Diffusion Coefficients for the System Toluene-Methylcyclohexane by Using Birefringent Interferometry

J. L. HALUSKA and C. P. COLVER

The University of Oklahoma, Norman, Oklahoma

This communication describes the use of the double Savart plate interferometer, introduced by Bryngdahl and Ljunggren (*1*), as applied to the measurement of molecular diffusion coefficients in liquids. Analysis of the birefringent interferometer has shown it to possess a high degree of precision unattainable by previous methods in which the optical power resolution limits the accuracy (*2*). A major advantage of this technique is that experiments can be performed by using very small concentration differences between diffusing solutions.

For the small concentration differences used in this work, Fick's second law with composition independent diffusion coefficient is presumed to be valid. The free diffusion model was used as a basis for the experimental measurements. The solution of Fick's second law under conditions of free diffusion may be written as

$$\frac{C_A(x,t) - C_{A0}}{C_{A1} - C_{A0}} = \frac{1}{2}\left[1 + \operatorname{erf}\left(\frac{x}{\sqrt{4D_{AB}t}}\right)\right] \qquad (1)$$

The interference patterns produced by the interferometer represent optical path gradients. The optical path is defined as the product of the refractive index of the solution and the geometrical path length through the diffusion cell. Over small concentration intervals, the refractive index may be assumed to vary linearly with composition. In this case, the optical path gradient is also representative of the concentration gradient, which is expressed as

$$\frac{\partial C_A(x,t)}{\partial x} = \frac{C_{A1} - C_{A0}}{2\sqrt{\pi D_{AB}t}} \exp\left[\frac{-x^2}{4D_{AB}t}\right] \qquad (2)$$

The diffusion coefficients are thus determined from the rate at which the interference fringe patterns change.

EXPERIMENTAL

The experimental apparatus consists of a double Savart plate interferometer, a constant temperature air bath, a flowing junction test cell, a helium-neon laser, and a 35 mm. still camera. The interferometer is shown schematically in Figure 1.

The optical bench of the interferometer is 20 ft. in length and is constructed of two 8 in. steel channel beams mounted on three rubber cushioned concrete pillars. The optical bench is unusually long so that long focal length lenses could be used to improve the quality of the collimated light passing through the diffusion cell.

Each of the optical components of the interferometer, including six lenses and two Savart plates, is mounted in an individual lens mount on a platform bolted to the optical bench. Each mount has at least 4 deg. of freedom adjustable to within 0.002 in.

High quality achromatic lenses are used throughout the optical system. Savart plates and optical flats are flat to within 200Å and parallel to within 15 sec.

The diffusion test cell is installed in a constant temperature air bath consisting of a double walled, insulated box equipped with internal control heaters, baffles, and air circulating fan. Bath temperatures are controlled to within 0.01°C. with a Hallikainen Thermatrol controller with temperature fluctuations being continually monitored by a Hallikainen Thermograph (Model 1154-C) strip chart recorder. Two NBS calibrated platinum resistance thermometers, one installed in the test cell and the other mounted on the wall of the bath, are used for temperature measurement.

A helium-neon gas laser is used as a source of light. The laser produces a polarized, coherent beam of red light at a wavelength of 6328 Å. at a maximum power output of 1 mw.

An experiment is conducted by forming a horizontal interface between two solutions in a flowing junction diffusion cell. The test cell used in the present study has been described in detail by Merliss (*3*). With the more dense solution on the bottom, a sharp boundary is formed between the two test solutions by withdrawing both fluids from horizontal exit slits centered along each side of the cell. After a satisfactory interface is established, fluid withdrawal is stopped, and the experiment is initiated. The decay of the interface by diffusion is followed by taking approximately thirty photographs of the interference patterns at known times. Photographs are taken with a Nikon F 35 mm. camera at specified times measured with 1/10 sec. elapsed time electric timer. The photographs show symmetric Gaussian shaped curves with increases in the degree of dispersion of the bell shape with time. A Sherr microprojector equipped with a 20X magnifying lens and a micrometer table capable of measurements to 5/100,000 in. along two axes is used to measure the profiles.

DATA INTERPRETATION AND REDUCTION

As depicted in Figure 2, the distance W across the Gaussian type of profiles is measured at a specified gradient level h on each photograph. Each measured distance is then scaled with the proper magnification factor determined from some reference distance in the cell.

