Quantitative Laser Beam Deflection Study of Liquid-Liquid Interdiffusion in the Water-Sugar System

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Purely concentration-gradient driven liquid-liquid interface laser beam deflection detection was studied theoretically and used experimentally to monitor the kinetics of diffusion between water and sugar as a simple model system. The combination of data from both sides of the interface was used to determine the initial position of the interface plane. The developed one-dimensional model of the dependence of the laser beam deflection on the diffusion parameters was found to be in good agreement with the experimental data, especially at early interdiffusion times. The model was thus able to yield the values for the diffusion coefficient D_s of sugar in water, and for the refractive index gradient $\partial n/\partial C_s$.

Keywords Laser beam deflection, diffusion, kinetics, liquid-liquid interface

Laser beam deflection (LBD), or otherwise known as the Mirage effect, has been increasingly utilized without optical heating to probe diffusion at the liquid-solid interface, in the form of chemical species concentration gradients and electrochemical species produced at working electrodes. When concentration gradients are monitored together with temperature gradients, decoupling the two effects can be done by detecting each deflection component at different laser probe beam intensity modulation frequencies, due to the widely different characteristic diffusion time constants between heat and mass transport.¹ Under purely mass transport transient conditions, a detailed theoretical analysis of the temporal evolution of the LBD signal in the presence of electrochemistry with constant concentration of electrode surface species (the assumed result of an ongoing electrochemical reaction) has been presented by Mandelis and Royce.² The analytical solutions to Maxwell's wave equation for the propagation of the probe beam parallel to the electrode surface demonstrated explicitly the dependence of the displacement of the intensity centroid and the dependence of the spot shape on the electrochemical product diffusion parameters of the system. Those theoretical predictions were found to be in agreement with experiment in the case of the diffusion of ferri-ferrocyanide redox species, 50 mM $\text{Fe}(\text{CN})_6^{3-}$ /50 mM $\text{Fe}(\text{CN})_6^{4-}$ in 0.5 M K_2SO_4 , produced electrochemically via a step voltage applied to a Pt electrode.³ Further studies of electrochemical

diffusion due to electrode voltage modulation without optical excitation have shown LBD modulation to be quite sensitive to concentration gradients generated by non-equilibrium electrochemical processes.^{4,5} The diffusion coefficient of Cu^{2+} in aqueous solution was also measured⁶ using the LBD signal drop with separation from the electrode surface in an electrochemical cell driving the reaction

in 0.01 M CuSO_4 +0.5 M H_2SO_4 electrolyte. In this case an ac potentiostatic voltage was applied to the electrode, the diffusion equation was solved for the one-dimensional $[\text{Cu}^{2+}]$ concentration wave at a fixed potential modulation frequency $f=0.5$ Hz, and the beam deflection was related to the gradient of the concentration wave, $\partial C(x,f)/\partial x$, and to the diffusion coefficient, whence the value $D=1.1 \times 10^{-5} \text{ cm}^2/\text{s}$ was deduced. Although the LBD detection technique has been increasingly used with solid-liquid interface systems, to our knowledge no study to date has addressed the problem of liquid-liquid interdiffusion, one of the most fundamental and important problems most frequently encountered between miscible fluids in the absence of an electrochemical interface. In this work the ability of the LBD technique to monitor the diffusion kinetics of such an interface has been studied both theoretically and experimentally, using one of the simplest well-known processes, the interdiffusion of sugar solutions and water. The successful determination of D demonstrates that this technique could be used for other, larger, molecules such as proteins and drugs. It thus could be used in practice for measurement of

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diffusivity in many biologically important solutions.

