

# Measurement of the Diffusion Coefficient of Miscible Fluids Using Both Interferometry and Wiener's Method<sup>1</sup>

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Measurements of the diffusion coefficient of two miscible liquids are reported. The liquids are various combinations of pure silicone oils and those to which small amounts of solvents are added to control the difference in density between the fluids. The liquids were placed in a quartz cell such that the interface is initially horizontal. As the fluids diffuse, the profile of the index of refraction near the interface is time dependent and is related to the local concentration of the diffusing fluids. The concentration gradient profile was measured by a shearing interferometer incorporating a Wollaston prism, as well as Wiener's method. In the latter technique, a 45° light sheet was passed through the test cell, and the local deflection of the light beam was measured. The average diffusion coefficient was obtained by analysis of the measured concentration gradient profile, assuming that the diffusion process is one-dimensional and is characterized by a constant value of the diffusion coefficient.

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**KEY WORDS:** diffusion coefficient; interferometry; miscible interfaces; Wiener's method.

## 1. INTRODUCTION

The dynamics of miscible interfaces is an active area of research that has been identified to benefit from experimentation in reduced gravity. The

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goal is to study the patterns assumed by the interface when one liquid is slowly displaced by another in a cylindrical tube, such that diffusion plays an important role in the dynamics. It has been suggested that nontraditional stresses in the fluids, caused by the steep variation of the concentration of the miscible fluids in the mixing zone, might be important in the dynamics [1]. These effects are overwhelmed by the flow caused by buoyancy under terrestrial conditions [2]. An improved understanding of the dynamics of multiphase porous media flows is deemed essential for progress in the fields of enhanced oil recovery, fixed bed regeneration, hydrology, and filtration [3–5].

The diffusion coefficient of the miscible fluids is a property that is important in the dynamics. Its values are vitally important to the proper design of the reduced gravity experiments. In particular, it determines the desirable range for the speeds of the displacing fluids, so that the effect of diffusion is not overshadowed by convective transport of mass. Petitjeans and Maxworthy [3] used a variation of Wiener's method, described in Ref. 6, to measure the diffusion coefficient. A focused laser beam was passed through a quartz cell in which two liquids were diffusing into each other across a horizontal miscible interface. The index of refraction at any location in the test cell is a function of time and depends on the local concentration of the fluids. As the beam traversed the test cell, it was bent vertically when it traversed a vertical gradient of concentration, and the deflection of the exiting beam was measured as a function of vertical position using a light detector. The deflection angle is related to the vertical gradient of the index of refraction, and hence to the concentration gradient within the test cell. The average diffusion coefficient was obtained by analysis of the measured concentration gradient profile, assuming that the diffusion process is one-dimensional and is characterized by a constant value of the diffusion coefficient.

The method used by Petitjeans and Maxworthy to measure the concentration gradient is a point measurement that requires the light beam and the detector to be traversed through the region of interest. Therefore, instantaneous measurement of the concentration gradient cannot be obtained everywhere near the interface. To overcome this limitation, we have used both interferometry and the original Wiener method, which used a  $45^\circ$  light sheet, to obtain the distribution of the index of refraction in the mixing region.

Specifically, in the first technique we have used a shearing interferometer incorporating a Wollaston prism, operating in the finite fringe mode, to visualize the concentration gradient in the mixing zone. The diffusion coefficient is obtained from the measured concentration gradient profiles following the procedure used by Petitjeans and Maxworthy. In

what follows, we describe the measurement techniques and the measured diffusion coefficients for various combinations of pure silicone oils and those to which small amounts of decane or carbon tetrachloride are added to control the mixture density.

