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Digital speckle pattern interferometric measurement of diffusion coefficients in hydrogels*

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Abstract: The technique of real-time digital speckle pattern interferometry is proposed to study diffusion of surfactants in hydrogel. The diffusion coefficient is simply and directly determined from the interferograms. An example of diffusion coefficient measurement of surfactant in agarose gel demonstrates the usefulness of the method. The results obtained are compared with the theoretical simulating values.

Key words: Hydrogel, Diffusion coefficient, Speckle pattern interferometry, Surfactant
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INTRODUCTION

The rate of diffusion of surfactants in gels is an important property both for the characterization of solute-gel interactions and for the design of novel applications of such materials (Kong et al., 1997). Conventionally, diffusion coefficients in gels are measured by monitoring the concentration of the diffusing solute in the solution outside the gel. Holographic interferometry technique offers a powerful tool for non-contact measurement. It had been used to measure diffusion coefficients in binary liquid systems in the past (Becsey et al., 1971; Bochner et al., 1976; Gabelmann-Gray et al., 1979; Szydlowska et al., 1982; Ruiz-Bevia et al., 1985). Recently, this technique was employed for liquid-gel or gel-gel system (Gustafsson et al., 1993; Kosar et al., 1995; Ruiz-Bevia et al., 1989). The method has several advantages. It is a direct method which avoids sampling and analysis of the liquid solution outside the gel. No mass balances are needed since the concentration in the gel is monitored directly. But holographic interferometry is based on photographic techniques, the process of film development makes their handling complicated. In this letter, we present digital speckle pattern interferometry (DSPI) and simple image processing to measure the diffusion coefficients in gels. The technique is also known as TV holography. A CCD camera is used as the recording device. The main advantages of DSPI are the ease of recording the holographic interferograms and analyzing the data and the possibility of observing the object in near real-time. Quantitative phase information can be obtained with phase measuring algorithms. In the present work, the diffusion process of surfactants in agarose gels was monitored by DSPI. The diffusion coefficients were simply and directly measured form the interferograms. The theoretical simulation of diffusion coefficients was also performed and compared with experimental results.

EXPERIMENTAL METHOD

Fig.1 shows a diagram of our DSPI apparatus. A continuous wave He-Ne laser emitting coherent light at 632.8 nm was used as the light source. The laser beam was divided into a reference beam and an object beam by a beam splitter. Each beam was focused through a pinhole spatial filter by a 25 × microscope objective, and

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then passed through collimating lenses. The object beam traversed the diffusion cell and the reference beam was reflected in the same way as the object beam. The two beams impinged on the CCD array. In order to produce a speckle interferogram it was necessary to introduce a ground glass plate as speckle source into the object beam. The interference fringes were recorded with a CCD camera. The diffusion cell was a 1.0×4.5 cm spectrophotometric cuvette with a 5 mm light path.

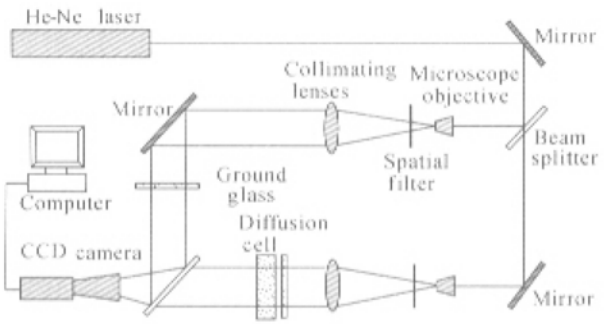

Fig. 1 Experiment arrangement for diffusion measurement in hydrogel by DSPI

In order to prepare agarose gels for diffusion measurements, a pure agarose solution at a specified weight percentage (1% to 3%) was prepared by mixing agarose powder and deionized water slowly heating to the solution boiling temperature. The solution was kept at this temperature until the agarose was completely dissolved, and then cooled down to approximately 40℃. Additional deionized water was added to compensate for the loss due to evaporation. The solution was stirred on a warm plate until it appeared homogeneous, then transferred using a syringe to a glass spectrophotometric cuvette, which was then cooled at room temperature for at least an hour to ensure complete gelation. A rectangular plastic was inserted into the cell to keep the gel upper surface in a plane. The surfactant solution used was 0.17 mol/L C_4PyCl solution.

