

Diffusion of Transient Radicals in Alcohols and Cyclohexane from Ambient to Supercritical Conditions Studied by the Transient Grating Method

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The translational diffusion coefficients of ketyl radicals produced by a hydrogen abstraction reaction in ethanol, methanol, and cyclohexane are investigated by the transient grating (TG) method, from liquid phase to the medium-density region in wide temperature ranges. It is found that the diffusion coefficient of the radical (D_r) is smaller than that of a stable molecule with a similar size (D_s) even under supercritical conditions. In the medium-density region, the values of D_r in alcohols are differently dependent on temperature over viscosity from those in cyclohexane. The activation energy of D_r was determined and compared with that of solvent viscosity. We found that D_r/D_s decreases with decreasing density in the medium-density region for cyclohexane. This tendency is explained in terms of the local density enhancement in the medium-density region. In alcohols, the density dependence of D_r/D_s is not significant.

1. Introduction

The knowledge of the translational diffusion coefficient, especially that of a transient intermediate, is indispensable for analyzing chemical reaction on the basis of diffusion-controlled theory.^{1,2} Many studies of the translational diffusion processes in solution have been performed by several experimental methods: tracer diffusion method, Taylor dispersion method, dynamic light scattering, NMR spin-echo measurements, and so on.^{3,4} However, the translational diffusion process of a reaction intermediate has been hardly investigated even under the ambient condition experimentally, because these traditional methods are not applicable to short-lived transient species. An electrochemical method may be used for transient charged particles (e.g., electrons emitted by X-ray) and the diffusion studies of metastable ions in supercritical fluids have been reported for a few decades.⁵ However, there has been almost no report on the diffusions of neutral short-lived molecules.^{6,7}

Recently, the transient grating (TG) method⁸ has been recognized as a very powerful technique for investigating various chemical reaction processes (e.g., thermalization process,⁹ thermal diffusion,^{10,11} mass diffusion,^{12–18} and nonradiative processes of organic molecules^{18–20} and proteins^{21,22}). Because the TG technique can detect translational movement with a high sensitivity within a short time range, the TG method is a suitable and powerful method to study the diffusion coefficient (D) of a short-lived molecule of relatively low concentration. Indeed, using this method, Terazima and co-workers have found that the diffusion coefficients of many radicals (D_r) are two or three times smaller than those of parent molecules (D_p), although the molecular sizes are similar to each other.^{12–17} They also examined the temperature dependence of D_r and D_p below room temperature, and found that the activation energies of D_r are larger than those of D_p .¹⁴ The origin of the

slow diffusion of the radicals has been attributed to an attractive intermolecular interaction between the radicals and solvent molecules. The origin of the attractive interaction has been investigated by Morita and Kato using ab initio calculations.^{23,24} They found that the electronic states of the radicals are more sensitive to the local solvent field. However, recently, Autrey et al. asserted that the slowness of radical diffusion in alcoholic solvents could be explained by the hydrogen bonds between ketyl radicals and solvent molecules.²⁵

Our interest in this paper is the effect of solvent density on the translational diffusion of radicals. Using the fluids under supercritical condition, so-called supercritical fluids,²⁶ we can continuously change the solvent density from the gaslike to the liquidlike densities. The effect of the attractive interaction between molecules is expected to enhance in the medium-density region of fluids, because solvent density around the solute is larger than is expected from the bulk density for the attractive solute. We investigated how this local density enhancement affects the diffusion process of the solute molecules. Although there have been a number of reports on the diffusion coefficients of various solutes in supercritical fluids,^{27–30} the effect of the local density has not been clarified. The effect of the local density enhancement on the solute diffusion was studied by Kimura and co-workers using molecular dynamics (MD) simulations for Lennard-Jones (LJ) fluids.³¹ By this simulation, the diffusion coefficient of the attractive solute (D_{solute}) was compared with that of solvent molecule (D_{solvent}) in a wide density range. The result shows that the ratio $D_{\text{solute}}/D_{\text{solvent}}$ decreases with decreasing the solvent density from the liquidlike region to the medium-density region. The analysis based on the generalized Langevin equation indicates that this decrease is primarily caused by the local density effect; that is, the increased local density around the solute causes larger friction. To verify this prediction experimentally, Kimura et al. measured the translational diffusion coefficients of radicals (D_r) in CF_3H and CO_2 in the medium-density region previously.¹⁵ The ratio of D_r to that of a stable molecule with a similar size (D_s) was evaluated in the range of reduced density $\rho_r = 1.2$ –