## 2. MEASUREMENT TECHNIQUES

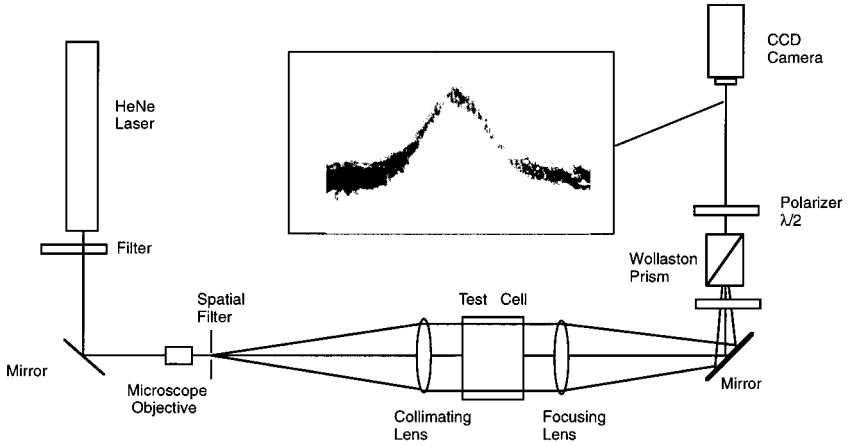
### 2.1. Shearing Interferometry Using a Wollaston Prism

A shearing interferometer measures the gradient of the index of refraction in a certain direction within a test cell [7]. We have used a Wollaston prism to shear the light beam. A collimated, polarized beam of light from a laser is passed through a transparent test cell. The light is then focused on a Wollaston prism, which splits the light into two beams that are slightly displaced from each other. When the beams are recombined, they produce interference fringes that indicates gradients in the index of refraction in the test medium. We have used the interferometer in what is called the finite fringe mode, where equidistant, parallel interference fringes appear in a uniform index of refraction field in the test cell. This is the case when only one of the fluids is present in the test cell. When the second fluid is introduced and diffusion occurs, the deviation or shift of a fringe from its undisturbed location is a measure of the index of refraction gradient within the test cell. We assume that the index of refraction within the test cell is only a function of the vertical coordinate. The light beam is passed through the test cell horizontally, and we assume that each ray of light traverses a path of constant refractive index, without refraction.

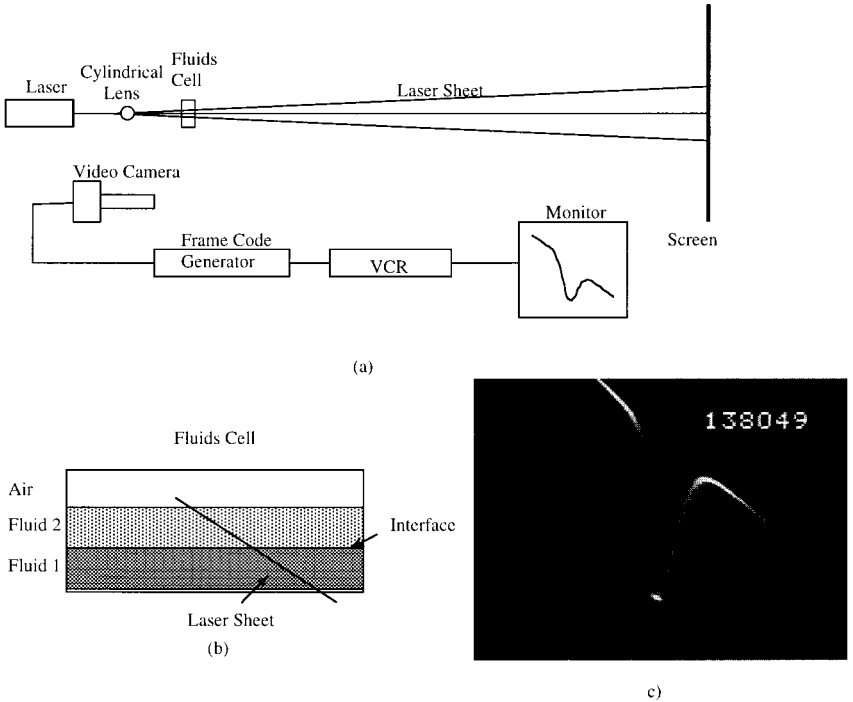
Figure 1 shows a schematic of the Wollaston prism shearing interferometer. The inset at the top of the figure shows the fringe shift that results from the diffusion across a decane–50 cSt silicone oil interface, contained in a quartz test cell of  $10 \times 10$ -mm cross section, at approximately 30 min after the fluids were brought into contact. This fringe represents the instantaneous profile of the gradient of the index of refraction near the interface of the diffusing fluids. To obtain this image, the Wollaston prism was rotated such that the interfering beams are nearly horizontally separated.

