A New Photoacoustic Method Diffusion study in Soft mater

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Introduction

Hydrogels are widely used in medicine, analytical methods, environmental protection, and others [1]. The study of ion, macromolecule, and nanoparticle diffusion through the spatial gel network is important both for practical applications and fundamental science. However, the experimental study of diffusion using conventional methods is usually costly and/or time-consuming.

In this work, we used a new variant of the photoacoustic (PA) technique to determine the effective diffusion coefficients of dyes. PA methods exhibit high sensitivity to the absorbed part of modulated radiation directed at the target object. Due to the properties of thermal waves and the variety of optical techniques, these methods offer high spatial resolution and flexibility. We used the "drum PA effect" [2] to generate an informative signal. This method allows the use of thin hydrogel layers (hundreds of microns or less) and the observation of changes in the concentration of the absorbing substance in the thin (much thinner than the layer thickness) near-surface region. For comparison, we used the method of optical contrast in digital images. Reducing the layer thickness enables a significant reduction in the experiment's time and the amount of reagents used.

Methods

Agarose gel was prepared by dissolving 180 mg of agarose (Sigma-Aldrich, Agarose For Routine Use) in 10 g of distilled water at 90°C with stirring for 10 minutes. Plates were made by pouring the pre-cooled solution into a gap (400 μm) between two glass plates, preheated to the same temperature. The gel plate was then cut into samples of 10 mm x 10 mm and 15 mm x 15 mm. Smaller samples were kept in the dye solution for one day. The dye concentration was 0.5 g of rhodamine 6G or 5 g of potassium dichromate (K2Cr2O7) per 100 g of water. Larger samples were kept in distilled water during this time.

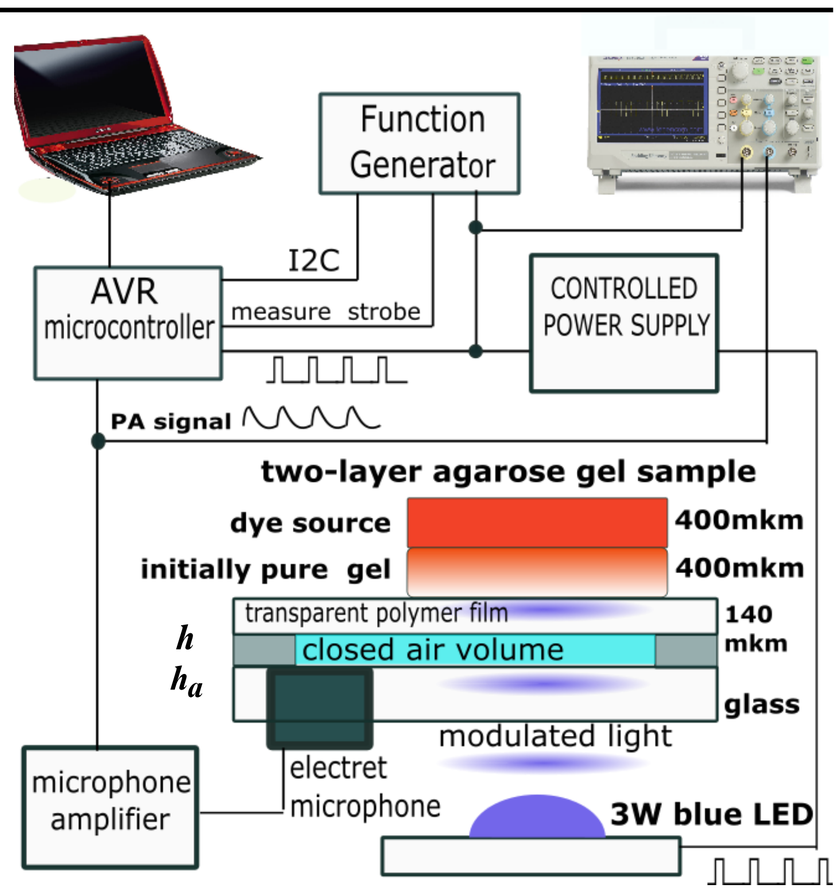


Fig.1 Experimental PA setup

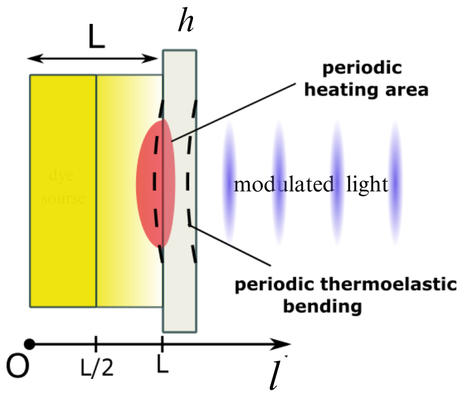


Fig.2 Experimental PA structure

$$P_d = \frac{3\alpha_T r^2}{h^2}\cdot\frac{\gamma P_0 I_0}{h_a \chi_s \sigma_s^2}\cdot\left(\frac{ch(\sigma_s h)-1}{\sigma_s h\cdot sh(\sigma_s h)}-\frac{1}{2}\right);\quad \sigma_s=\frac{j+1}{\mu_s};\quad \mu_s=\sqrt{\frac{T\chi_s}{\pi c\rho}} \qquad (1)$$

The experimental PA setup is shown in Fig.1, and the geometry of the experimental structure is shown in Fig.2. The inner closed volume of the PA cell was formed between the glass base plate and the polyethylene membrane (h=140 μm) with a circular opening in the polyester plate, connected to glass and polyethylene with double-sided tape. The air gap thickness was about 200 μm, and the diameter was 8 mm. Additionally, a channel with a width of 2 mm and a length of 15 mm was made in the specified remote plate to connect the cavity to the electret microphone. The two-layer system consisting of a dyed and undyed gel plate was placed on the surface of the polyethylene plate with the sample without dye facing down. Periodically modulated blue LED light was directed onto the surface of the two-layer sample through both transparent layers (windows) of the cell.