By defining t_i as the time at which the maximum distance across the gradient profile occurred, the gradient [Equation (2)] at t_i and $2x_i$ may be equated with the gradient at any other data pair $2x$ and t because the measurements are made at a constant gradient level:

$$\frac{1}{t}\exp\left[\frac{-(2x)^2}{8D_{AB}t}\right] = \frac{1}{t_i}\exp\left[\frac{-(2x_i)^2}{8D_{AB}t_i}\right] \qquad (3)$$

Note that at the time t_i

$$(2x_i)^2 = 8D_{AB}t_i \tag{4}$$

Substitution of Equation (4) in Equation (3) yields

$$(2x)^2 = 8D_{AB}t\left[1 + \ln\left(\frac{t_i}{t}\right)\right] \tag{5}$$

Equation (8) relates the fringe separation $2x$ to the coordinate time, the time of maximum fringe separation, and the diffusion coefficient for an infinitely sharp initial interfacial condition. Because it is not possible to establish a perfect interface between test solutions, a zero time correction must be determined and added to each experimentally recorded time. By considering the zero time correction, the final expression is given by

$$(2x)^2 = 8D_{AB}(t + t_o)\left[1 + \ln\left[\frac{t_i + t_o}{t + t_o}\right]\right] \tag{6}$$

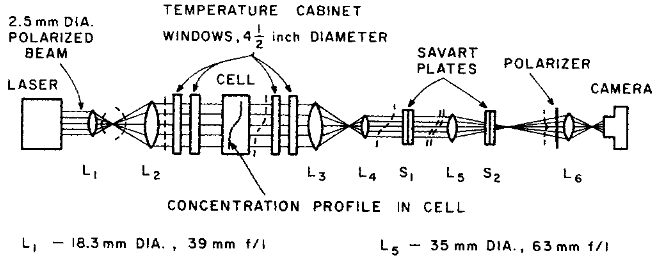
Determination of the diffusion coefficient and the zero time correction is accomplished by a regression analysis. A Gauss-Newton nonlinear least-squares technique (which minimizes the sum of the squared deviation between predicted and observed values) is used to obtain the experimentally determined value of diffusion coefficient and zero time correction.

RESULTS AND DISCUSSION

Values of the diffusion coefficient for the sucrose-water system were determined at 25 ± 0.01°C. Reagent grade sucrose having a stated purity of better than 99.9 wt. % and distilled, deionized water were used in preparing the test solutions. Three values at an average concentration of 0.75 g. sucrose/100 ml. of solution and one value at a concentration of 0.05 g. sucrose/ml. are presented in Figure 3 together with the data of other investigators (*2*, *4* to *7*). For these data, the initial concentration difference between test solutions was held to within 0.1 wt.% in each case. The three diffusion coefficients at 0.75 g./100 ml. have an average absolute deviation of 0.17% from their mean value of 5.175×10^{-6} sq. cm./sec. These data compare most favorably with the previously reported data.

Diffusion coefficients were obtained for the toluene-methylcyclohexane system at 25°, 45°, and 60°C. over the entire concentration range (Table 1 and Figure 4). The toluene and methylcyclohexane used in the determinations were Baker analyzed reagents and had a stated purity of 99.9 wt.%. In these measurements, the initial concentration difference between the two diffusing solutions was kept within 0.4 wt.%.

The diffusion coefficients at infinite dilution were compared with the predicted diffusion coefficients calculated from the Othmer-Thakar (*8*), Lusis-Radcliff (*9*), and Wilke-Chang (*10*) equations. The Lusis-Radcliff equation provides the best predictive technique for methylcyclohexane as solute with an average error of approximately



L_1 – 18.3 mm DIA., 39 mm f/1
L_2, L_3 – 4 1/8 inch DIA., 60 inch f/1
L_4 – 35 mm DIA., 200 mm f/1
L_5 – 35 mm DIA., 63 mm f/1
L_6 – 36 mm DIA., 100 mm f/1

NOTE:
DASHED LINES REPRESENT SHAPE OF LIGHT FRONT AT POINT INDICATED

Fig. 1. Interferometer lens arrangement.