### 2.2. Wiener's Method

A schematic of the experimental setup for Wiener's method is shown in Fig. 2. A test cell containing the diffusing fluids is illuminated by a laser light sheet, at a  $45^\circ$  angle to the interface. As the light traverses the test cell, the exiting rays are bent vertically when they cross a vertical gradient of



**Fig. 1.** Schematic of a Wollaston prism shearing interferometer. Shown in the inset is the fringe shift caused by diffusion across a decane-50 cSt silicone oil miscible interface.



**Fig. 2.** Schematic of Wiener's method: (a) experimental setup, (b) test cell and light sheet location, and (c) image showing the deflection of the light sheet.

concentration. The angle of deflection of the light exiting the test cell is given by

$$\alpha = \frac{n}{n_a} \int \frac{1}{n} \frac{\partial n}{\partial x} dz \quad (1)$$

where  $n$  (with respect to the value  $n_a$  for air) is the refractive index of the fluid,  $x$  is perpendicular to the mixing front, and  $z$  is the direction of propagation of the undisturbed laser light. Figure 2c shows a typical image of the light exiting the test cell. The concentration gradient at a given  $x_{in}$  along the light sheet is proportional to the deflection  $x_{out} - x_{in}$  of the exiting light. The plot of  $x_{out} - x_{in}$  versus  $x_{in}$  therefore represents the profile of the concentration gradient in the test cell.

### 2.3. Diffusion Coefficient Calculation

We assume that the two fluids are pure, and therefore, only binary diffusion occurs. Let  $\rho_1(x, t)$  and  $\rho_2(x, t)$  represent the mass concentration (mass of species per unit volume of the fluid) of the two fluids at a vertical location  $x$  and a given time  $t$ . Far away from the interface,  $\rho_{1\infty}$  and  $\rho_{2\infty}$  are the density of the two fluids. It is convenient to define  $c = \rho_1(x)/M_1\rho_{1\infty}$  as the dimensionless molar concentration of fluid 1, where  $M_1$  is the molecular weight of fluid 1. A similar dimensionless concentration for fluid 2 may be defined. For stationary liquids, the governing equation for diffusion is [8]

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (2)$$

Strictly speaking, this equation is valid only when the binary diffusion coefficient  $D$  as well as the local density in the fluid is constant. We will extract the diffusion coefficient from our experiments assuming that the above equation is valid. The boundary conditions are

$$c \rightarrow 1 \quad \text{as } x \rightarrow \infty \quad \text{and} \quad c \rightarrow 0 \quad \text{as } x \rightarrow -\infty \quad (3)$$

This solution for the concentration gradient is

$$\frac{\partial c}{\partial x} = \frac{1}{2\sqrt{\pi Dt}} e^{-x^2/4Dt} \quad (4)$$

The dimensionless concentration gradient profile for fluid 2 is identical to that for fluid 1. Assuming that the refractive index is linearly proportional

to the concentration of the two fluids, the gradient of the refractive index has a similar profile.

