

Application of laser beam deflection technique to study the diffusion process in electrolyte solutions

ACHAMMA KURIAN¹, C V BINDHU, S S HARILAL, RIJU C ISSAC,
V P N NAMPOORI and C P G VALLABHAN

Laser Division, Department of Physics, Cochin University of Science and Technology, Cochin 682 022, India

¹Also at Department of Physics, Catholicate College, Pathanamthitta 689 645, India

MS received 27 June 1994

Abstract. A simple method based on laser beam deflection to study the variation of diffusion coefficient with concentration in a solution is presented. When a properly fanned out laser beam is passed through a rectangular cell filled with solution having concentration gradient, the emergent beam traces out a curved pattern on a screen. By taking measurements on the pattern at different concentrations, the variation of diffusion coefficient with concentration can be determined.

Keywords. Laser beam deflection; diffusion coefficient.

PACS Nos 05·60; 42·20; 42·60

1. Introduction

Laser beam deflection (LBD) technique is an effective and sensitive method for studying the refractive index gradient (RIG) created in a medium by various causes like temperature and concentration variations [1]. In this method, a laser beam with a gaussian profile is allowed to pass through a well defined region in which the refractive index gradient has been created by some physical effect. The amount of deflection suffered by the laser beam is a direct measure of RIG that has been caused in the defined region and hence yields the value of the parameters of the physical processes that create the RIG. Various features of the LBD method has been extensively discussed in the literature [2, 3]. In this work we have used the LBD method to study the different processes in electrolytic solutions. The variation of the diffusion coefficient with concentration has been worked out using the above method.

The concentration dependence of diffusion coefficient has been studied by various workers using different techniques. Some of such techniques are conductometric method [4], isotopic tracer method [5] and interferometric method [6]. All these techniques involve the study of the concentration of diffusing species at a particular point as a function of time. This is repeated at various spatial points. In the present method it is possible to determine the diffusing properties in the diffusing medium simultaneously at various spatial points. This will help us to identify the presence of any spatial anisotropy in the medium.

2. Principle

The schematic of the experimental set up is shown in figure 1. Laser beam is passed through a cylindrical lens mounted with its axis at 45° to the vertical. The emerging fan of rays then passes through a rectangular glass cell containing the liquid. The fanned out laser beam is deflected at the interface and the curved image of the deflected beam can be obtained on the screen kept at a distance from the cell. The magnitude of beam deflection [7] is

$$z = ad \frac{\partial n}{\partial y} \quad (1)$$

where a is the distance between the cell and the screen, d the thickness of the cell and $\partial n/\partial y$ is the refractive index gradient. Since $\partial n/\partial y$ is proportional to concentration gradient $\partial C/\partial y$, one can write

$$z = Kad \frac{\partial C}{\partial y}$$

where K is a constant.

Introducing a horizontal coordinate x on the screen for the rays passing through the depth y in the cell, and with an appropriate choice of origin, x is related to y through the expression

$$x = (a + b) \frac{y}{b} \quad (2)$$

where b is the distance from the cell to the origin of the fan of rays. The magnitude of deflection is different for different concentrations. In the case of electrolytic solutions, diffusion coefficient (D) depends on concentration. Then the diffusion equation can be written as [8]

$$\frac{\partial C}{\partial t} = D(C) \frac{\partial^2 C}{\partial y^2} + \frac{dD(C)}{dC} \left(\frac{\partial C}{\partial y} \right)^2 \quad (3)$$

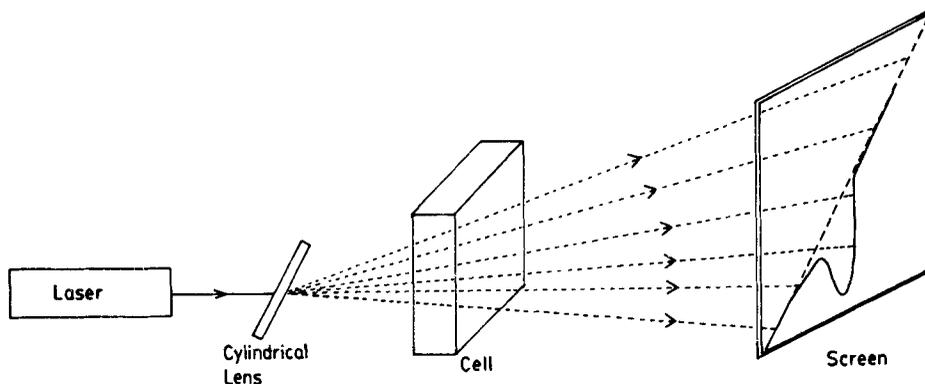


Figure 1. Schematic diagram of the experimental set-up.

