

Diffusion Process of Methyl Red in Organic Solvents Studied by the Transient Grating Method

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Time dependence of the transient grating (TG) signal after the photoexcitation of methyl red (MR) is investigated in organic solvents, especially in benzene, ethanol, and 2-propanol. The origin of the TG signal, which represents the mass diffusion of MR, is attributed to the phase grating. The cis form of MR, which has a slightly smaller molecular size than the trans form, is found to diffuse more slowly than the trans form in alcoholic and aldehyde solutions. The measured diffusion coefficients (D) in the three solvents are compared with theoretically calculated values. It is shown that the measured D are in good agreement with the values calculated by using the modified Stokes–Einstein equation. Diffusion coefficients in 2-propanol at low temperatures are also measured and compared with the calculated values.

1. Introduction

The translational diffusion process in solution is one of the most fundamental processes in chemistry and physics and has attracted many investigators for a long time. Although there are several methods used for the measurement of the diffusion coefficient (D), measuring D is still reputed to be difficult.¹ Therefore D is sometimes estimated from the viscosity and the Stokes–Einstein relationship, which does not always guarantee a reliable value as shown later. Recently, a transient grating (TG) (or holographic grating) technique has been recognized gradually as a direct and sensitive method to study the diffusion process.

In the TG experiment, a sinusoidal pattern is created by the interference of two excitation beams. If the sample contains photochemically active molecules, these molecules are converted to other species in the bright region but not in the dark region. This site-selective excitation induces a spatially modulated distribution of chemical species and it causes a spatially modulated refractive index and/or absorption coefficient. This modulation (grating) diffracts another probe beam entering in this region. The signal decays as the modulation smears out by the diffusion. Therefore, the decay of the TG signal reflects the diffusion process of the probe molecule. Since this method has the advantage that it detects the diffusion in a short distance, the measurement time is dramatically reduced. On the basis of this advantage, the TG method has been applied to measure D of short-lived radicals² or of dye molecules in polymer solutions,^{3–10} polymer glasses,^{11–13} a gel,¹⁴ and liquid crystals.¹⁵ Also because of the high sensitivity of this method, the concentration of the probe dye molecule can be low enough not to perturb the solution dynamics.

In these measurements of dye molecules, methyl red (MR) has been preferably used.^{3–7,11,12,14,15} The photochromic properties of MR are associated with the trans–cis isomerization through its azo linkage. In spite of the extensive usage in slow diffusional matrices, the character of the TG signal of MR in ordinary solution has not been studied. In order to apply this dye to probe the diffusion dynamics, however, it is desirable to know the fundamental properties of the TG signal in ordinary solutions of small molecules.

In this paper, we aim to elucidate the decay characteristics of the TG signal after the photoexcitation of MR for studying the diffusional processes in organic solvents with a pulsed laser and a fast detection system. We show that the TG technique is a convenient means to study the diffusion processes in solution. It is also shown that the decay characters of the TG signal in solution are substantially different from those found in polymers. Al-

though we have examined the TG signal in a number of organic solvents such as methanol, ethanol, 2-propanol, 1-butanol, 2-butanol, benzene, toluene, acetone, diethyl ether, and acetaldehyde, here we choose benzene, ethanol, and 2-propanol solvents as representative systems for extensive analysis and discussion. From the photochemical point of view, we are particularly interested in the diffusion process in 2-propanol, because this solvent has been used frequently in studying photochemical reactions. Since unusually stable radical pairs have been detected in 2-propanol at low temperatures and this has been attributed to the slow diffusion,¹⁶ D in 2-propanol is also measured at low temperatures.

2. Experiment

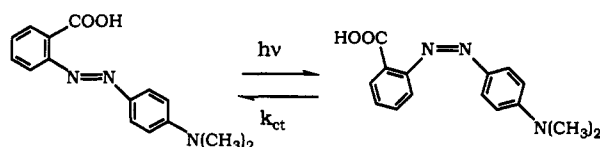
The experimental setup for the TG experiment has been reported previously.¹⁷ Transient grating is created by the interference of two excitation beams from an excimer laser-pumped dye laser (Lumonics Hyper 400, Lumonics Hyper Dye 300) with a 10-ns pulse width. The repetition rate of the excitation pulse was typically ~ 3 Hz to ensure that most of the cis form of MR is converted back to the trans form before the next excitation pulse arrives. A He–Ne laser was brought into the crossing region at the Bragg condition for the probe beam. The diffracted signal was detected by a photomultiplier (Hamamatsu R928) and averaged by a digital oscilloscope (Tektronix 2430A). The crossing angle θ of the two excitation beams was varied from 0.86° to 5.71° . The relaxation time was measured as a function of the crossing angle. The temperature of the solution was varied by flowing temperature-regulated methanol around a copper sample holder with a temperature control system (Lauda RSD6D).