The maximum value of the concentration gradient is at  $x=0$  and is given by

$$m = \left( \frac{\partial c}{\partial x} \right)_{\max} = \frac{1}{2\sqrt{\pi Dt}} \quad (5)$$

For positive  $x$ , let  $x = \frac{1}{2}\delta_{1-(1/e)}$  at the location where  $\partial c/\partial x = (1-(1/e))m$ . Using the solution given above, we can then obtain the diffusion coefficient to be

$$D_{1-(1/e)} = \frac{\delta_{1-(1/e)}^2}{[-16 \ln(1-(1/e))]t} = \frac{\delta_{1-(1/e)}^2}{7.334t} \quad (6)$$

Similarly, let  $x = \frac{1}{2}\delta_{1/e}$  at the location where  $\partial c/\partial x = (1/e)m$ .  $D_{1/e}$  is then obtained to be

$$D_{1/e} = \frac{\delta_{1/e}^2}{16t} \quad (7)$$

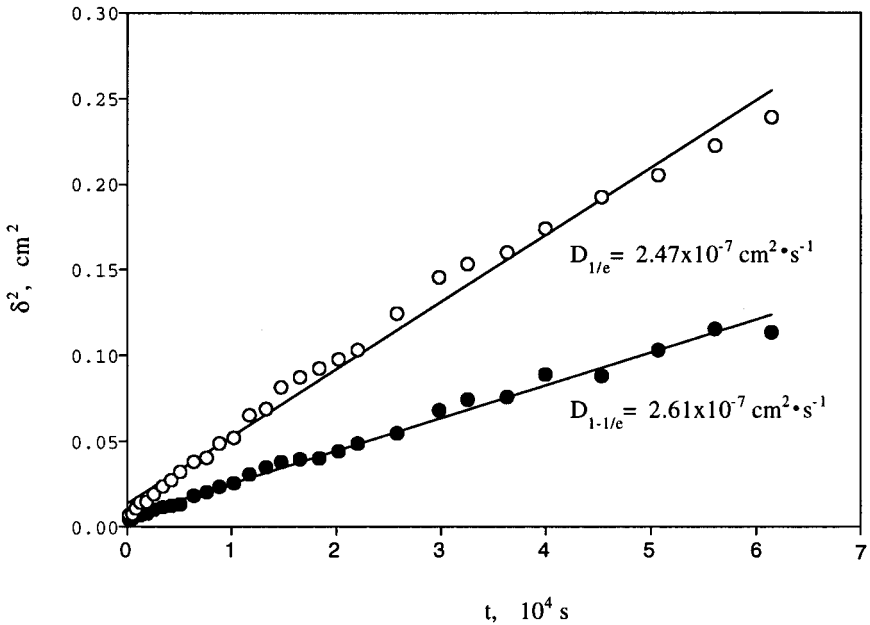


Fig. 3. Plot of  $\delta^2$  (see Section 2.3) versus time, for the diffusion of a 10 cSt–1000 cSt silicone oil fluid pair. The diffusion coefficient is obtained from the slope of the best-fitting line.

