MICRO-FLUIDIC DIFFUSION COEFFICIENT MEASUREMENT

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Abstract

A new method for diffusion coefficient measurement applicable to micro-fluidics is presented. The method utilizes an analytical model describing laminar dispersion in rectangular micro-channels. The method was verified through measurement of fluorescein diffusivity in water and aqueous polymer solutions of differing concentration. The diffusivity of fluorescein was measured as $0.64 \times 10^{-9}\mathrm{m}^2/\mathrm{s}$ in water, $0.49 \times 10^{-9}\mathrm{m}^2/\mathrm{s}$ in the 4 gm/dl dextran solution and $0.38 \times 10^{-9}\mathrm{m}^2/\mathrm{s}$ in the 8 gm/dl dextran solution.

Keywords: diffusion coefficient, dextran, fluorescein, dispersion

1. Introduction

The goal of μTAS is to perform chemical analysis on small volume samples [1]. A major application area of μTAS involves biological samples. Biological samples can be characterized as polymer solutions in terms of their mass transport and rheological properties [7]. The presence of biological constituents or polymers results in diffusivities that may not be predicted *a priori*. At scales typical of μTAS, fluid flow is laminar and constituents mix via diffusion. Therefore in order to design μTAS systems for use with complex biological samples the diffusivity of constituents of interest in these samples must be known.

A new method for measuring constituent diffusivities in complex fluids is presented. The new method minimizes sample volume and has the potential to measure diffusivity in opaque solutions. The method has advantages over methods such as a diaphragm cell [2] in that no membrane is required and flow is continuous. The method also has advantages over Taylor dispersion [3] and SPLITT fractionation [4] in that the measurement is made in a much shorter channel.

2. Theory

An analytical model derived from the species conservation equation was used in this diffusion coefficient measurement method. Concentration distributions calculated using this model are equivalent to those calculated using other analytical solutions that appear in the literature [1]. The solution expresses constituent concentration distributions in a rectangular channel for the case where convection is the dominant mode of transport along the channel and diffusion is the dominant mode of transport across the channel. The solution is parametric in terms of the Peclet number $\mathrm{Pe} = Uh/D$, where U is the average channel velocity, h is half the channel dimension in the diffusion direction, and D is the diffusivity of the constituent of interest in the liquid solution of interest. The

Peclet number is the ratio of mass transport by convection along the channel to mass transport by diffusion across the channel.

The model is applied to flow in a T-channel in which a sample fluid containing a constituent of interest flows in the channel with a mixing stream that does not contain the constituent of interest. The form of the analytical solution used assumes that both streams are identical, except for the presence of the diffusing constituent in only one stream entering the T-channel. Thus a single Peclet number characterizes dispersion (combined convection and diffusion) in both streams. The particular form of the analytical solution used assumes equal flow rates in each stream. Therefore the interface between the two streams is at the center of the channel. The form of the analytical solutions used is:

$$\gamma(\frac{x}{h},\frac{z}{h}) = \sum_{n=1}^{\infty} \frac{-2}{\pi\ (2n-1)} \exp\left[-\left(\frac{\pi\ (2n-1)}{2}\right)^2 \frac{x}{h\ Pe}\right]\ \sin\left[\frac{(2n-1)}{2}\ \frac{\pi\ z}{h}\right], \quad (1)$$

where x and z are the dimensions along and across the channel respectively, and γ is the non-dimensional concentration,

$$\gamma = \frac{c - c_{eq}}{c_{20}}, \quad (2)$$

c is the concentration, c_{eq} is the equilibrium (fully mixed) concentration, and c_{20} is the entering concentration in the sample stream. The origin is at the center of the channel where the two streams first meet. Details of this derivation for the more general case where a different Peclet number applies in each stream are contained in [5].

3. Experimental

The method was used to measure the diffusion coefficient of fluorescein in water and in two aqueous dextran solutions. Concentrations of 4 gm/dl and 8 gm/dl of MW 70000 dextran were used to create the two aqueous polymer solutions. The diffusivity of fluorescein in the two dextran solutions was effected by the presence of the large dextran molecules.

The demonstration experiments utilized a T-channel to bring the sample stream containing fluorescein into contact with the mixing stream that did not contain fluorescein. The T-channel cross-section was approximately 400 μm by 50 μm, and was manufactured using wet anisotropic etch. The flow rate for each input stream was controlled using syringe pumps (Kloehne Co. Ltd, Las Vegas Nevada). Flow rates of 9 nl/s and 20 nl/s in each stream were used.

Images of fluid filled micro-channels at and just downstream of the junction of the two input legs of the T-channel were obtained through a 2.5X objective Zeiss ICM 405 Inverted Microscope (Zeiss Germany) equipped with a fluorescent filter set appropriate for fluorescein (480nm excitation and 510nm capturing). A charge coupled device (CCD) camera (AIMS Technology, Japan) and frame capturing software (Apple Computer Inc., Cupertino California) were used to collect image data. The captured color image was converted to TIFF format with Adobe Photoshop (Adobe, San Jose California). Figure 1 shows a typical captured image. The captured color image was converted into red, green, and blue spectra intensities using NIH image (National Institutes of Health, Atlanta Georgia). The green spectra intensity was directly proportional to fluorescein concentration. Calibration was done by normalizing green spectra intensity across the

channel to intensity at locations of known concentration, plots of non-dimensional concentration were created (Fig. 2).

