Diffusivity study of transparent liquid solutions by imaging beam deflection

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ABSTRACT

A non-interferometric technique to measure the diffusion coefficients of transparent liquid solutions is proposed. The technique can be realized using a white light source. The bending of the light beam caused by the non-linear refractive index distribution existing within the experimental cell (glass cell) containing the diffusing solutions, is utilized to find the diffusivity values. The bending of the light beam is imaged using an optically active material or a birefringent material, placed between two crossed polarizers and a CCD camera. As different portions of a plane wavefront passing through the diffusion cell travels different thickness inside the optically active/birefringent medium, the local refractive index variation is converted into a spatial variation of output intensity. The diffusion coefficient could be calculated from a single image of beam bending or by using images at two different instances of time.

Key Words: Diffusion coefficient, Beam deflection

1. INTRODUCTION

Diffusion is the movement of molecules due to their thermal energies under the influence of a concentration gradient. The study of diffusion is important in fields as diverse as chemical engineering, biology, pollution control, separation of isotopes etc. Knowledge of diffusivity is necessary for the design of chemical equipments and for mass transfer studies. Diffusivity is therefore one of the most important fundamental property of a chemical system. There are many methods to determine diffusion coefficients of transparent liquid solutions. Optical methods are one of the most accurate methods used to determine diffusivity values. The optical method includes conventional interferometry, holographic interferometry and electronic speckle pattern interferometry. But the disadvantage of most of optical methods is that they impose stringent optical requirements, which are difficult to employ in industrial environments. So it becomes necessary to develop new methods for diffusivity measurement that are easy to implement and cheap. In this paper we propose a new method to measure diffusion coefficients of transparent binary liquid solutions using white light source and a birefringent/optically active medium. The method discussed is non-interferometric. Light rays passing through a non-uniform refractive index medium bend towards regions of higher refractive index. The amount of the ray bending at various instances of time will depend upon the refractive index gradient existing inside the medium and hence on the diffusion coefficient. Therefore by measuring the bending of the ray the diffusion coefficient can be determined. This is achieved by using an optically active/birefringent crystal to convert the beam bending into a spatially varying intensity pattern. A wavefront sensing device using birefringent crystal has already been developed. The output intensity caused by a wavefront passing through a birefringent plate placed between a pair of crossed polarizers will depend upon the distance each portion of the wavefront traveled through the birefringent medium. Therefore wavefronts traveling more distance will produce more output intensity and vice-versa. The same principle applies for optically active materials. The property of these mediums to rotate the plane of polarization of the incident plane polarized is utilized to determine the diffusion coefficients of transparent liquid solution.
2. EXPERIMENTAL SETUP AND THEORY

The experimental setup used is shown in Fig. 1. The light from a white source is collimated and made monochromatic by using a optical filter. The collimated light passes through a polarizer. The polarized light then passes through the cell containing the diffusing solutions. A linear polarization rotator (LPR), which can be either an optically active crystal or a birefringent crystal and an analyzer, which is also a polarizer with its polarization direction at 90° to P, placed after the cell converts the beam deflection occurring inside the cell into a spatially varying intensity distribution. This intensity distribution is imaged using an imaging lens and a CCD camera.

Half of the experimental cell is filled with solution of lighter concentration. The heavier concentration solution is introduced below the lighter concentration solution, using a capillary tube mechanism. The process of diffusion starts after the experimental cell is filled.

The solution inside the cell can be considered as consisting of layers having spatially varying refractive indices. This position depended refractive index will give rise to a deflection of the incident beam (Fig. 2). As diffusion progresses the refractive index of these layers will also change, thereby changing the angle of deflection. If this deflection can be recorded, it could be used for diffusion coefficient measurements. The theoretical explanation is as follows.

**Free diffusion process**
Solution of the Fick’s second law which governs free diffusion process²¹,²² in a binary liquid system consisting of liquids having concentrations \( C_1 \) and \( C_2 \) (\( C_2 > C_1 \)), separated at \( x=0 \) when \( t=0 \), considering diffusion along only one direction (x-axis) is given by²²

\[
C(x,t) = \frac{C_1 + C_2}{2} + \frac{C_2 - C_1}{2} \left[ \frac{2}{\sqrt{4Dt}} \int_0^{\sqrt{4Dt}} \exp\left(-\eta^2\right) d\eta \right] 
\]

where \( C(x,t) \) is concentration at position \( x \) and time \( t \) and \( D \) is the diffusion coefficient, which is a constant for the concentration range between \( C_1 \) and \( C_2 \). The bracketed term is the error function²³ of \( \sqrt{2\pi Dt} \).

For the narrow range of concentrations over which the experiments were conducted, the refractive index inside the experimental cell can be considered as a linear function of concentration. Therefore the refractive index can be written as

\[
n(x,t) = \left( \frac{dn}{dC} \right)_b C(x,t) + n_0
\]
Fig. 2: Refractive index profile inside the diffusion cell and the resulting beam deflection

where \( n_0 \) is a constant and \( (dn/dC)_0 \) is the mean value of the derivative for the applied concentration range. As the diffusion process progresses the concentration gradient and hence the refractive index changes. The refractive index distribution inside the diffusion cell is non-uniform (Eq. 2) resulting in the bending of light rays entering the cell. The amount of bending will depend on the refractive index gradient and for a ray entering at \( z=0 \) and \( x \), considering diffusion along only the \( x \) direction is given by\(^{19,20}\):

\[
\theta (x,t) = \int_0^l \left( \frac{dn(x,t)}{dn} \right) dx = l \left( \frac{dn}{dC} \right) \left( \frac{C_1 - C_2}{2} \right) \exp \left( -\frac{x^2}{4Dt} \right)
\]

where \( l \) is the length of the diffusion cell and \( n \) is the refractive index at point \( x \).