Methyl red was purified by recrystallization. Spectroscopic grade solvents methanol, ethanol, 2-propanol 2-butanol, acetone, and benzene (purchased from Wako Chemical Co.) and 1-butanol, toluene, diethyl ether (Nakarai Co.), and acetaldehyde (Merk Co.) are used without further purification. Concentration of MR was 7.4×10^{-4} M.

3. Analysis

The principle for measuring D has been described in previous papers.^{3–15} Here we briefly summarize the method and what is different from the previous treatments. The trans form is the stable form of MR at room temperature in solution. After photoexcitation of MR to the excited singlet state, it is converted to the cis form and the cis form is gradually converted back to

SCHEME I



the trans form in the dark (Scheme I). In this paper, we neglect the isomerization process from the trans to cis forms in the dark. Usually this process is known to be negligible. Upon irradiation of the sample with the spatially modulated laser beam, the refractive index (n) and absorption coefficient (k) become nonuniform and are periodic functions of the position. While the change of the absorption coefficient (δk_p) is only due to the inhomogeneous distribution of the cis and trans forms of MR, that of the refractive index (δn) comes from the thermal expansion of the medium (δn_{th}) as well as the inhomogeneous distribution of the isomers (δn_p). The grating due to the absorption coefficient and refractive index terms are called the amplitude and phase gratings, respectively. In the previous papers,³⁻¹⁵ the contribution of δn_{th} was usually neglected. However, as shown later, this contribution is important for analyzing the results. We therefore continuously monitor the TG signal from just after the pulsed laser excitation to the complete decay of the signal due to the mass diffusion.

The refractive index and absorption coefficient in the sample solution after the excitation is given by

$$n(x,t) = n_0 + \delta n_p(x,t) + \delta n_{th}(x,t) \quad (1a)$$

$$k(x,t) = k_0 + \delta k_p(x,t) \quad (1b)$$

where n_0 and k_0 are respectively the unperturbed refractive index and absorption coefficient of the solution. By solving the thermal and mass diffusion equations including the back photochemical process from cis to trans with the rate constant k_{ct} , Fourier components of each term, $\delta n_{th}(q,t)$, $\delta n_p(q,t)$, and $\delta k_p(q,t)$ are given by

$$\delta n_p(q,t) = \delta n_1 \exp(-D_c q^2 t) + \delta n_2 \exp(-(D_c q^2 + k_{ct})t) \quad (2a)$$

$$\delta k_p(q,t) = \delta k_1 \exp(-D_c q^2 t) + \delta k_2 \exp(-(D_c q^2 + k_{ct})t) \quad (2b)$$

$$\delta n_{th}(q,t) = \delta n_{th}^0 \exp(-D_{th} q^2 t) \quad (2c)$$

and

$$\delta n_1 = -[\Delta c] \delta n_{th}^0 \frac{D_c q^2 - D_t q^2}{D_c q^2 - D_t q^2 + k_{ct}}$$

$$\delta n_2 = [\Delta c] \left(\delta n_c - \delta n_{th}^0 \frac{k_{ct}}{D_c q^2 - D_t q^2 + k_{ct}} \right)$$

$$\delta k_1 = -[\Delta c] \delta k_{th}^0 \frac{D_c q^2 - D_t q^2}{D_c q^2 - D_t q^2 + k_{ct}}$$

$$\delta k_2 = [\Delta c] \left(\delta k_c - \delta k_{th}^0 \frac{k_{ct}}{D_c q^2 - D_t q^2 + k_{ct}} \right)$$

where subscripts c and t represent the cis and trans forms, respectively, for the corresponding properties. D_{th} is the thermal diffusion coefficient and $[\Delta c]$ is the concentration change of the cis form by the photoexcitation. Here, we have neglected a coupling term between the thermal and mass diffusion, which is usually very small in the organic solvents we examined at room temperature. Since the peaks of the absorption spectra of the cis and trans forms are located at shorter wavelengths than that of the He-Ne laser, both δn_c and δn_t should be positive. Under the thick grating and the weak diffraction conditions, the TG signal