Theory

The diffusion problem

Figure 1 shows the geometry of the interdiffusion system. This consists of a cuvette of thickness L containing two liquids, the molecularly heavier of which (*i.e.* the liquid with the higher density such as a sugar solution, S) occupies the lower half-space ($y < 0$), and the lighter one (*e.g.* water, W) lies entirely above the initial interface placed at $y=0$ at time $t=0$. The total depth of liquid S is y_0 ($y_0 < 0$). Figure 1a shows schematically the deflection of a probe laser beam which is incident perpendicular to the wall of the cuvette at the position $y=y_1$. The origin of y is the elevation where two liquids were brought in contact at $t=0$. Parallel to Fig. 1a, Fig. 1b shows the concentration profiles $C_S(y, t)$ at instants $t=0$ and $t>0$. When we assume a semiinfinite W column and a finite S column, as existed in the experiment, conservation of the diffusing species requires

$$\frac{\partial^2}{\partial y^2} C_S(y, t) = \frac{1}{D_S} \frac{\partial}{\partial t} C_S(y, t) \quad (2a)$$

with boundary and initial conditions:

$$C_S(y < 0, t=0) = C_{S0} \quad (2b)$$

$$C_S(y > 0, t=0) = 0 \quad (2c)$$

$$\left. \frac{\partial C_S(y, t)}{\partial y} \right|_{y=y_0=-|y_0|} = 0. \quad (2d)$$

D_S is the diffusion coefficient of the liquid S (sugar) in the liquid W (water). Using a Laplace transform approach yields the solution to Eq. (2):

$$\hat{C}_S(y, s) = \frac{C_{S0}}{s} \left\{ 1 - \frac{1}{2} \left[e^{qy} + e^{-q(2|y_0|+y)} \right] \right\} \quad (3)$$

where $\hat{C}_S$ is the Laplace transform of the concentration, s

is the Laplace variable, and $q=(s/D_S)^{1/2}$. Inversion of Eq. (3) into the time domain gives the profile

$$C_S(y, t) = \frac{C_{S0}}{2} \left[\operatorname{erfc}\left(\frac{y}{2\sqrt{D_S t}}\right) - \operatorname{erfc}\left(\frac{2|y_0|+y}{2\sqrt{D_S t}}\right) \right] \quad (4)$$

where the complementary error function is defined as

$$\operatorname{erfc}(q) = \frac{2}{\sqrt{\pi}} \int_q^\infty e^{-x^2} dx \quad (5a)$$

with the useful property:

$$\operatorname{erfc}(-|y|) = 2 - \operatorname{erfc}|y|. \quad (5b)$$

In the limit of semiinfinite S ($y_0 \rightarrow -\infty$), Eq. (4) simplifies to the expression derived by Crank.⁷

The LBD problem

For small concentrations $C_S(y, t)$ it is reasonable to assume² a linear dependence of the liquid refractive index on C_S :

$$n(y, t) = n_0 + \left(\frac{\partial n}{\partial C_S} \right)_{C_S=0} C_S(y, t) \quad (6)$$

where

$$n_0 = n_{H_2O} \approx 1.33 \quad (7)$$

and higher order terms, $C_S^2(y, t)$, in the Taylor expansion, Eq. (6), have been neglected. In many experimental instances, and for small concentrations C_{S0} , it is furthermore true⁸ that the value of $\partial n / \partial C_S$ is independent of C_S , *i.e.*

$$\left. \frac{\partial n}{\partial C_S} \right|_{C_S=0} = \left. \frac{\partial n}{\partial C_S} \right|_{C_S>0} \quad (8)$$

which facilitates this analysis and was found to be valid within experimental error. Using an optical path extremum (Fermat's) method, the optical path p of the probe laser beam of Fig. 1a can be rigorously described by:

$$dp = dx + dy \Rightarrow dp = dy \sqrt{\left(\frac{dx}{dy}\right)^2 + 1} \quad (9)$$

and by Fermat's principle

$$\int_S n(y, t) dp = \text{minimum}. \quad (10)$$

It can be shown that Euler's equation for this extremum can be satisfied by the following functional form⁸

$$\frac{n(y, t)(dx/dy)}{\sqrt{(dx/dy)^2 + 1}} = C_1 \text{ (a constant independent of } y). \quad (11)$$