Energy conversion during the FA effect:

Periodic heating → thermoelactic bending → dV → dP_{air} → photoacoustic signal

Results and Discussion

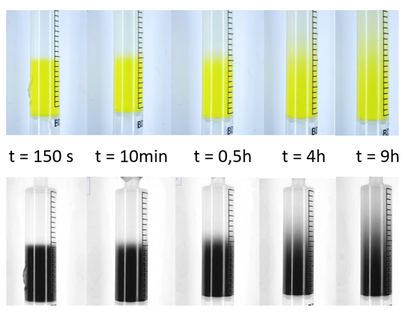
Figure 3 shows the temporal evolution of the PA response shape (one period) during the diffusion process of rhodamine. The change in the amplitude of the first harmonic of the response Fourier series for samples with rhodamine and potassium dichromate over time is presented in Fig.4. The values of effective diffusion coefficients (D) were obtained by overlaying the amplitude dependence (Pd) of the PA signal (concentration dependence of the dye calculated using the known formula (2)). It was assumed that under weak light absorption (in the absence of PA saturation), Pd~C(L) at the boundary between the dye and polyethylene.

$$C = \frac{C_0}{2}+\frac{2C_0}{\pi}\sum_{m=0}^{\infty}(-1)^m\frac{\cos\frac{(2m+1)\pi\ell}{L}}{2m+1}e^{-\frac{(2m+1)^2\pi^2D^2t}{L^2}} \qquad (2)$$

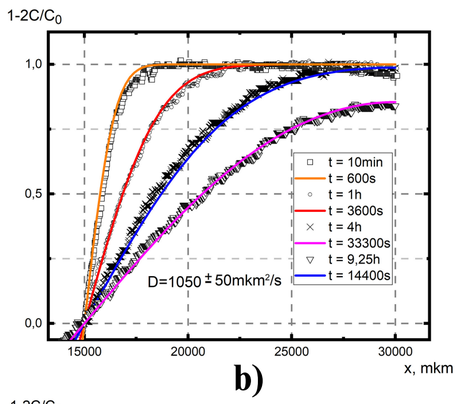
For control, a standard method of changing the optical contrast of a mathematically identical one-dimensional structure of larger size was used (Fig.6).

Fig.3 Evolution of the waveform of the PA signal

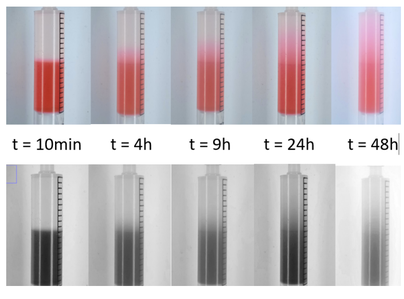
Fig.4 Vary PA signal amplitude over time (scatter). The lines represent theoretical dependencies calculated using expression (2).



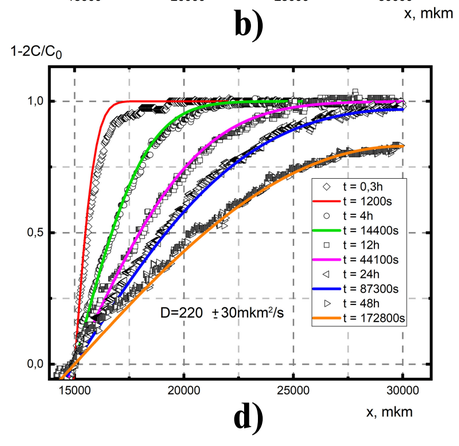
a)



b)



c)



d)

Fig.6 Optical contrast method

Digital images of a gel-filled syringe at various time points during the diffusion process (a, c). The normalized values in the blue channel of the digital image (scatter) and the calculated values (1-2C/C0) according to expression (2) are shown as lines (b, d).

Table 1 presents the values of D obtained by both methods for comparison. The errors of the PA method are mainly due to the error in determining the gel layer thickness. The errors of the optical contrast method are due to:

a) the lack of temperature control,
b) scattering of light by the pure gel reflected from the dyed gel layers,
c) nonlinearity of the camera matrix.

	D_{PA} ($*10^{-6}$ sm^2/s)	D_{OC} ($*10^{-6}$ sm^2/s)
Rhodamine G	1,9±0,2	2,2±0,3
potassium dichromate	10,0±0,5	10,5±1,5

Tab.1 Experimental values of the effective diffusion coefficient obtained by the PA method and the optical contrast method

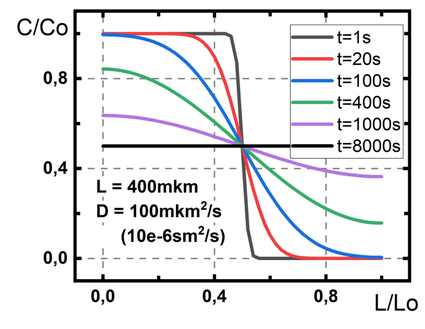


Fig.5 Change over time of the calculated (expression 2) value of the concentration of the dye

Conclusion

Thus, it is demonstrated:

1. the proposed PA method is applicable for estimating the values of diffusion coefficients of light-absorbing particles in transparent hydrogels, including those with strong light scattering;
2. using polyethylene as the working medium for the drum PA effect improves the signal-to-noise ratio in the PA method;
3. the method significantly (by orders of magnitude) reduces the experiment time;
4. the method is simple and requires minimal inexpensive equipment.

References

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