DIFFUSION COEFFICIENT CALCULATION

In the DSPI technique, the intensity distribution $I(x, y)$ of speckle correlation fringes corresponding to the refractive index variation can be calculated from two intensities at different time by subtracting and taking the modulus. The process can be shown mathematically (Song et al., 1997; Dyrseth et al., 1997) as

$$I^2(x, y) = 8A_0^2(x, y)A_r^2(x, y) \cdot \sin^2(\Delta\varphi(x, y)/2) \tag{1}$$

where $A_o^2(x, y)$ and $A_r^2(x, y)$ are the real amplitudes of the object and the reference beams, respectively. $\Delta\varphi(x, y)$ is the phase difference due to the refractive index variation in the diffusion process.

The diffusion process is governed by Fick's law, which for 1-D diffusion can be expressed as (Crank, 1975)

$$\partial C/\partial t = D(\partial^2 C/\partial t^2) \tag{2}$$

where D, the diffusion coefficient, is independent of the concentration in the interval of concentrations considered. The diffusion equation and boundary condition in the solute-gel system in a cell can be expressed as

$$\begin{aligned} &\frac{\partial C}{\partial t} = D_g \frac{\partial^2 C}{\partial x^2}, \quad 0 < x < l_g, \\ &\frac{\partial C}{\partial t} = D_s \frac{\partial^2 C}{\partial x^2}, \quad -l_s < x < 0, \\ &D_g \frac{\partial C}{\partial x} = D_s \frac{\partial C}{\partial x}, \quad x = 0, \\ &\frac{\partial C}{\partial x} = 0, \quad x = -l_s, x = l_g, \end{aligned} \tag{3}$$

where D_g and D_s are diffusion coefficients in gel and in solution, respectively. l_g and l_s are the gel length and solution length, respectively.

If we consider this as an infinite system, the solution of this equation, in the case of two media initially separated at the point $x = 0$ is

$$C(x, t) = A + B\int_0^{x/2\sqrt{Dt}} \exp(-\eta^2)\mathrm{d}\eta \tag{4}$$

where constants A and B satisfy the initial conditions.

As a result of the diffusion process occurring in the cell, the concentration gradient changes as a function of time. If the refractive index varies linearly with the concentration, the change of the index of refraction between times t_1 and t_2 can be expressed as

$$n(x, t_1) - n(x, t_2) = K[C(x, t_1) - C(x, t_2)] \quad (5)$$

where K is a constant.

When the interferogram is formed, a series of interference fringes appears superimposed on the image of the cell whenever the following condition is satisfied,

$$n(x, t_1) - n(x, t_2) = (2k + 1)\lambda/2d \quad (6)$$

where k is the interference order, λ is the wavelength of the light used, and d is the thickness of the gel that the light goes through. Thus, for the fringe of the pth order that appears in position x_1, we may obtain,

$$(2p + 1)\lambda/2d = K[C(x_1, t_1) - C(x_1, t_2)] \quad (7)$$

and for the qth order fringe that appears in position x_2,

$$(2q + 1)\lambda/2d = K[C(x_2, t_1) - C(x_2, t_2)] \quad (8)$$

Combining Eqs. (7) and (8), we have

$$[C(x_1, t_1) - C(x_1, t_2)]/(2p + 1) = [C(x_2, t_1) - C(x_2, t_2)]/(2q + 1) \quad (9)$$

the diffusion coefficient being that value satisfies meets the Eq. (9).

EXPERIMENTAL RESULTS

Fig. 2(a) shows the original DSPI fringe pattern with carrier fringes. This pattern was obtained by subtracting two images acquired at t_1 = 6300 s and t_2 = 9000 s in surfactants diffusing in 2wt% agarose gel. After digital image processing, including filtering speckle noise, extracting the fringe skeletons and thinning the skeletons, we obtained the skeletonized fringes shown in Fig. 2(b) used for automatic measurement of the diffusion coefficient.