The boundary condition for normal incidence at $x=0$ is (Fig. 1a):

$$\lim_{x \rightarrow 0} \left(\frac{dx}{dy} \right) = \infty,$$

Fig. 1 Details of the geometry of liquid-liquid interdiffusion as probed by LBD. (a): the LBD trajectory at instant $t > 0$, with the laser beam incident at position $y=y_1 < 0$; (b): the corresponding concentration profile of S, $C_S(y, t)$, at instants $t=0$ and $t > 0$.

so that

$$C_1 = n(y_1, t). \quad (12)$$

Equations (11) and (12) show that the trajectory $x = x(y, t)$ of the probe laser beam incident at $y = y_1$ is given in differential form by:

$$dx(y, t) = \frac{dy}{\sqrt{n^2(y, t) - n^2(y_1, t)}} \times n(y_1, t). \quad (13)$$

The total bending distance $\Delta y(t)$ over the cuvette thickness L is found by integrating Eq. (13)

$$L = n(y_1, t) \int_{y_1}^{y_1 + \Delta y(t)} \frac{dy}{\sqrt{n^2(y, t) - n^2(y_1, t)}}. \quad (14)$$

In principle, explicit integration yields $\Delta y(t)$; however, in practice, Eqs. (4) and (6) result in a non-closed form for the integral. Note that the denominator of the integrand in Eq. (14) is always real and positive, since the refractive index increases with increasing solute concentration, C_s ; therefore, for $|y| > |y_1|$ on the $y < 0$ side, we find $n(y, t) > n(y_1, t)$, as shown in Fig. 1b. The important path integral in Eq. (14) can be solved analytically upon introducing the (experimentally verifiable) small deflection approximation:

$$(\Delta y)_{\max} \ll L. \quad (15)$$

A Taylor expansion of $n(y, t)$ about $y = y_1$ gives from Eqs. (4) and (6), and in the limit $|y_0| \gg |y_1|$:

$$n(y, t) \approx n(y_1, t) - \frac{\delta n}{\sqrt{\pi D_{st}}} (y - y_1) \exp\left(-\frac{y_1^2}{4D_{st}}\right) \quad (16)$$

where:

$$\delta n \equiv \frac{1}{2} \left(\frac{\partial n}{\partial C_s} \right)_{C_s = C_s(y_1)} C_{s0} \ll n_0. \quad (17)$$

Now, Eq. (14) can be conveniently written:

$$L = -\frac{n(y_1, t)}{F(y_1, t)} \int_0^{\Delta y(t)} \frac{dz}{\sqrt{z^2 + 2[n(y_1, t)/F(y_1, t)]z}} \quad (18)$$

with the definition:

$$F(y_1, t) \equiv \frac{\delta n}{\sqrt{\pi D_{st}}} \exp\left(-\frac{y_1^2}{4D_{st}}\right). \quad (19)$$

This integral can be readily solved:

$$|\Delta y(y_1, t)| = 2R(y_1, t) \sinh^2[L/2R(y_1, t)] \quad (20)$$

where

$$R(y_1, t) \equiv n(y_1, t)/F(y_1, t). \quad (21)$$

Beam refraction and signal detection

Although Eq. (20) describes the maximum deflection of the probe laser beam at $x = L$ when incident at position $x = 0$, $y = y_1$, the deflection detected at distance $x = l + L$

Fig. 2 The effect of refraction at the optical detector plane $x = l + L$. For $l \gg L$, it may be assumed that $\overline{AB} \approx \overline{A'B}$.

must include the change in direction of the beam after it exits from the cuvette. This is due to refraction at the wall $x = L$, which is the cell-air interface. It is well-known that refraction can significantly alter the measured value of the angular deflection⁸, thus introducing error of several degrees in the data. Figure 2 shows the beam exit geometry in the presence of refraction. At $x = L$, Snell's law requires

$$\sin[\beta(y_1, t)] = n[y_1 + \Delta y(y_1, t)] \sin[\alpha(y_1, t)]. \quad (22)$$

