Mass diffusion measurements in liquid crystals by a novel optical method

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(Received 10 August 1977)

Binary mass diffusion measurements have been performed in fluid media doped with photochromic dye molecules. A periodic concentration of tagged molecules is created by illuminating the sample with a fringe intensity pattern. The photo induced change of refractive index and/or absorption of the dye molecules creates an optical grating which is observed through Bragg diffraction of an auxiliary laser beam. When the flash excitation is switched off, this grating will relax since photoexcited molecules will diffuse into nonphotoexcited zones and vice versa. The main advantages of this method are that: (1) the duration of the experiment is strongly reduced compared to classical tracer methods since diffusion lengths, defined by the fringe spacing, are small (1–100 μm); (2) the possibility of studying anisotropic diffusion is readily available; and (3) small sample volumes are required. Results are reported on the diffusion of methyl red in a homogeneously aligned sample of MBBA. In the nematic phase, the diffusion is faster along the local optical axis than perpendicular, the anisotropic ratio $D_{\parallel}/D_{\perp}$ being 1.6 ± 0.1 at 22 °C, in good agreement with previous tracer data. The temperature dependence yields an activation energy of 5.8 ± 0.7 kcal/mole for $D_{\parallel}$ and 6.0 ± 0.8 kcal/mole for $D_{\perp}$. In the isotropic phase, the activation energy is found to be 10 ± 1.5 kcal/mole.

INTRODUCTION

Self and binary mass diffusion of organic molecules in solutions have been extensively studied with a large number of physical techniques. NMR,[1] neutrons,[2] Rayleigh light scattering,[3] radioactive tracers.[4] Several reviews[5] can be found in the literature, from which it appears that each technique has its advantages and drawbacks. What we have in mind here is the measurement of small diffusion coefficients, in the range 10^{-7} to 10^{-11} cm^2/sec. Typical examples are: diffusion in the various liquid crystalline phases[6] or in polymer solutions[7] and also protein diffusion on cell surfaces.[8] So far, the most precise data in these various examples have been obtained by tracer techniques (radioactive, fluorescent dye, ...) However, the duration of the experiment is often prohibitive since diffusion has to be observed on macroscopic distances (0.1–1 cm)[7,9] and diffusion time increases as the square of the diffusion length. In this letter, we present an optical method using photochromic dye molecules as tracers and in which the diffusion length can be easily reduced down to a few μm, without any loss of accuracy. Applications to binary mass diffusion measurements in the nematic and isotropic phase of MBBA yield results in good agreement with previous literature data though experimental time was considerably lower. It also allows for easy and precise measurements of the anisotropic components of the diffusivity parallel and perpendicular to the local optical axis.

THEORY

The new method is derived from the forced Rayleigh scattering technique developed for thermal diffusivity measurements in liquids and solids.[10] Here, interferences between two coherent plane waves issued from a pulsed high power laser, the "writing laser," create a periodic (wave vector q) concentration of photoexcited molecules, by bringing the photochromic dye molecules in the bright fringes to higher excited states. To this concentration distribution is associated a phase and/or absorption optical grating[11] since the optical polarizability of the dye molecules has been modified in the photochromic process. Following the flash excitation, the concentration distribution will be gradually smeared out by diffusion. Thus the optical grating will relax with a time τ characteristic of the translational mass diffusion coefficient D. (We assume here that the optical grating does not relax through a trivial intramolecular relaxation process).

Let us first calculate the concentration distribution $C_1(x, t=0)$ of photoexcited molecules at the end of the writing laser flash. As $c_1(x)$ will be proportional to the local photoexciting light intensity one can write:

$$c_1(x, t=0) \propto c_1(x=0, t=0)\cos^2 qx\,, \tag{1}$$

the origin of time being chosen at the end of the laser flash. Equation (1) assumes that the problem is one dimensional. Indeed, it is well known that interference between two coherent plane waves forms a linear array of stripes (perpendicular to the 0x axis). However, this assumption is strictly valid only if the sample absorbance at the writing wave length λ_0 is small enough so that the concentration of photoexcited molecules throughout the sample thickness l(0z axis) is approximately uniform. More quantitatively, if α^{-1} is the characteristic absorption length of the sample at λ_0 (for a given dye concentration), one should have $\alpha^{-1} \gg l$. If $\alpha^{-1} \sim l$, the problem can still be considered one dimensional, in first approximation, with the supplementary condition that $l \gg i$, where i is the fringe spacing. In this latter case, mass diffusion along the 0x axis is still dominant over diffusion along 0z. This initial concentration distribution of photoexcited molecules relaxes by mass diffusion according to Fick's law as:

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0021-9606/78/6806-2725$01.00

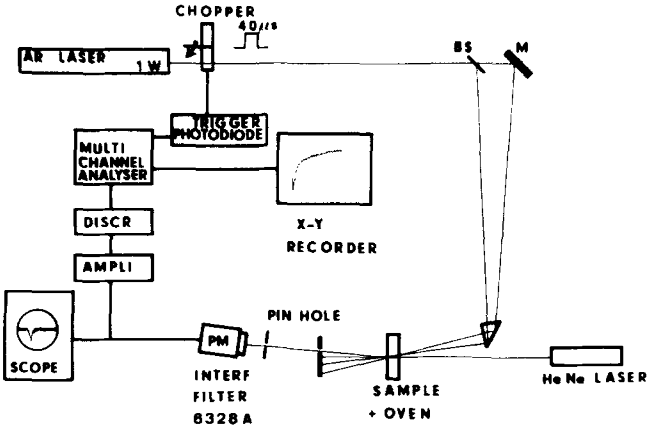


FIG. 1. Experimental set up.

$$\frac{\partial c_1(x,t)}{\partial t} - D\frac{\partial^2 c_1(x\,t)}{\partial x^2} = 0,$$

which gives:

$$c_1(x,t) = c_1(x,0)e^{-t/\tau}$$

with $\tau = 1/Dq^2$. This concentration distribution acts as an optical grating for the reading laser beam. Diffraction theory states that this beam will be diffracted into various diffracted orders. On a screen in the far field, the first order diffracted beam will appear as two bright dots at distance $d = (\lambda_1/i)L$ to the direct beam (L, the distance from the sample to the viewing screen, λ_1 the reading wavelength). The scattered electric field $E(t)$ is proportional to the amplitude of the concentration distribution.[12] As this is the diffracted intensity $I(t)$ which is detected, we will analyze its time dependence in the next paragraph.

EXPERIMENTAL DATA ANALYSIS

The time analysis of the diffracted intensity can be correctly described only if coherence properties of the scattered electric field are taken into account. This problem is well known in quasielastic Rayleigh light scattering.[13] The various scattered electric fields $E_n(t)$ emitted by different parts in the illuminated volume are collected on the phototube over less than one coherence area, so they add up constructively. In that case, the output voltage $Va(t)$ is proportional to $I(t) = |\sum_n E_n(t)|^2$. In the summation we have included scattered electric fields due to the concentration distribution (signal term), but also those due to unavoidable static defects (background term). The former decay with time like $\exp -t/\tau$, while the latter are time independent. Then $Va(t)$ writes:

$$Va(t) = \alpha^2(E_s e^{-t/\tau} + B)^2,$$

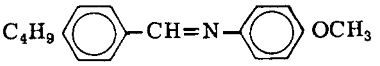
where α^2 is a proportionality factor. The two limiting cases, $E_s \gg B$ or $E_s \ll B$ correspond to the so-called homodyne or heterodyne regimes.[13] In this experiment, we process the data by first determining the $\alpha^2 B^2$ value at long times ($t \gg \tau$) and then plotting on semilog scales $[V_a(t)^{1/2} - \alpha B]$ vs time. The curve should be a straight line of slope τ^{-1}. This yields a direct determination of the mass diffusion coefficient, D, knowing the grating wave vector q from the geometrical conditions.

EXPERIMENTAL SET UP

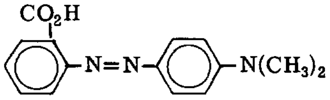
The experimental set up is shown on Fig. 1. The linear fringe pattern which produces the periodic distribution of photoexcited molecules is obtained by splitting the main beam of a 1 W Ar$^+$ laser (Spectra Physics model 165, $\lambda_0 = 5145$ Å) into two beams of equal intensity, converging on the sample. The fringe spacing i can be varied from 5–70 μm, by adjusting the angle Θ between the two interfering beams. The Ar$^+$ laser beam is chopped mechanically to give light pulses of 40 μsec duration, with an adjustable repetition rate from 20 msec –33 min. The exciting laser power was generally kept below 200 mW, giving energy pulses of 8 μJ. The reading laser is a 2 mW He–Ne (Spectra Physics model 133, $\lambda_1 = 6328$ Å) with a beam diameter $a = 1$ m/m. At a distance $L = 130$ cm, the diameter of the coherence area is $\sim\lambda_1 L/a$, i.e., ~ 1 mm. The first order diffracted intensity is detected over less than one coherence area with an RTC-56TVP photomultiplier fitted with a 500 μm pinhole. The phototube output is amplified and fed into a multichannel analyzer (Intertechnique BM 25) used in the multiscaler mode. The time dependence of the diffracted intensity is recorded after each exciting pulse and averaged over 1000 pulses to improve the accuracy (it should be emphasized that single pulse data are already quite good). The data are then processed with an HP 9825 calculator using a least square fit to extract the relaxation time according to the procedure described above.