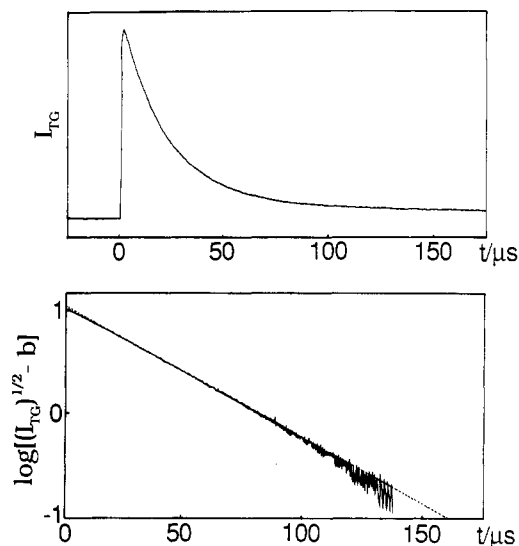


Figure 1. (a, Top) Fast dynamics of the TG signal after the excitation of methyl red in ethanol at room temperature with $\theta = 1.15^\circ$. The main contribution of the signal comes from the thermal grating. The population grating signal is nearly constant in this time scale. (b, Bottom) Plot of $\log((I_{TG})^{1/2} - b)$ vs t .

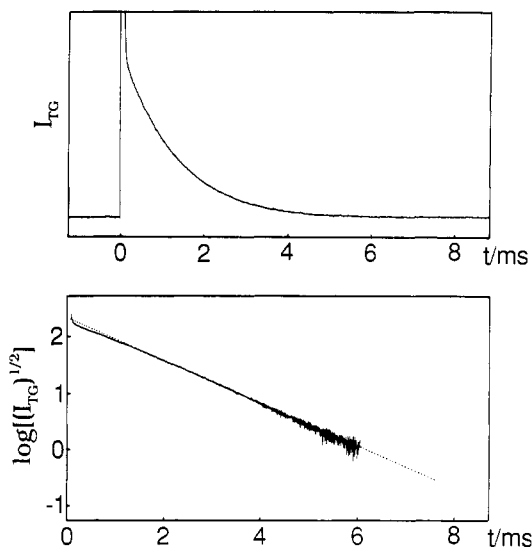


Figure 2. (a, Top) Time dependence of the TG signal, which represents the mass diffusion of MR in ethanol at room temperature with $\theta = 1.15^\circ$. (b, Bottom) Semilog plot of the $I_{TG}^{1/2}$.

intensity $I_{TG}(t)$ at a grating vector q is given by

$$I_{TG}(t) = A(\delta n_{th}(q,t) + \delta n(q,t))^2 + B(\delta k(q,t))^2 \quad (3)$$

4. Results and Discussion

4.1. Characters of the TG Signal in Ordinary Solution. Figures 1-4 show the time dependence of the TG signal after the excitation of MR in benzene, ethanol, and 2-propanol. In the early time region after the excitation, the TG signal due to the thermal grating dominates (Figure 1a). This signal gradually decays owing to the thermal diffusion and then the signal due to the population grating becomes apparent (Figures 2a-4a). The TG signal intensity due to the population grating relaxes to the baseline level at a sufficiently long time. Some authors claimed that the apparent lifetime of *cis*-MR is strongly affected by the probe beam.^{7,12} However, the decay rate of the TG signal does not vary even if the probe laser power is reduced to $\sim 1/10$ under our experimental conditions. Also we confirm that the decay rate does not depend on the repetition rate of the excitation laser from 4 to 2 Hz.