To calculate $\alpha(y_1, t)$ it can be seen from Fig. 1a that

$$\tan \alpha = \frac{dy}{dx} \Big|_{y=y_1 + \Delta y}. \quad (23)$$

Combining with Eq. (13), the identity

$$\sin \alpha = \frac{\tan \alpha}{\sqrt{1 + \tan^2 \alpha}} \quad (24)$$

gives

$$\sin[\alpha(y_1, t)] = \frac{\sqrt{n^2(y_1 + \Delta y) - n^2(y_1)}}{n(y_1 + \Delta y)} \quad (25)$$

so that

$$\sin[\beta(y_1, t)] = \sqrt{n^2(y_1 + \Delta y) - n^2(y_1)}. \quad (26)$$

Now, from Fig. 2, the expression for $\overline{AB}(y_1, t)$ is

$$\overline{AB}(y_1, t) \approx \overline{A'B}$$

for $l \gg L$, or, equivalently, $\overline{AA'} \ll \overline{AB} = l \tan[\beta(y_1, t)]$ or

$$|\overline{AB}| \approx Ll \frac{Q(y_1, t)}{\sqrt{1 - \left[\frac{L}{n_0}\right]^2 Q^2(y_1, t)}} \quad (27)$$

where, from Eqs. (16) and (19) the function Q can be written approximately as

$$Q(y_1, t) = F(y_1, t) \left\{ \frac{1 + L^2/2R^2(y_1, t)}{\sqrt{1 + L^2/R^2(y_1, t)}} \right\} \quad (28)$$

Equations (27) and (28) completely define the solution to the LBD problem with refraction taken into account.

Experiment and Results

Fresh solutions of commercially available sugar in room temperature water were prepared and poured in a cuvette made of plexiglas, to a depth such that the semi-infinite approximation, $y_0 \rightarrow -\infty$ in Eq. (4), was valid for all diffusion times of interest. Since $D_b \sim O(10^{-6} \text{ cm}^2/\text{s})^9$, no concentration increases due to reflections at the boundary $y=y_0$ were expected. Room temperature water was then introduced on top with a pipet, producing an undisturbed, homogeneous interface at $t=0$, with two separate layers, as per Fig. 1b. A 2 mW He-Ne laser was used with the incident beam perpendicular to the cuvette side at $x=0$. The intensity of the laser was chopped with a mechanical chopper at 20 Hz, with the chopper placed on the exit side of the beam, so as to avoid any possible contribution to the deflection due to synchronous photothermal wave effects.¹⁰ Such effects would, nevertheless, be negligible, as sugar solutions are transparent in the red to near infrared range around the 632.8 nm He-Ne probe beam wavelength. Chopping was introduced in these experiments only to enable us to use lock-in detection with its concomitant high noise rejection efficiency. The emerging chopped beam was intercepted by a silicon photodiode at $x=l+L$, Fig. 2, mounted on a vertical micrometer stage moving along the plane AB. A lock-in amplifier was used to demodulate the photodiode signal and to determine accurately the position $\overline{AB}(y_1, t)$ of the beam intensity maximum. The cuvette was also mounted on a vertical stage, allowing the positioning of the laser beam, y_1 , across either side of the liquid-liquid interface. Subsequently, during several experiments the time evolution of $\overline{AB}(y_1, t)$ was monitored. A typical curve of the time evolution of the LBD signal is shown in Fig. 3. In that figure a range of intermediate-time data points is missing; these points correspond to times during which the experiment remained unattended overnight, which is the con-

sequence of the very slow diffusion of sugar, along with our lack of automation for our experiments. Note from the time span of the t -axis that the entire experiment of Fig. 3 lasted for more than 18 hours. Similar comments can be made about the missing ranges of data in Fig. 4. Returning to Fig. 3 the minimum in the curve can be found from Eqs. (27), (28) upon setting:

$$\left. \frac{\partial}{\partial t} \overline{AB}(y_1, t) \right|_{t=t_{\min}} = 0. \quad (29)$$