The analytical model was then used to determine the value of $x/h\ Pe$ that best matched the measured concentration distribution at different values of x along the channel. A least squares technique was used to determine the best match to within 0.002 $x/h\ Pe$. A least squares linear curve fit of this data allows one to calculate the slope of these curves (Fig. 3). The inverse of the slope of these curves is the Peclet number. The Peclet number was then used to calculate the diffusivity of fluorescein in all 3 solutions.

$$D = \frac{U\ h}{Pe} = \frac{Q\ h}{2\ h\ d\ Pe} = \frac{Q}{2\ d\ Pe}, \tag{3}$$

where d is the channel depth, and Q is the flow rate.

4. Results and Discussion

Using the technique described above the diffusivity of fluorescein in water was measured as $0.64 \times 10^{-9}\mathrm{m}^2/\mathrm{s}$ at the 9 nl/s flow rate and $0.66 \times 10^{-9}\mathrm{m}^2/\mathrm{s}$ at the 20 nl/s flow rate. These values compare favorably with values reported in the literature that range from 0.5 to $0.6 \times 10^{-9}\mathrm{m}^2/\mathrm{s}$ [7].

The effect of dextran in solution on fluorescein diffusivity is shown in Fig. 4. The diffusivity falls with increasing dextran concentration. Figure 4 also includes data from the literature [6]. In [6] the diffusivity of a probe molecule through polymer solutions was measured. The ratio of probe size to polymer size was similar to the ratio of fluorescein size to dextran size for the data reported here.

Concentration measurement across the entire channel is not required to determine diffusivity. If half the channel were visible, the technique could still be applied to the visible half. In this way the diffusivity of a constituent in an opaque sample stream, such as blood, could be measured. In that case, however, the analytical model must include the effects of varying Peclet [5].

References

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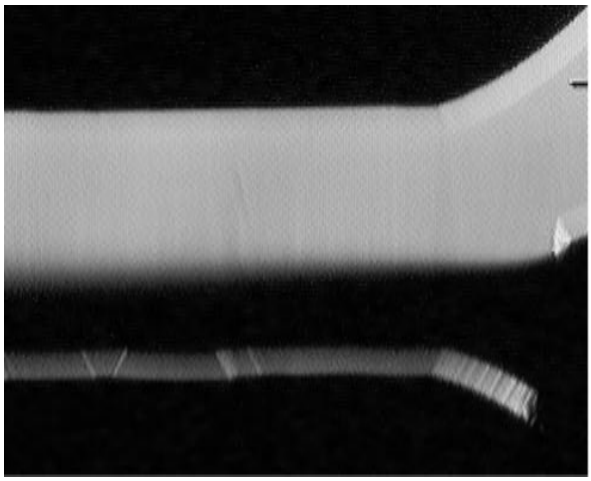

Fig. 1. Fluorescein Diffusion in Water

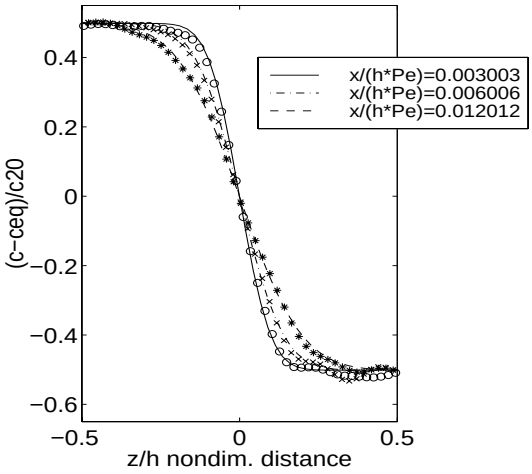

Fig. 2. Matching Concentration Profiles

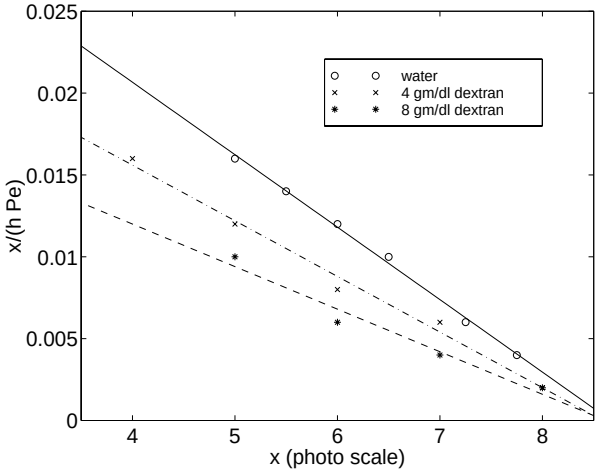

Fig. 3. Matching Curve Slopes

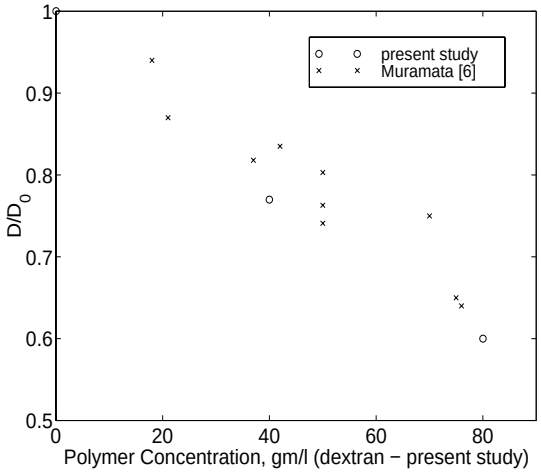

Fig. 4. Diffusivity in polymer solutions