Table I. Measured Diffusion Coefficients

Fluids	Diffusion coefficient ( $\text{cm}^2 \cdot \text{s}^{-1}$ )			Technique <sup>d</sup>
	$D_{1-(1/\epsilon)}$	$D_{1/\epsilon}$	$D_{\text{Wiener}}$	
1000 cSt/100 cSt <sup>a</sup> silicone oils	$(4.36 \pm 0.30) \times 10^{-8}$	$(4.79 \pm 0.22) \times 10^{-8}$	$(1.69 \pm 0.06) \times 10^{-8}$	WM
	$(5.11 \pm 0.73) \times 10^{-8}$	$(5.41 \pm 0.75) \times 10^{-8}$	—	WPI
1000 cSt/50 cSt silicone oils	$(4.37 \pm 0.97) \times 10^{-8}$	$(5.07 \pm 1.31) \times 10^{-8}$	—	WPI
1000 cSt/10 cSt silicone oils	$(2.61 \pm 0.10) \times 10^{-7}$	$(2.47 \pm 0.10) \times 10^{-7}$	$(3.14 \pm 0.15) \times 10^{-7}$	WM
	$(2.83 \pm 0.72) \times 10^{-7}$	$(2.34 \pm 0.68) \times 10^{-7}$	—	WPI
1000 cSt/1 cSt silicone oils	$(4.17 \pm 0.23) \times 10^{-6}$	$(2.48 \pm 0.21) \times 10^{-6}$	$(1.93 \pm 0.08) \times 10^{-6}$	WM
	$(2.65 \pm 0.32) \times 10^{-6}$	$(1.93 \pm 0.29) \times 10^{-6}$	—	WPI
1000 cSt silicone oil + decane <sup>b</sup> /10 cSt silicone oil	$(3.28 \pm 0.12) \times 10^{-7}$	$(3.09 \pm 0.13) \times 10^{-7}$	—	WM
1000 cSt silicone oil/ $\text{CCl}_4$ + 100 cSt silicone oil <sup>c</sup>	$(2.71 \pm 0.43) \times 10^{-8}$	$(3.02 \pm 0.36) \times 10^{-8}$	—	WM
100 cSt silicone oil/decane	$(2.82 \pm 0.09) \times 10^{-6}$	$(3.02 \pm 0.12) \times 10^{-6}$	—	WM
50 cSt silicone oil/decane	$(1.54 \pm 0.40) \times 10^{-6}$	$(2.63 \pm 0.68) \times 10^{-6}$	—	WPI

<sup>a</sup> 1 cSt =  $10^{-4} \text{ m}^{-2} \cdot \text{s}^{-1}$ .

<sup>b</sup> Mixture density =  $0.964 \text{ g} \cdot \text{cm}^{-3}$ .

<sup>c</sup> Mixture density =  $0.97 \text{ g} \cdot \text{cm}^{-3}$ .

<sup>d</sup> WM, Wiener's method; WPI, Wollaston prism interferometry.

Wiener [6] obtained the diffusion coefficient by measuring the maximum deflection  $\gamma$  of the light beam that exits the test cell. From the solution given above, it can be shown that  $\gamma = (|n_1 - n_2| d) / (2 \sqrt{\pi D t})$ , where  $d$  is the width of the test cell. The diffusion coefficient is given by

$$D_{\text{Wiener}} = \frac{(n_1 - n_2)^2 d^2}{4\pi\gamma^2 t} \quad (8)$$

The values of  $\delta_{1-(1/e)}$ ,  $\delta_{1/e}$ , and  $\gamma$  have been obtained from the measured refractive index gradient profiles, for various values of  $t$ . A plot of  $\delta^2$  versus  $t$  was then generated (a typical plot is shown in Fig. 3). Values for the diffusion coefficient, together with its 95% confidence interval, were obtained by finding the best fitting straight line to such plots, using linear regression.

### 3. RESULTS

Table I shows the measured diffusion coefficients for several liquid pairs, chiefly silicone oils. These fluids are currently planned to be used in the reduced gravity experiments described in Ref. 2, and the diffusion coefficients are unknown, to the best of our knowledge. In some instances, small quantities of solvents such as decane or carbon tetrachloride were added to one of the fluids so that the density of the two fluids were the same. We have obtained a diffusion coefficient for such cases assuming that the simple theory of binary diffusion holds. In all cases, we have reported the 95% confidence interval for the measured diffusion coefficients, obtained from the regression analysis. The diffusion coefficient measured by Wiener's original method appears to be the least accurate, perhaps because the refractive index of the fluids must be known more precisely at the wavelength of the light used. In the case of diffusion across a 1000 cSt/1 cSt interface, the difference in the diffusion coefficients obtained by the various techniques is large. This pair has the largest density difference ( $\Delta\rho/\rho = 0.19$ ) among all the fluid pairs we have used. It is possible that the simple model of diffusion we have used does not hold for this pair.

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