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2.0 scaled by the critical density ρ_c . The result showed that the ratio (D_r/D_s) increases slightly for anion radicals and is almost constant for neutral radicals with decreasing the solvent density. It was concluded that the local density enhancement on the diffusion was not observed, probably because the density region examined in their study was not wide enough. In particular, data in a high-density region was limited.

In this study, we measured the diffusion coefficients of the transient ketyl radicals created by hydrogen abstraction reactions from liquid-phase toward the medium-density region. We chose ethanol, methanol, and cyclohexane as solvents. The TG signals were measured with a high-pressure cell withstanding high temperature, and the diffusion coefficients of the ketyl radicals (D_r) were determined in the density range of $\rho_r = 1.5\text{--}3.0$ (in ethanol). At first, we discuss D_r in comparison with the Stokes–Einstein relationship and also compare them with solute diffusion in supercritical CO_2 . Next, we examined the temperature dependence of D_r . We will discuss the Arrhenius equation of the diffusion coefficients in relation with that of the solvent viscosity. Finally, we will consider the density dependence of D . We evaluate the ratio D_r/D_s and discuss the local density enhancement on the translational diffusion.

2. Experimental Section

(a) Materials. Transient ketyl radicals were created by the photoexcitation of benzophenone (BP) in ethanol (EtOH), methanol (MeOH), and cyclohexane (CyHx), and acetophenone (AP) in EtOH. In the following, we will abbreviate the solution BP in EtOH as “BP/EtOH”, and so on. EtOH, MeOH, and CyHx of spectroscopic grade were purchased from Nakalai Tesque and used without further purification. BP (Nakalai Tesque) was recrystallized from ethanol before use. AP (Wako Pure Chem. Ind.) was used without further purification. The estimated concentration of BP was about 5×10^{-2} M ($\text{M} \equiv \text{mol dm}^{-3}$) in all three solvents, and that of AP was about 0.5 M in EtOH. Oxygen in sample solution was removed by bubbling nitrogen for more than 10 min to avoid the quenching reaction.^{13,32}

(b) Apparatus and Experimental Conditions. The high-pressure optical cell made of Hastelloy with two sapphire windows, and the pressure- and temperature-control systems were described elsewhere.¹¹ The internal volume of the cell is about 0.3 cm³. The optical path length is about 2 mm. We also used a HPLC pump (JASCO PU-1580) to compress and transfer the sample solutions. The temperature and the pressure were kept within ± 1 K and ± 0.1 MPa.

The experimental arrangement for the TG measurement was almost the same as described before,¹⁹ except for the equipment of the cell. Briefly, we used a third harmonic pulse (~ 8 ns) from a Nd:YAG laser (355 nm; Spectra-Physics GCR-170) or a pulse from a XeCl excimer laser (308 nm; Lambda Physik COMPEX 102) for the excitation. As a probe laser, we used a He–Ne CW laser (633 nm; Uniphase). The TG signal was detected by a photomultiplier and averaged about 250 times by a digital oscilloscope (Tektronix 2430A) and a personal computer. The repetition rate of the excitation pulse was about 3 Hz. The angle of the crossing pump pulses is in the range from 1.5×10^{-2} to 9.0×10^{-2} rad.