Condition (29) is equivalent to $\partial Q(y_1, t)/\partial t=0$, which gives $\partial F(y_1, t)/\partial t=0$ as the only minimum point. From Eq. (19) one thus obtains

$$t_{\min} = y_1^2 / 2D_s. \quad (30)$$

Therefore, knowledge of $(y_1, t_{\min})$ immediately determines the diffusion coefficient D_s . However, the measured position of the laser beam, distance y_1 , which was also nominally the distance between the incident laser probe beam at $x=0$ and the initial (sharp) liquid-liquid interface could not accurately represent the position of the interface, because the interface was of finite thickness at the beginning of our measurements. In order to overcome this problem, it was assumed that the actual initial liquid-liquid interface at $t=0$ was at $y=Y$, so that the laser beam was actually located at a distance y_1+Y away from the interface on the sugar side. Equation (30) is thus modified accordingly, so that the maximum deflection occurred at time

$$t_{\min}^s = (|y_1| + Y)^2 / 2D_s. \quad (30')$$

A simultaneous and similar measurement to that of Fig. 3 on the other (the water) side of the interface, with the laser beam at position y_2 , yielded a minimum at time

$$t_{\min}^w = (y_2 - Y)^2 / 2D_s. \quad (30'')$$

Note that there is no inherent need to perform measurements on both sides of the interface. Any two measured points y_1 and y_2 can be chosen on the same side and the measured two $t_{\min}$ will give the same information. The diffusion coefficient, D_s , and the unknown interface offset value, Y , were then calculated from Eqs. (30', 30'') with the knowledge of the measured values y_1 and y_2 . Figure 4 shows the fit of Eq. (27) to the data of Fig. 3, with the quantity δn as the only adjustable parameter and the value $D_s = 2.599 \times 10^{-6} \text{ cm}^2/\text{s}$ obtained from the modified Eq. (30) as discussed above. Similar measurements with other sugar concentrations yielded variations of $\pm 0.35 \times 10^{-6} \text{ cm}^2/\text{s}$ on the above value. This value is to be compared with the literature value⁹ of $0.254 \text{ cm}^2/\text{d}$, or $2.9 \times 10^{-6} \text{ cm}^2/\text{s}$. The agreement between these two values is satisfactory, in view of the fact that neither our sample supplier nor the literature-cited provide any information on the structure and molecular weight of the sugar used in these experiments. The best-fit value for δn in Fig. 4 was found to be

$$\delta n = 0.67. \quad (31)$$

Fig. 3 LBD signal from commercial sugar (specific gravity 1.2296)/water interdiffusion. $y_1=2.529 \text{ mm}$, $l=13.4 \text{ cm}$, $L=5.0 \text{ mm}$; $t_{\min}=12300 \text{ s}$, $F_{\min}=0.142 \text{ mm}^{-1}$.

Fig. 4 Theoretical fit of Eq. (27) to the data of Fig. 3 with the value of $D_s = 2.599 \times 10^{-6} \text{ cm}^2/\text{s}$ obtained from Eqs. (30', 30'') and $\delta n = 0.67$: (a) early diffusion; (b) late diffusion. The offset distance Y was found to be -6.51 mm .

Although the fit of the theory to the data is excellent at early times ($t < 2 \times 10^4 \text{ s}$), the late-time group of the data points in Fig. 4b is not very well represented by the theoretical model. This discrepancy, though not entirely understood at present, is not important to the overall quantitative aspects of this work, as the pertinent interdiffusion parameters D_s and δn can be obtained from the early data alone. A plausible explanation may lie in the potential time-dependence of the effective average diffusion coefficient $\langle D_s \rangle$ of the molecularly composite sugar mixture used in these experiments (sucrose plus other sugars of unknown molecular weights). In such a case long-term diffusion in water would tend to spatially separate out the various sugar groups, with the lighter molecules diffusing faster, so that the average diffusion coefficient value might exhibit measurable deviations at the long-time end of the experiment. Future experimentation with pure sucrose is expected to test this hypothesis.

