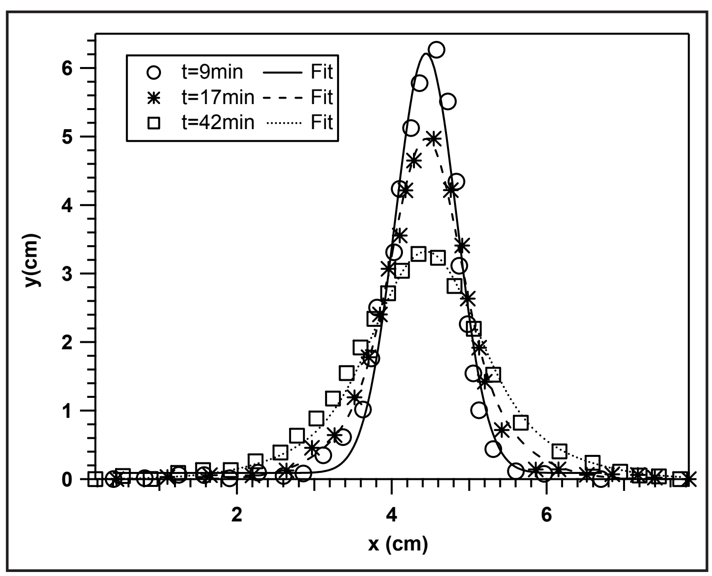

Figure 4. *Experimental data with fit using Eq. (5).*

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