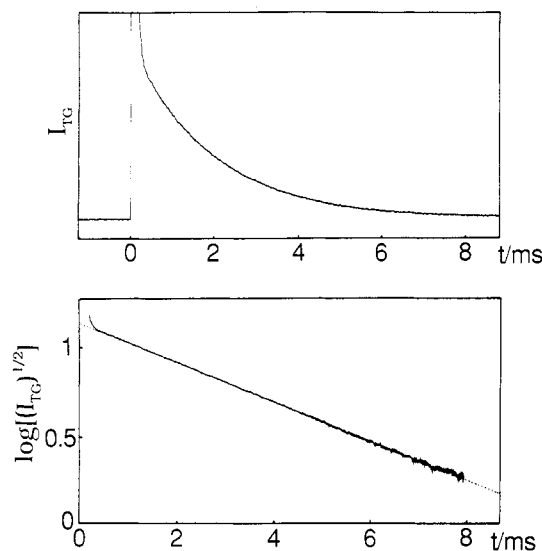


Figure 3. (a, Top) Time dependence of the TG signal, which represents the mass diffusion of MR in benzene at room temperature with $\theta = 1.15^\circ$. (b, Bottom) Semilog plot of the $I_{TG}^{1/2}$.

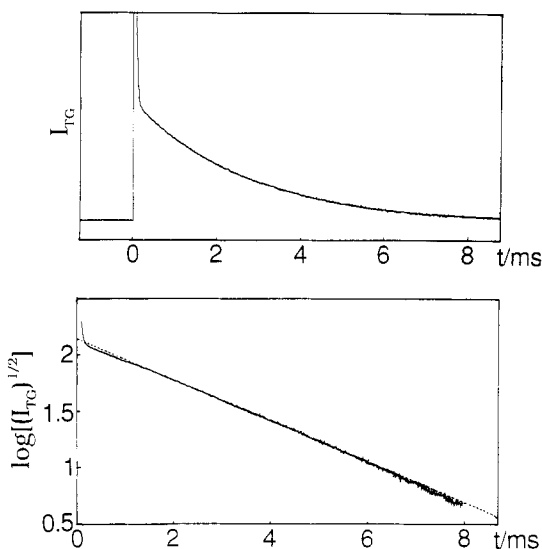


Figure 4. (a, Top) Time dependence of the TG signal, which represents the mass diffusion of MR in 2-propanol at room temperature with $\theta = 1.15^\circ$. (b, Bottom) Semilog plot of the $I_{TG}^{1/2}$.

Although we should first know whether the TG signal due to the mass diffusion comes from the δn_p term or the δk_p term (or mixture of both) in order to analyze the data, the origin has not been clarified so far. Here we try to identify the origin in the following way. In principle, if we fit the TG signal by eq 3, we should know the relative contribution of δn and δk terms. However, the fitting cannot be accurate enough to distinguish the small difference without knowing $D_{th}q^2$. Therefore we first determine $D_{th}q^2$ by fitting the square root of the TG signal with a function

$$a \exp(-D_{th}q^2 t) + b \quad (4)$$

where a and b are constants satisfying $a \gg b$. This is a good approximation, even if the TG signal comes from the amplitude or/and phase gratings, as long as δn_p and δk_p are sufficiently smaller than δn_{th} and both $D_c q^2$ and $D_t q^2$ are sufficiently smaller than $D_{th}q^2$. After the determination of $D_{th}q^2$, we examine if the experimental decay curve can be fitted by eq 3. We find that the $\delta k(q,t)^2$ term in eq 3 is negligible in all the solvents we used. Therefore we conclude that the phase grating is dominant in our experiments.

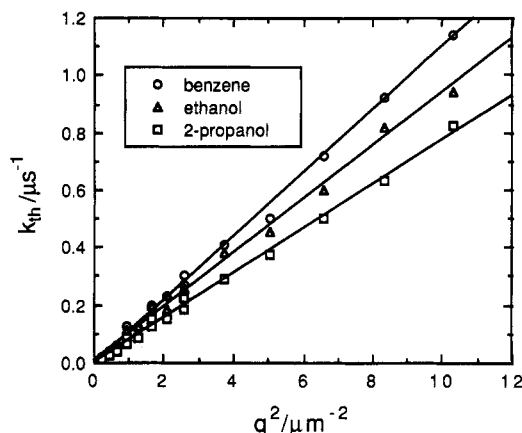


Figure 5. Plot of the decay rate constants of the thermal grating (k_{th}) vs q^2 at room temperature in benzene, ethanol, and 2-propanol.