Besides the best-fit approach to the calculation of the δn value, a simple method will now be presented which gives a fairly accurate numerical expression for δn directly from the data curve of Fig. 3, without recourse to fitting. If Eq. (30) is substituted in Eq. (19), the minimum value of $F(y_1, t)$ is

$$F_{\min}(y_1, t_{\min}) = \frac{\delta n}{\sqrt{\pi e D_s t_{\min}}} \quad (32)$$

or

$$\delta n = 2.066 F_{\min} y_1. \quad (33)$$

From numerical simulations of Eq. (28), the approximation

$$Q(y_1, t) \approx F(y_1, t) \quad (34)$$

is very good, with $L/R(y_1, t) \ll 1$. Equation (27) may be simplified:

Fig. 5 Data reconstruction of refractive index, n , dependence on molar concentration, M , of sucrose from Ref. 11. n_0 is the refractive index of pure water. The data were obtained upon exposure to sodium yellow light.

$$|\overline{AB}(y_1, t)| \approx L I F(y_1, t)$$

or

$$F_{\min}(y_1, t_{\min}) = \frac{|\overline{AB}(y_1, t_{\min})|}{L I} \quad (35)$$

In the set-up of Fig. 2 and the curve of Fig. 3 with $y_1 = 2.529 \text{ mm}$, Eq. (35) gives $F_{\min}(y_1, t_{\min}) = 0.142 \text{ mm}^{-1}$. Therefore, Eq. (33) gives $\delta n = 0.744$, an estimate within 11% from the best-fit value of 0.67. Similar or better accuracies were also recorded using other sugar concentrations. This quick method can be used with liquid-liquid systems to give good approximations to the otherwise difficult to estimate $\partial n / \partial C$ coefficients. For the sugar-water system, the $\delta n = 0.67$ value results in the condition $\delta n < n_0$, which is weaker than condition (17). The excellent fit of the theory to the data of Fig. 4a, however, is a strong indicator that, despite the weaker condition, the first-order Taylor expansion remains a very good approximation and higher terms in the Taylor expansion, Eq. (16), are not required. Assuming the $\delta n = 0.67$ value, and that our samples consisted entirely of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (molecular weight 342 and specific gravity 1.2296), the most important commercial sugar, the defining equation (17) for δn yields for the first time

$$\frac{\partial n}{\partial C_s} = \frac{2 \times 0.67}{3.595 \text{ mol/l}} = 0.373 (\text{mol/l})^{-1}. \quad (36)$$

A qualitative comparison of our value for $\partial n / \partial C_s$ can be made with the measured dependence of the refractive index on the concentration of pure sucrose.¹¹ Figure 5 shows the published data in Ref. 11 reconstructed and exhibiting essentially linear behavior. The slope of the curve yields

$$\frac{\Delta n}{\Delta M} \approx 0.405 (\text{g-mol/l})^{-1} \quad (37)$$

which compares reasonably well with our extracted value, in view of the fact that i) the He-Ne optical wavelength used was different from the sodium yellow light of Ref. 11; and ii) the sucrose content of our commercial sugar sample was unknown. The use of the methodology described in this paper can, indeed, replace a tedious and time-consuming series of experiments of different concentrations $M=C_s$ in order to extract the $\partial n/\partial C$ value, by measuring the refractive index gradient at a single concentration. It should also be proven valuable in cases where the $\partial n/\partial C_s$ is not constant, corresponding to a non-linear curve in the plot of Fig. 5.

A quantitative LBD study was undertaken for beam deflections purely due to concentration gradients in two interdiffusing liquids. The excellent fit of the experimental data curve with the developed theory, especially at early times, was consistent with the D_s value calculated from the deflection at $t_{\min}$, and was shown to yield high accuracy measurements of the diffusion coefficient. It was also found to be a new and simple method to measure the refractive index gradient with concentration, which is conventionally a complicated task.⁸ $\partial n/\partial C$ is a measure of the degree to which the laser beam bends towards the denser liquid region in its trajectory across the cuvette, as well as a physical property of every liquid solution. Future applications to biomedical diffusion problems may be expected using this technique.

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