Binary mass diffusion coefficients have been measured for the nematic liquid crystal *p*-methoxybenzilidene *p*-*n*-butyl aniline (MBBA) doped with low concentrations of methyl red. Methyl red is a dye of the azobenzene series, which are well known to undergo *trans* to *cis* photoisomerism when photoexcited in their absorption band.[14] When dissolved into MBBA, methyl red absorbs practically no 6328 Å incident radiation. On the other hand, about 50% of the energy is absorbed at 5145 Å for dye concentration of 5×10^{-4} (weight) in 200 μm thick samples. This corresponds to $\alpha^{-1} \sim 300$ μm (let us recall that one must have $\alpha^{-1} \gg i$).

The characteristic lifetime of the photoexcited *cis* state is of the order of several seconds[15] which is long enough for our diffusion experiments. Methyl red was also chosen because these dye molecules are similar in size and shape to MBBA molecules.



(MBBA)



(MR)

One can thus expect the binary mass diffusion coefficient to approximate rather well the true self diffusion coefficient of MBBA. The liquid crystal was placed between two silicon monoxide coated glass plates (2 cm × 1.5 cm) separated by a teflon spacer, typically 200 μm thick. Deposition of the SiO coating under oblique inci-

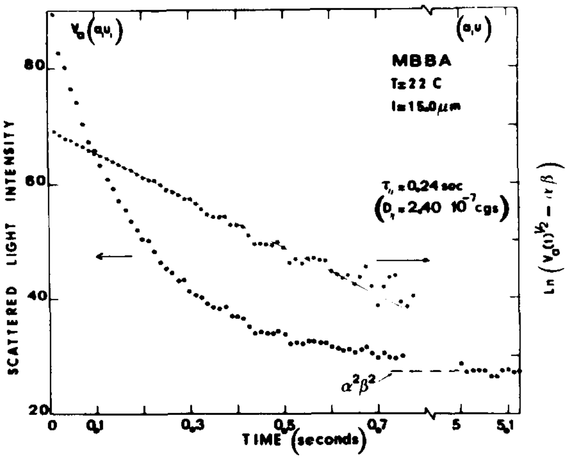


FIG. 2. Left hand side scale: output voltage of the phototube versus time, as obtained on the multichannel analyzer after a 100 pulses averaging. Right hand side scale: semilog plot of the raw data following the procedure described in the text. The best fit gives a decay time $\tau_{\parallel} = 0.24$ sec for the mass diffusion parallel to the long molecular axis, fringe spacing = 15.0 μm; $T = 22$ °C.

dence[16] insures the homogeneous alignment of the nematic liquid crystal with its optical axis parallel to the glass walls. Since sample areas smaller that 5 mm^2 are sufficient for the experiment the best aligned regions, essentially free of disclinations[6] are selected by visual inspection under the microscope. Measurements were made in the nematic phase between 22 and 44 °C in the two geometries, i.e., fringes parallel and perpendicular to the nematic optical axis, respectively, and also in the isotropic phase up to 55 °C.

RESULTS

Figure 2 shows a typical plot of $\mathrm{Ln}[V_a(t)^{1/2} - B]$ vs time in the nematic phase at 22 °C for mass diffusion. The data can always be fitted with a straight line, for diffusion parallel ($D_{\parallel}$) and perpendicular ($D_{\perp}$) to the nematic optical axis, respectively. The accuracy of the determination of τ and of the measurement of i is about 1%. The dependence of τ with the fringe spacing $i = 2\pi/q$ is given on Fig. 3. i was varied between 10 and 70 μm. At low i values, $\tau_{\parallel}$ and $\tau_{\perp}$ are proportional to i^2 and all points align on two straight lines passing through the origin. This is indeed in agreement with a diffusion process for which the characteristic time increases as the square of the diffusion length. Assuming that $\tau = 1/Dq^2$, one then gets: $D_{\parallel} = 2.4 \pm 0.1$ 10^{-7} cm^2/sec; $D_{\perp} = 1.5 \pm 0.1$ 10^{-7} cm^2/sec at 22 °C. At large i values, τ saturates and tends towards a constant value independent of the experimental geometry. We interpret this limiting value of τ as the intramolecular relaxation time τ intra corresponding to the spontaneous deexcitation of the photoexcited state of methyl red molecules. τ intra is found to be ~2 sec, and independent of both the fringe spacing and the geometry as opposed to the relaxation time by mass diffusion τ studied above. τ intra is rather strongly dependent with temperature and care was taken to work at low enough fringe spacing when temperature was varied.