The diffusion coefficient is calculated separately for each pair of fringes with the same interference order. The results are presented in Table 1. The diffusion coefficients obtained from Eqs. (4) and (9) are based on infinite diffusion system, and those obtained from Eqs. (3) and (9) are based on a finite system in which the surfactant C_4PyCl diffusion coefficient in water, $D_s = 1.26$ cm^2/sec, was used. We can note that the coefficients obtained from the two treatments are very close to each other. We think that in the primary time in the diffusion process, we can treat the diffusion process as an infinite system. Table 2 shows the experimental results for 1 wt% agarose gel with different gel length (1.4, 1.9 and 2.5 cm).

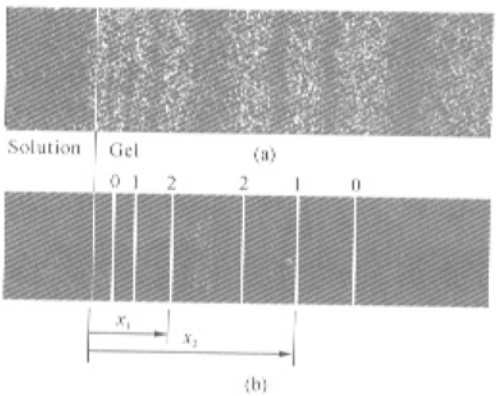

Fig. 2 (a) Original DSPI correlation fringes, and (b) the corresponding keletonized fringes, for t_1 = 6300 s, t_2 = 9000 s, 2 wt% agarose gel

The experimental results showed no significant differences in the standard deviations between diffusion into the gel with different length. The main sources of errors came from the coarseness of the fringe pattern which limits the accurary of locating of the fringe peak in the digital image processing. Fig. 3 shows the experimental and theoretical values of surfactants in 1 wt%, 2 wt% and 3 wt% agarose gel. The theoretical value was simulated by theory from literature (Phillips et al., 1990).

Table 1 Diffusion coefficient values from the fringes shown in Fig. 2

Interference Order	x_1 (cm)	x_2 (cm)	Eqs. (4) and (9) D(cm^2/sec × 10^{-5})	Eqs. (3) and (9) D(cm^2/sec × 10^{-5})
0	0.47	1.28	0.964	0.968
1	0.67	1.21	0.934	0.937
2	0.85	1.09	0.945	0.945

Table 2 Diffusion coefficients ($cm^2/sec\ 10^{-5}$) of C_4PyCl in 1wt% agarose gel (gel length: Exp. I 1.4 cm, II 1.9 cm and III 2.5 cm)

t_1(second)	t_2(second)	Exp.I	Exp.II	Exp. III
4500	8100	1.042	0.9734	1.001
5400	7200	1.047	0.9476	1.012
5400	9000	1.061	0.9882	1.049
6300	9000	1.076	1.017	1.022
6300	9900	1.049	0.9870	1.056
6300	10800	1.043	0.9641	1.083
7200	10800	1.051	0.9448	1.087

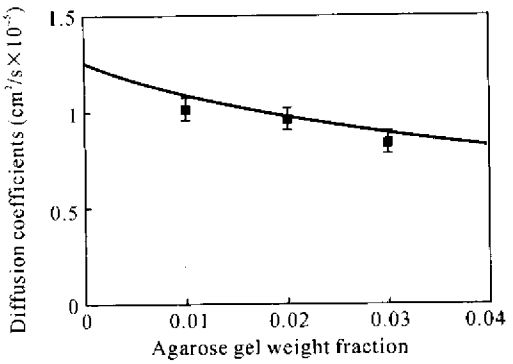

Fig.3 Diffusion coefficients of C4PyCl as a function of agarose gel weight fractio. Solid curve is predicted from the theory of lietrature (Phillips et al., 1990)

CONCLUSIONS

DSPI method is valid for measurement of diffusion coefficients in hydrogel. The method is simple and accurate. Furthermore, we need only know times t_1 and t_2 and measure the distances at which the interference fringes appear. Moreover, it is possible to obtain several diffusion coefficient values from each interferogram and an accurate mean value can be calculated, in contrast to other methods which obtain only one value. The accuracy is higher than when conventional techniques are used and the diffusion process can almost be visualized with digital speckle pattern interferometry, whereas with conventional techniques, the diffusion coefficient has to be measured by means of indirect methods.

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