Laser beam deflection technique

Substituting $x = y/t^{1/2}$, (3) becomes

$$\frac{d^2 C}{dx^2} + \frac{x}{2D} \frac{dC}{dx} + \frac{D'}{D} \left(\frac{dC}{dy} \right)^2 = 0 \quad (4)$$

where

$$D' = \frac{dD}{dC}.$$

These nonlinear equations defining D as an arbitrary function of C cannot be integrated. Usually the method is to find $D(C)$ experimentally and (4) can be written as

$$\frac{d}{dx} \left(D \frac{dC}{dx} \right) = - \frac{X}{2} \frac{dC}{dx} \quad (5)$$

and

$$D(C) = - \frac{1}{2} \frac{dx}{dC} \int x dC \quad (6)$$

Right hand side of (6) can be evaluated experimentally. One of the simplest forms of $D(C)$ is to write

$$D(C) = D_0 + D_1 C^{1/2} + D_2 C + D_3 C^{3/2} + \dots \quad (7)$$

such that

$$|D_{i+1}| \ll |D_i|.$$

For low concentration, $D(C) = D_0$ which corresponds to concentration independent case. Taking a step-like variation of concentration in a plane within the medium we can write

$$\left(\frac{\partial C}{\partial y} \right)_i = - \frac{C_0}{2\sqrt{\pi Dt}} \exp(-y^2/4Dt) \quad (8)$$

which is a gaussian function, and will be of the same shape traced out by the deflected beam at the boundary as seen from figure 1. Thus we write the shape of the beam trajectory inside the liquid as

$$Z(y) = K \exp(-y^2/4Dt) \quad (9)$$

As time evolves, the boundary smears out until the concentration gradient disappears. This will result into the broadening of the gaussian function. From (7) one can evaluate D from the half width ($y_{1/2}$) of the gaussian function as

$$D = \frac{y_{1/2}^2}{4t \ln 2} \quad (10)$$

3. Results and discussion

Figure 1 shows the experimental configuration used for the determination of D . Laser beam from a frequency stabilized 10 mW He-Ne laser (Spectra Physics) of wavelength 632.8 nm is passed through a cylindrical lens. A glass rod of diameter half centimeter

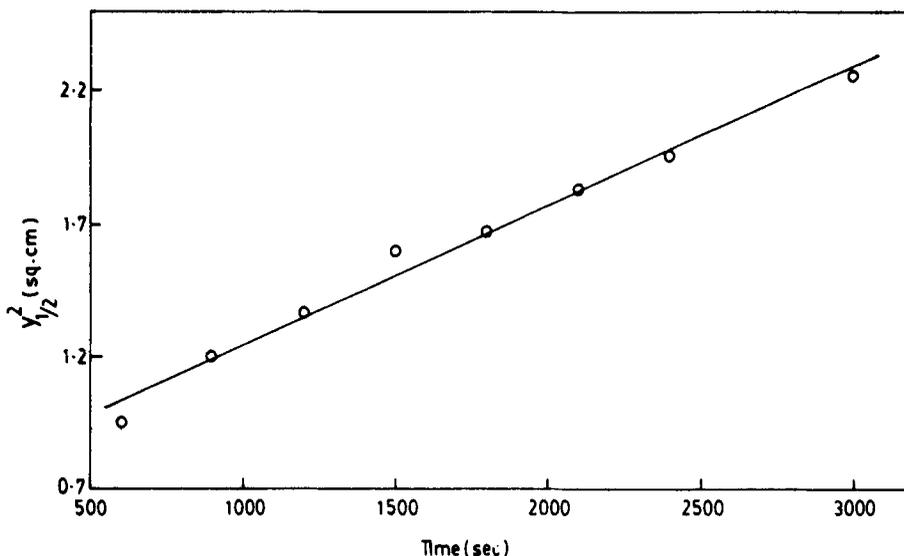


Figure 2. Variation of $y_{1/2}^2$ with time.

mounted 45° to the vertical can be used in the place of cylindrical lens. The solvent (water) is poured into the cell and an equal amount of aqueous solution of BaCl_2 with appropriate concentration is carefully micropipetted to the bottom of the cell in order to minimize the initial mixing of the liquids. One can thus create a clear boundary between the solvent and solution so as to create a step-like variation of concentration. The emerging rays from the cylindrical lens while passing through the solution gets deflected at the interface. The image due to the emergent beam is traced out on a graph paper at different intervals of time after the interface is formed. The depth of the different layers of the liquid is calculated using equation (2) and the value of dC/dy is calculated using (1). A graph is plotted connecting dC/dy and y . The half width of the curve at half maximum ($y_{1/2}$) of dC/dy is measured for a particular time. This is repeated for different values of time. A graph is plotted between $y_{1/2}^2$ and t (figure 2) and its slope can be used to evaluate D . The above experiment is repeated for different concentrations of the solution.