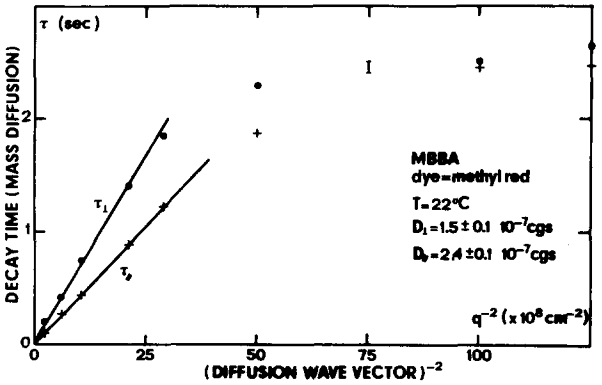


FIG. 3. Experimental decay times for mass diffusion vs the inverse square of the grating wave vector for parallel and perpendicular geometries. $T = 22$ °C. From the slope, one gets $D_{\parallel} = 2.4 \pm 0.1$ 10^{-7} cm^2/sec and $D_{\perp} = 1.5 \pm 0.1$ 10^{-7} cm^2/sec.

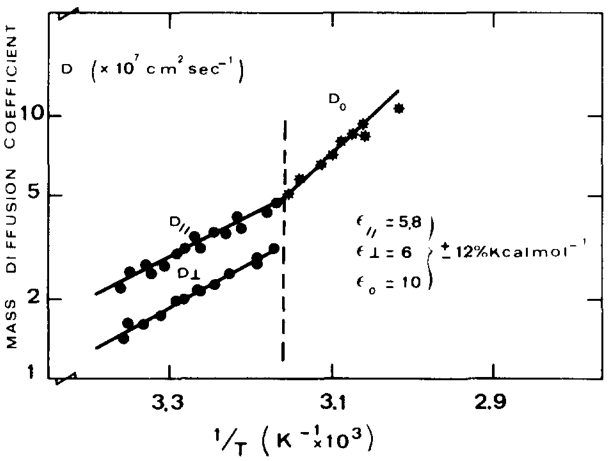


FIG. 4. Temperature dependence of $D_{\parallel}$, $D_{\perp}$, and D_0 in the nematic and isotropic phases MBBA.

The temperature dependence of $D_{\parallel}$ and $D_{\perp}$ in the nematic phase and of D_0 in the isotropic phase is plotted on Fig. 4. In the nematic phase, the anisotropic ratio $D_{\parallel}/D_{\perp}$ decreases from 1.6 at 22 °C down to 1.33 at 42 °C. Above the transition temperature to the isotropic phase, the diffusion is isotropic and the results are independent of the geometry. It should be noted that D_0 shows no observable discontinuity at the nematic to isotropic phase transition.

Numerous determination of $D_{\parallel}$ and $D_{\perp}$ have been made in the nematic phase around room temperature. Although there is a considerable scattering in the data published in the literature[17] we believe that most reliable results are obtained from tracer experiments. A particular easy comparison can be made with the results obtained by a macroscopic dye tracer technique[9] since methyl red was used in both experiments. The agreement with our present data is excellent since $D_{\parallel}$ was reported to be 2.6 ± 0.3 10^{-7} cm^2/sec and $D_{\perp} = 1.6 \pm 0.3$ 10^{-7} cm^2/sec at 22 °C. The temperature dependence of D has been much less studied. In the absence of a satisfying microscopic theoretical description of the translational diffusion in liquid crystalline phases, the temperature dependence is generally described as an activated energy process. Here, we obtained from Fig. 4 that the activation energy for $D_{\parallel}$ is $\epsilon_{\parallel} = 5.8 \pm 0.7$ kcal/mole, for $D_{\perp}$ is $\epsilon_{\parallel} = 6.0 \pm 0.8$ kcal/mole, and for D_0 is $\epsilon_0 = 10 \pm 1.5$ kcal/mole. $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ have very close values. This has already been observed by several authors in different materials (*p*-azoxyanizole,[18] one of the substituted phenyl-4-benzoyloxybenzoates,[17] terephtal-bis-butyl aniline).[19] We confirm here their observation on MBBA also, contrary to a previous report.[20] Our results for $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are in good agreement with the values of 5.0 and 5.4 kcal/mole obtained from NMR measurements on partially deuterated MBBA.[21] Literature values for ϵ_0 are rather scattered between 6.0 and 9.5 kcal/mole,[20-22] to be compared with our 10 ± 1.5 kcal/mole determination.