TABLE I: Thermal Diffusion Coefficients (D_{th}) and Translational Diffusion Coefficients of MR (D) in Various Solvents Determined by the TG Method, Calculated by Eq 6 (D_{SE}) and Eq 7 (D_{SW}), and Self-Diffusion Coefficients (D_{self})^a

solvent	D_{th}	D_{th}^b	$D_c (\sim D_t)$	D_{SE}	D_{SW}	D_{self}
benzene	11.0	10.1	1.35	0.64	1.20	2.09 ^c
ethanol	9.33	8.93	0.90	0.36	0.92	0.89 ^d
2-propanol	7.81	6.81	0.56	0.18	0.59	0.48 ^e

^a The unit of D_{th} is $10^{-8} \text{ m}^2 \text{ s}^{-1}$ and D of mass diffusion is $10^{-9} \text{ m}^2 \text{ s}^{-1}$.
^b Calculated from the relationship $D_{th} = \kappa / C_p \rho$, where κ is the heat conductivity, C_p the specific heat capacity, and ρ the density. Data are taken from ref 24. ^c Reference 25. ^d Reference 26. ^e Reference 27.

The determined decay rate constant $k_{th} (=D_{th}q^2)$ is plotted against q^2 in Figure 5. In all the solvents, the plots show good linear relations as predicted and, from the slopes of the plots, D_{th} of the solvents are calculated (Table I). These values are in good agreement with the literature values.

4.2. Diffusion Process at Room Temperature. After the complete decay of the thermal grating signal, the square root of the population grating signal should decay biexponentially as predicted by eq 3. Actually, in some polymer hosts, the TG signal shows a decay-rise-decay curve that can be fitted by a double-exponential function with significantly different values of $D_c q^2 + k_{ct}$ and $D_t q^2$. The semilogarithm plots of $I_{TG}(t)$ of the population grating signals in our systems are shown in Figures 2b–4b. Contrary to the dramatic double-exponential curve observed in polymers,^{37,11,12,14,15} it appears that the decays in solution are expressed well by a single-exponential function at a first glance. A closer examination shows that, however, $\log(I_{TG}(t))$ vs t deviates slightly downward from the straight line calculated by the least-square method from the data in the later time region. For example, the deviation is conspicuous from 0.2 to 1 ms in Figure 2b. This deviation is clear in ethanol and 2-propanol but it is not seen in benzene. In principle, the rate constants $D_c q^2 + k_{ct}$ and $D_t q^2$ can be extracted separately from the biexponential curve-fitting analysis based on eq 3. However, due to the minor deviation from the single-exponential decay even in 2-propanol and ethanol, it is very difficult to determine reliable values individually. The fact that the deviation from a single-exponential decay is small indicates $D_t q^2 + k_{ct} \sim D_c q^2$ or $D_t \sim D_c$ since $k_{ct} \ll D_c q^2$ and $D_t q^2$. Then the general equation (3) is reduced to

$$\delta n_p = [\Delta c](\delta n_c - \delta n_t) \exp(-(D_c q^2 + k_{ct})t) \quad (5)$$

The preexponential factor should be negative because there is no observable dip between the thermal grating signal and the population grating signal and the population grating signal. From the previous discussion given in section 3, we know that δn_c and δn_t are positive. Therefore, we conclude $\delta n_c < \delta n_t$. This relationship is considered to be reasonable because the absorption

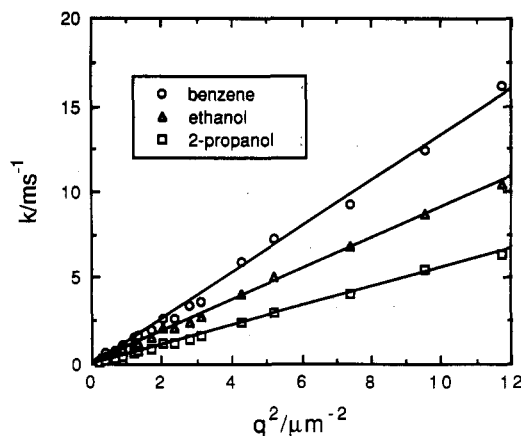


Figure 6. Plot of the decay rate constants (k) of $I_{TG}^{1/2}$ vs q^2 at room temperature in benzene, ethanol, and 2-propanol.

peak of the trans form is located at a longer wavelength than that of the cis form.¹¹