TABLE 1. EXPERIMENTAL VALUE OF DIFFUSION COEFFICIENTS FOR THE TOLUENE-METHYLCYCLOHEXANE SYSTEM

Mole fraction toluene	$D_{AB} \times 10^5$, sq.cm./sec. 25°C.	45°C.	60°C.
0.003	1.64	2.18	2.73
0.347	1.61	2.16	2.63
0.681	1.73	2.40	2.94
0.998	2.20	3.09	3.66

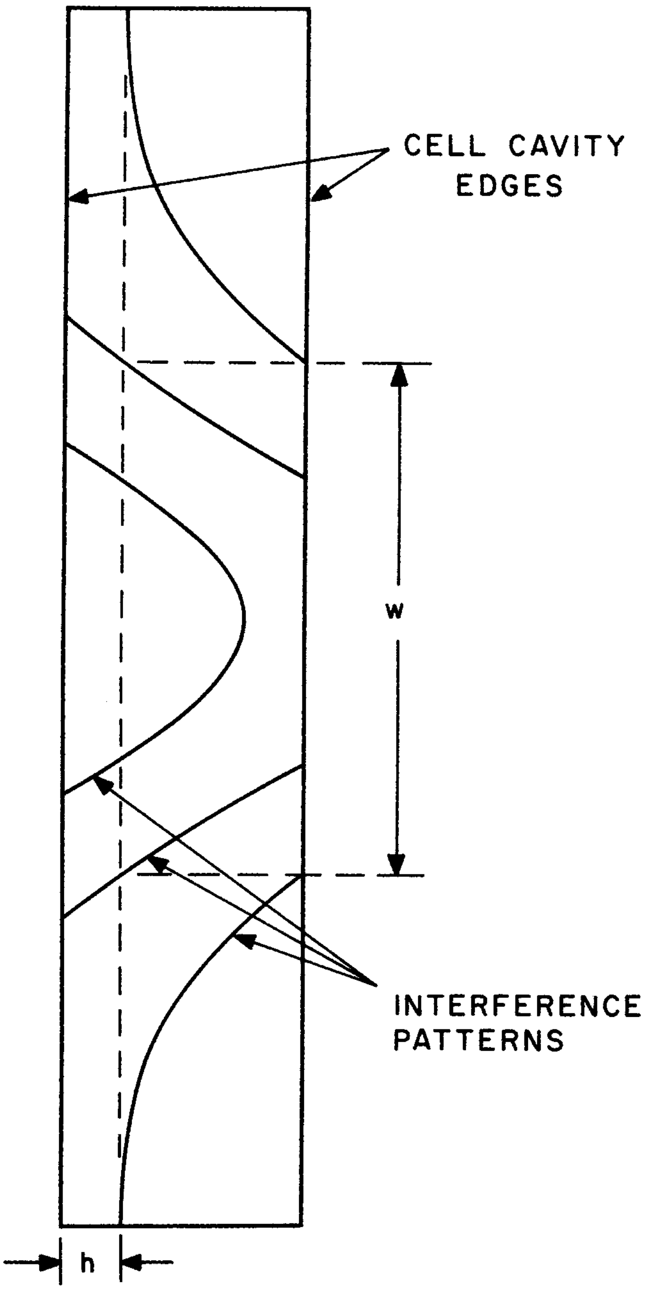


Fig. 2. Illustration of measurement made on each actual interference pattern.

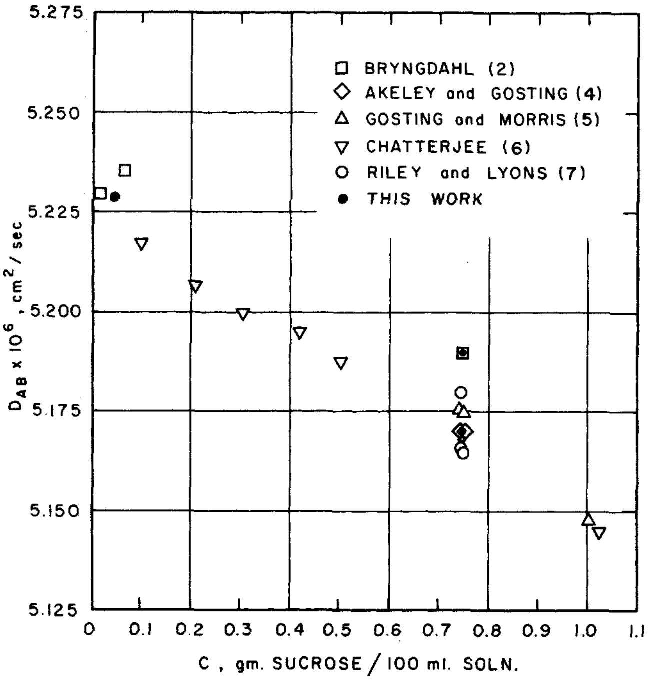


Fig. 3. Diffusion coefficients for the sucrose-water system at 25°C.