**3. SIMULATIONS AND DISCUSSIONS**

The change in bending angle along the diffusion direction for different times is shown in Fig. 3 average concentration \( C_{av} = 0.9959 \) mol l\(^{-1}\) of ammonium dihydrogen phosphate. It can be seen that the rays are bending in the same direction for the upper and lower part and the maximum bending occurs at the interface. As the time progresses the angle of bending also decreases. As the bending depends upon the refractive index profile inside the cell, the diffusivity values could be determined from the amount of bending. The amount of bending is imaged using the polarization rotator.

Fig. 3: Change in bending angle with diffusion direction at different instances of time
When a birefringent crystal is used, the incident plane polarized light is split into two eigen waves, which travel with different phase velocities due to different effective refractive indices. These waves are combined at the exit face of the crystal and the polarization direction of the resulting wave depends upon the propagation length and hence on the beam bending. The rotation of plane of polarization of the plane polarized light is caused by the retardation, which is depends upon the difference of refractive indices along the two principal directions and hence on the angle of incidence. The analyzer will convert this spatially modulated polarization direction into a spatially varying intensity pattern.

In the case of an optically active medium, the incident plane polarized light is split into a right circularly polarized light and a left circularly polarized light, which travel with different velocities inside the medium due to different refractive indices. They will combine at the exit face to form a plane polarized light with its plane of polarization rotated by an amount which depends upon the difference of refractive indices existing for the lest and right circular polarizations. Here also the amount of rotation at the exit face is spatially varying due to varying propagation lengths of different points on the wavefront. The analyzer will convert this polarization pattern into an intensity pattern.

The diffusivity values could be determined from the images of the beam bending in two ways 1) from a single image and 2) using two images.

**Technique using a single image**

The intensity at the CCD plane for rays entering the diffusion cell at two positions \( x_1 \) and \( x_2 \) at an instance of time \( t \) could be written using Eq. (3) as.

\[
I(x_1,t) = \frac{A}{\sqrt{t}} \exp \left( -\frac{x_1^2}{4Dt} \right) \quad \text{and} \quad I(x_2,t) = \frac{A}{\sqrt{t}} \exp \left( -\frac{x_2^2}{4Dt} \right)
\]

where \( A = \frac{1}{n} \left( \frac{dn}{dC} \right) \left( \frac{C_1 - C_2}{2\sqrt{nD}} \right) \) is a constant. Due to bending these local output intensities will be different. Taking the ratio of the local output intensities

\[
\frac{I(x_1,t)}{I(x_2,t)} = \exp \left( -\frac{x_1^2 - x_2^2}{4Dt} \right)
\]

and diffusion coefficient can be written as

\[
D = \frac{x_2^2 - x_1^2}{4t \ln \left[ \frac{I(x_1,t)}{I(x_2,t)} \right]}
\]

Therefore by finding the ratio of the intensities (gray levels) at two positions in the diffusion cell will yield the diffusion coefficient.

**Technique using two images**

From Eq. (3), the change in intensity due to bending for a ray entering the diffusion cell at position \( x \) for two different instances of time \( t_1 \) and \( t_2 \) is given by

\[
\delta I = I(x,t_2) - I(x,t_1) = A \left[ \exp \left( -\frac{x^2}{4Dt_2} \right) - \exp \left( -\frac{x^2}{4Dt_1} \right) \right]
\]

The graphical representation of Eq. 7 is shown in Fig. 4 (average concentration \( C_{av}=0.9959 \ \text{mol l}^{-1} \)). It can be seen that this curve has three extremes. These extremes can be found by differentiating Eq. 7 with respect to \( x \) and equating to zero. This yields

\[
\sqrt{t_1} \exp \left( -\frac{x^2}{4Dt_2} \right) = \sqrt{t_2} \exp \left( -\frac{x^2}{4Dt_1} \right)
\]

One of the solutions of Eq. (9) is \( x=0 \), the interface. The other two solutions can be found by taking its logarithm. This leads to the other two solutions \( x_1 \) and \( x_2 \). Using \( x_1 \) and \( x_2 \), the equation for diffusion coefficient can be written as,
Fig. 4: Change in angle of deflection in the diffusion direction ($t_1=240s$, $t_2=900s$)

\[ D = \frac{d^2 [I(t_2) - I(t_1)]}{16 \ln\left(\frac{x_2^{3/2}}{x_1^{3/2}}\right)} \]  

(9)

where $d = x_1 - x_2$ is the separation between the two extremes. By subtracting, intensity pattern at time $t_2$ from time $t_1$, the separation between the extreme points can be obtained. Substituting this in Eq. (9) yields the diffusion coefficient.

**Simulations**

Figures 5a to 5c shows the simulated images for Ammonium dihydrogen solution of concentration 0.9959 mol l$^{-1}$. Fig. 5a and 5b are the simulated images at times 240 seconds and 600 seconds respectively. Fig. 5c is the difference image of Fig. 5a and 5b. Using a single image or the difference image one could calculate the diffusion coefficient.
4. CONCLUSIONS

A method for diffusion coefficient from the beam bending due to the non-linear refractive index using a birefringent/optically active crystal is proposed. The diffusion coefficient could be calculated from a single image or using two images. The main advantage of the method is that it is non-interferometric and could be performed with white light. From the simulated images, it can be seen that, the method yields accurate results.

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