The variation of D with the concentration of electrolytic solutions is due to the presence of attractive and repulsive forces between the ions [8]. Variation of D as a function of \sqrt{C} are given in figure 3 showing well defined minima for BaCl_2 at $\sqrt{C} = 0.4523$ molar. In the low concentration region, the distance between the different cations (or anions) decreases as concentration is increased so that increased attractive force between them causes decrease in the mobility of the ions, thereby decreasing the diffusion rate. Above an optimum concentration the mean free path between the cations (or anions) becomes small so that repulsive force predominates thereby enhancing the mobility of the ions and increase in D . Figure 3 compares the results obtained from the present method with those of conductometric method [3] in the case of BaCl_2 solution. Results are in close agreement. In the low concentration region the experimental results coincide with those predicted by Onsager-Fuoss theory [9].

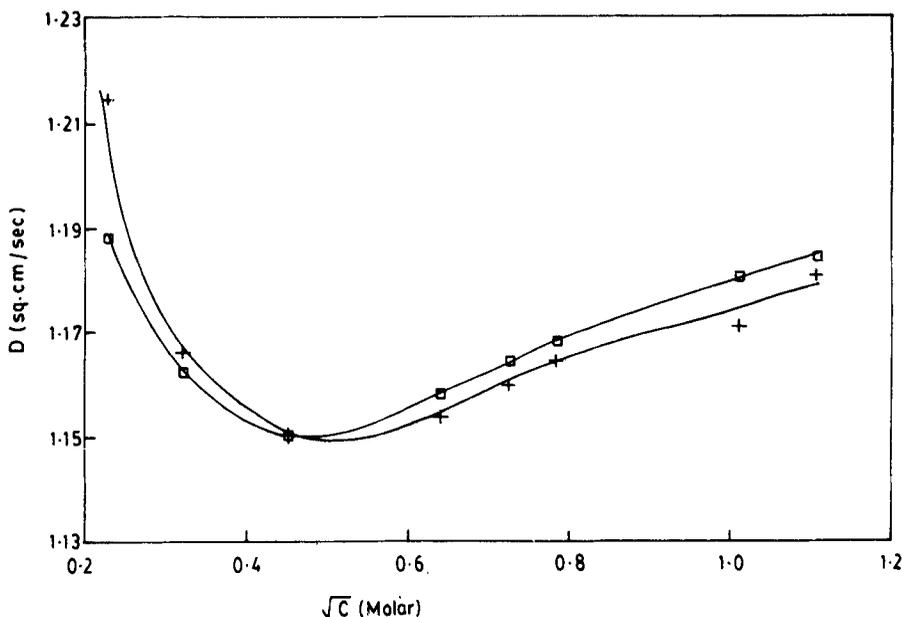


Figure 3. Variation of diffusion coefficient with concentration for BaCl_2 (+ – using the present LBD method, □ – using conductometric method).

4. Conclusions

Concentration dependence of diffusion coefficient of ions can be explained on the basis of various ion-solvent and ion-ion interactions. At infinite dilutions, number densities of the ions are small so that, ion-ion and ion-solvent molecular interactions are less. However as concentration increases such interactions get enhanced so that transport properties will become concentration dependent. One can therefore write D as a polynomial in C so that

$$D(C) = D_0 + D_1 C^{1/2} + D_2 C + D_3 C^{2/3} + \dots$$

The technique described in the present work can also be used to evaluate temperature dependence of refractive index of liquids. Such temperature coefficient of refractive index is an important quantity to study various thermo optical phenomena like photothermal deflections and thermal lens effect. Another possible extension of the work is to study the phase transition in binary liquids in which disappearance of the distortions in the image will indicate transition from multicomponent to homogeneous conditions of the liquid mixture.

Acknowledgements

Financial assistance from DST (India) is greatly acknowledged. AK and CVB are thankful to University Grants Commission (India) for financial assistance and SSH is grateful to CSIR (India) for research fellowship.

References

- [1] Shojiro Nemoto, *Appl. Opt.* **31**, 6690 (1992)
- [2] A J Barnard and B Ahlborn, *Am. J. Phys.* **43**, 573 (1975)
- [3] A C Boccara, D Fournier and J Badoz, *J. Appl. Phys.* **36**, 130 (1980)
- [4] H S Harned, *Chem. Rev.* **40**, 461 (1947)
- [5] J H Wang and J W Kennedy, *J. Am. Chem. Soc.*, **72**, 2080 (1949)
- [6] V Vitagliano and D A Lyons, *J. Am. Chem. Soc.*, **78**, 1549 (1956)
- [7] Reeta Vyas and R Gupta, *Appl. Opt.*, **27**, 4701 (1988)
- [8] W Jost, *Diffusion of Solids, Liquids, Gases*, III edn. (New York, Academic Press, 1952)
Ch. I and XI
- [9] L Onsager and R M Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932)