The minor deviation downward from the single-exponential fitting is considered to be due to the first term in eq 2a. To explain the time dependence and the downward deviation, δn_1 should be positive and $D_c q^2 + k_{ci} < D_i q^2$. Both conditions are satisfied under the condition $D_c < D_i$, although the difference should be very small. According to a calculation of the molecular volume of the cis and trans forms based on the molecular structure and the van der Waals radii, we find that the cis form has a slightly smaller molecular size than the trans form. The smaller *cis*-MR isomer was also concluded by an independent group.⁷ Therefore, the above observation indicates that the smaller cis form of MR has a smaller diffusion coefficient than the larger trans form. Similar unexpected results with much larger differences have been observed in polymer hosts previously and it has been interpreted as due to a strong interaction between the cis isomer and the polymer hosts.⁷ Besides ethanol and 2-propanol, similar deviations are observed in methanol, 1-butanol, 2-butanol, and acetaldehyde. Importantly, however, such deviations are not observed in benzene, acetone, toluene, and diethyl ether, indicating that the difference between D_c and D_i is much smaller. The solvent dependence suggests that the interaction between the solvent and MR is likely due to the hydrogen-bonding interaction. Probably the bended structure of the cis form is more easily affected by the hydrogen bonding with the solvent. The large difference between D_i and D_c in the polymer hosts⁷ is explained by the slow diffusion in the polymers, that is, the specific interaction becomes apparent because the absolute values of D in polymers are small. In contrast, the relatively large D by the hydrodynamic motion of solvent almost masks the small difference in solution.

The decay rate constants of the TG signal cannot be determined accurately even by using a double-exponential fitting procedure because of the small difference between D_c and D_i and also because of the small contribution of the first term in eq 2a. We calculate the decay rate by the least-square fitting of the relatively slow decay parts. The uncertainty due to this deviation from a single-exponential decay is estimated to be less than $\pm 5\%$. The obtained rate constants are plotted against q^2 in Figure 6. Here we calculate q^2 at each crossing angle from the decay rate constant of the thermal grating signal (k_{th}) and D_{th} to correct a small error in measuring the crossing angle. D_s obtained from the slopes of the plots are listed in Table I. In all the solvents, the intercept k_{ci} is very small and this is consistent with long lifetimes of the cis form in the dark (an order of seconds).

According to the Stokes-Einstein (SE) relation, the diffusion coefficient of a spherical molecule of radius r in a continuum

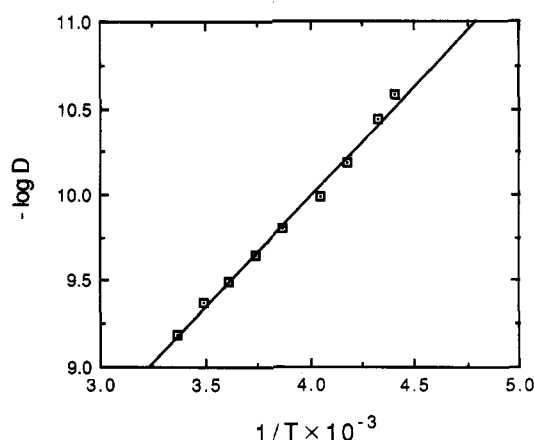


Figure 7. Plot of $-\log D$ vs $1/T$ in 2-propanol (squares) and the calculated temperature dependence of D_{SW} (line).

solvent of viscosity η is given by^{1,18}

$$D_{SE} = kt/f\pi\eta r \quad (6)$$

The value of f is 4 for the slip boundary condition and 6 for the stick boundary condition. If the molecule is a prolate or oblate ellipsoid, f is calculated by the equation derived by Perrin.¹⁸ In the table, we also list the calculated D based on the Stokes-Einstein relation. The calculated D_{SEs} are much smaller than those observed.

The underestimate of D by the SE relation has been frequently reported, especially for relatively small solutes compared with the solvent size.¹⁹⁻²² However, the fact that the difference becomes larger in order of benzene, ethanol, and 2-propanol indicates that the molecular size is not the only cause of the difference. Interestingly, D of MR in ethanol and 2-propanol is larger than the self-diffusion coefficients of solvents (D_{self}) that have much smaller molecular sizes than that of MR.