DISCUSSION

We have demonstrated that forced Rayleigh scattering can be used to measure mass diffusion coefficients in liquid crystals. In this method, one measures the relaxation time of an optically-induced, spatially periodic, concentration distribution of photochromic molecules. Several advantages over previously described techniques are apparent.

(1) A wide range of D values can be investigated typically from 10^{-5} to 10^{-11} cm^2/sec. With the classical tracer techniques, the only other method to cover such a wide range of D, the measurement of very low D implies extremely long experimental times, of the order of several days.[7,9,17,20] Indeed, it is necessary to let the tagged molecules diffuse over macroscopic distances (0.1–1 cm) if accurate results are needed. Here the diffusion length is equal to the fringe spacing (1–100 μm). The duration of the experiment is reduced as the square of the ratio of the diffusion length, i.e., up to 8 orders of magnitude.

(2) In anisotropic materials, the components of the mass diffusivity tensor can be measured by adjusting the spatial orientation of the linear fringe pattern relative to the principal axes of the sample.

(3) Very small samples areas are needed. Well defined diffraction patterns can be obtained with less than ten fringes in the illuminated volume. Therefore, experiments are in principle feasible with samples area ~ 100 μm in diameter. This may be useful for studying materials which are either scarcely available, (biological molecules, some liquid crystals) or difficult to align on large surfaces (smectic phases).

(4) The extreme sensitivity of the Forced Rayleigh scattering has already been discussed elsewhere.[10,15] Refractive index changes of 10^{-7} or optical absorption changes of 10^{-5} are sufficient to give a detectable signal. This is quite useful for solutions with very weak photochromic properties.

The main limitation of this method is the necessity of using photochromic dopants if the sample is not photochromic by itself. Therefore, the true self-diffusion coefficient is usually not measured. However, it is generally agreed that diffusivity of impurities correctly describe that of the solvent molecules when their sizes are comparable.[23] Another possibility would be to photobleach directly the solvent molecules with the writing laser beam. The method is then the analog of the fluorescence photobleaching recovery developed by Axelrod *et al.*.[24] The advantage of using an optical fringe pattern to selectively bleach the sample is a much better definition of the diffusion lengths, thereby allowing for greater accuracy in the measurement of diffusion coefficients. We have already seen that if photochromism is used to tag the diffusing molecules, the intramolecular relaxation time must be longer than the translational diffusion time τ. We do not think that this is a serious limitation since by reducing the fringe spacing to 1 μm, τ can be kept below 1 sec, even for D as low as 10^{-10} cm^2/sec. Moreover, photochromic molecules with very long life time (tens of minutes and more), can be found, spiropyrans being the best known examples.[25]

So far, we have not mentioned that as in every forced Rayleigh scattering experiment, part of the absorbed energy is converted into heat, building up a thermal grating.[10] This grating is superimposed over the one due to the photoexcited molecules, which has been discussed at length here. Following the optical flash excitation, it will relax by thermal diffusion with the same square dependence on the fringe spacing. However, the thermal diffusivity coefficient is 10^2–10^4 times smaller than the mass diffusion coefficient, and the two relaxations are thus widely separated in the time domain. Thermal diffusivity measurements in MBBA doped with methyl red gives D thermal ~ $0.5\ 10^{-3}$ cm^2/sec[26] to be compared with $D_{\parallel} \sim 2\ 10^{-7}$ cm^2/sec for mass diffusion. The sample heating due to the pulsed laser absorption was negligible in all cases, being calculated to be less that 10 m°K with typical 40 μsec pulses of 200 mW power.

Too high exciting laser power had also to be avoided for a completely different reason. It was observed experimentally that above a given energy threshold, the relaxation process could no longer be described by a single exponential. We have no definite explanation for this fact. In some cases, the detected diffracted light intensity was increasing at first, suggesting an autoexcitation of the dye molecules. Similar effects were observed when increasing the dye concentration, at a given input energy level. It is indeed well known that photochromic properties are generally concentration dependent.

CONCLUSION

We have demostrated on liquid crystals that the forced Rayleigh scattering method is an interesting procedure for measurements of translation mass diffusion coefficients. The results seem to be as reliable and accurate as those obtained with more classical tracer techniques, although duration of the experiments is considerably reduced. Therefore, we suggest that this novel optical method can be applied to a wide variety of problems: anisotropic liquid crystalline phases, polymer solutions, biological molecules in solutions or *in situ*.

ACKNOWLEDGMENT

We are very grateful to R. Guglielmetti for many helpful discussions on photochromism. The SiO evaporation was performed by C. Boix.

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