8%. The Wilke-Chang expression gives the best results for the temperature dependence of the infinite dilution ceffificients with toluene as the solute, the average error being approximately 3%. The Othmer-Thakar equation was found to yield errors of 30% at the higher temperatures.

The experimental results at each temperature were compared with the equation of Vignes-Cullinan (*11, 12*), Darken (*13*), and Rathbun (*14*) over the entire composition range. Activity values used in these equations were determined from the thermodynamic data of Schneider (*15*). The diffusion isotherms indicate a negative deviation from linearity which is characteristic of liquid solutions which deviate positively from Raoult's law. The curve in Figure 4 represents the Vignes-Cullinan expression

$$D_{AB} = \left({D^0{}_{BA}}^{x_A} \; {D^0{}_{AB}}^{x_B} \right) \frac{d \ln a}{d \ln x} \qquad (7)$$

Agreement with the experimental points is within 5%, with the predicted diffusion coefficients being consistently lower in value. Values predicted by Darken's equation were nearly identical to those of the Vignes-Cullinan equation. This similarity is seemingly a result of the near ideality of the toluene-methylcyclohexane system. Rathbun's equation, which has largely been tested with binaries consisting of an associating and a nonassociating component, was found to yield values that were greater than the experimental data, with maximum deviations of about 7% occurring in the 0.3 to 0.7 toluene mole fraction concentration range.

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NOTATION

a = activity
c_i = concentration of species i, (g.)(mole)/(liter)

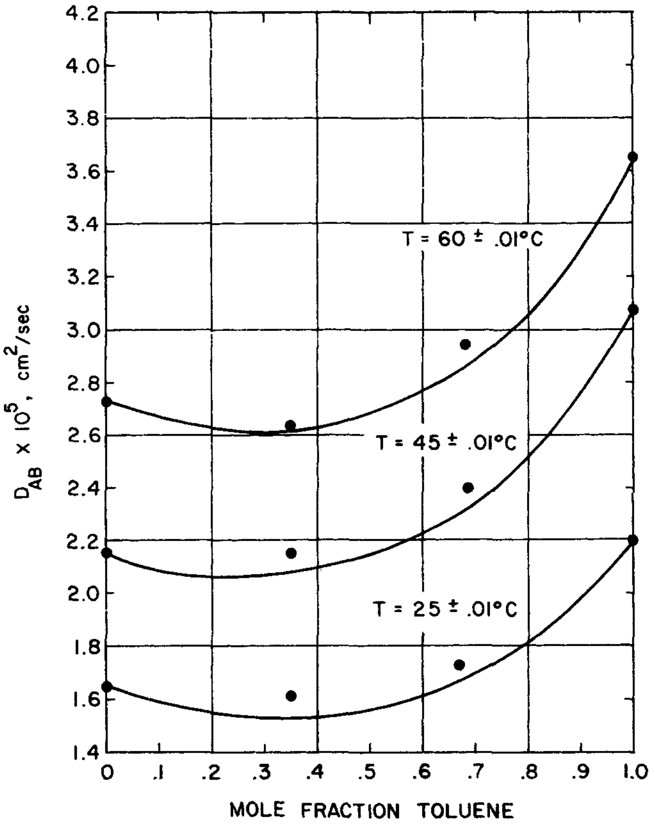

Fig. 4. Molecular diffusion coefficients for the toluene-methycyclohexane system.

D_{ij} = binary diffusion coefficient for species i and j, sq. cm./sec.
erf(y) = error function as $\int_0^y e^{-y^2} dy$
h = reference distance to specified gradient level on all image, cm.
t = time, sec.
t_o = zero time correction, sec.
t_i = time of maximum fringe expansion, sec.
w = distance measured across interference profile, cm.
x_i = mole fraction of species i

Superscript

0 = infinite dilution of indicated species

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