So far, many modifications of the SE theory have been proposed. For example, Spornol and Wirtz modified the SE equation by taking into account the finite size of the solvent molecule and rough interactive potential between solute and solvent by introducing an empirical microfriction factor f_{SW} ²³

$$D_{SW} = kT/6\pi\eta r f_{SW} \quad (7)$$

$$f_{SW} = \left(0.16 + 0.4 \frac{r_A}{r_B}\right) (0.3 + 0.4 T'_A - 0.25 T'_B)$$

where r_A and r_B respectively represent the radii of the solute (r_A) and the solvent (r_B). Further, the reduced temperatures, T'_A and T'_B , are calculated by

$$T'_X = (T - T_X^f)/(T_X^b - T_X^f)$$

by using the freezing (T_X^f) and boiling (T_X^b) points of the solute ($X = A$) or the solvent ($X = B$). This correction method has been recommended by several groups.^{21,22} The calculated D_s based on this equation are listed in the table. The results show that the calculated D_{SW} and experimental D values agree very well.

4.3. Diffusion in 2-Propanol at Low Temperatures. On the basis of the time-resolved EPR measurements of ketyl radicals in 2-propanol at low temperatures, it has been suggested that the radical diffusion in the radical pair might be slower than expected from the viscosity¹⁶ because of the solvent structures, which hold radicals together. This abnormal behavior may manifest itself in the diffusion process at low temperature. Therefore the diffusion coefficients at low temperatures in 2-propanol are examined. Figure 7 shows the temperature dependence of D_c measured from the decay rate constant of the TG signal at $\theta = 5.71^\circ$ ($\Lambda = 2.0 \mu m$). Since the isomerization from cis to trans is slow enough at low temperatures, the decay rate constant is

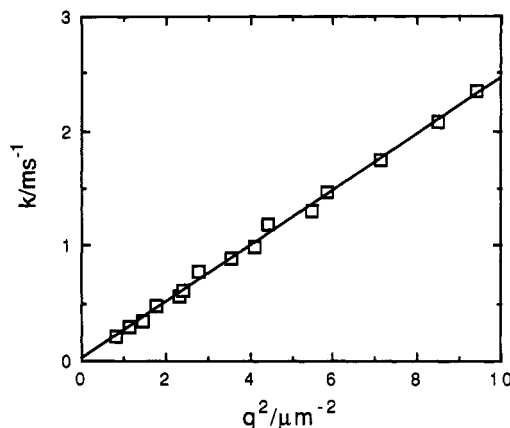


Figure 8. Plot of the decay rate constants (k) of $I_{TG}^{1/2}$ vs q^2 in 2-propanol at $-46.5\text{ }^{\circ}\text{C}$ (squares) and the least-square fit of the data (line).

nearly equal to $D_c q^2$. The slope of this plot, which gives an activation energy (E_a) of the Arrhenius-type expression,

$$D(T) = D_0 \exp(-E_a/kT) \quad (8)$$

agrees well with the activation energy of η calculated from

$$\eta(T) = \eta_0 \exp(-E_\eta/kT) \quad (9)$$

This is expected from eq 7, since D_{SW} is inversely proportional to η . Calculated $D_{SW}(T)$ from eq 7 and $\eta(T)$ are also shown in Figure 7. The calculated and experimental values are in excellent agreement. Furthermore, in Figure 8, the decay rate constants are plotted against q^2 at $-46.5\text{ }^{\circ}\text{C}$. The plot shows a linear relationship between k and q^2 from $\Lambda = 2.0$ to $\Lambda = 7.8\text{ }\mu\text{m}$. Therefore we conclude that the diffusion process of MR in 2-propanol at low temperature is similar to that at room temperature at least within our experimental conditions, from $24\text{ }^{\circ}\text{C}$ to $-46.5\text{ }^{\circ}\text{C}$ and from $\Lambda = 2.0$ to $7.8\text{ }\mu\text{m}$. No abnormal behavior is observed at low temperatures in the present experiment.

5. Summary

Diffusion coefficients of methyl red in organic solutions are measured by the transient grating technique. Contribution of the phase grating is revealed to be dominant in the TG signal. The cis form, which has a smaller size, possesses smaller D than that of the trans form. This unexpected result is attributed to the hydrogen-bonding interaction between MR and the solvents. The diffusion coefficients of MR are much larger than those calculated by the Stokes–Einstein equation in all the solvents we examine and even larger than the self-diffusion coefficient of the solvent in ethanol and 2-propanol. The experimentally obtained

D s at room temperature as well as at low temperatures agree well with the values calculated by the modified Stokes–Einstein equation according to Spornol and Wirtz. It is shown that the TG technique is a convenient means to study the translational diffusion process in solution. Further, the capability of measuring very fast response will make the TG method a very powerful method for studying the solution dynamics.

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