For measuring D of the radicals induced by the photoexcitation, we have to rule out a possibility of sample corrosion or undesirable side reactions under high-temperature conditions. According to the absorption study by Bennet and Johnston, BP and acetone in supercritical water (at 673 K and 27.6 MPa) are stable in 3 h.³³ Therefore, we do not need to consider the thermal decomposition of ketones. However, ketones and alcohols can

TABLE 1: Critical Parameters of Solvents and the Experimental Conditions in This Study

	T_c/K	P_c/MPa	$\rho_c/\text{kg m}^{-3}$	measurement points		
				T/K	P/MPa	ρ_r
EtOH	516.3	6.18	276	331	0.1–50	2.80–2.96
				404	1–50	2.52–2.74
				471	5–50	2.11–2.48
				518	8–50	1.53–2.28
				543	13–50	1.50–2.18
MeOH	512.6	8.10	276	295	0.1–50	2.86–3.00
				387	2–50	2.53–2.74
				418	2–50	2.38–2.64
				453	3–50	2.16–2.52
				513	8.5–50	1.43–2.28
CyHx	553.5	4.07	273	540	15–50	1.45–2.15
				400	0.3 ^a –30	2.46–2.62
				450	0.9 ^a –30	2.24–2.47
				500	1.9 ^a –30	1.95–2.32
				540	3.3 ^a –30	1.56–2.20
				573.	6–30	1.37–2.09

^a Saturation pressure. ^{*} ρ_r denotes the reduced density by the critical density of the solvent.

react into acetal at high temperatures (it is reported that acetone in sub- or supercritical methanol reacts quickly³⁴). We measured the time profile of transient absorption (TA) spectra of ketyl radicals, to ensure that the hydrogen abstraction reaction occurs and that the radicals survive under supercritical conditions. We measured the TA spectra of these radicals by using a xenon lamp (USHIO SX-UI500XQ) as a probe beam. The absorption was sampled by a photomultiplier through a monochromator (Shimadzu SPG-100S). To determine the lifetime of the radicals, we also measured the time dependence of the transient absorption signal at a single wavelength using a green He–Ne laser (Uniphase; CW, 543.5 nm) under the same experimental conditions as the TG measurement.

(c) PVT Relations and Other References. In a calculation of the density of MeOH from pressure and temperature, we used the equation of state recommended by IUPAC.³⁵ For EtOH, the densities were evaluated according to the procedure in our previous paper.^{11,36} For CyHx, we interpolated the densities reported at various pressures and temperatures from medium-density to the liquidlike density regions.³⁷ For analyzing the TG signals and determining the grating wavenumber q , we need the value of thermal diffusivities $D_{th} = \lambda(\rho C_p)^{-1}$, where λ , ρ , and C_p denote thermal conductivity, density, and isobaric specific heat, respectively. For CyHx, we calculated the thermal diffusivity from the reported thermal conductivity and the isobaric specific heat.³⁸ For MeOH and EtOH, thermal conductivities are reported.³⁹ Isobaric specific heats of MeOH were calculated from the equation of state given by IUPAC.³⁵ For EtOH, we used isobaric specific heat of 96% EtOH aqueous solution,⁴⁰ because that of pure EtOH is not available. In addition, we used the thermal diffusivities of the supercritical MeOH and EtOH evaluated in our previous paper.¹¹ The values of viscosity for MeOH, EtOH, and CyHx were taken from refs 39 and 41. In some cases, we made extrapolation of the reported values to estimate the viscosity. In the calculation of the above properties, we did not consider any solute effect. We consider that the solute effect does not influence the following discussion seriously.⁴²

3. Results

Table 1 summarizes the state points we have investigated. First, we discuss the result of the TA spectra at the highest temperature in our measurements. Next, we present the result of the TG signals and the way of signal analysis.

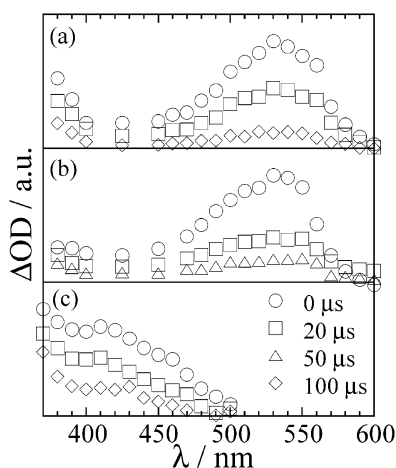


Figure 1. Transient absorption spectra of (a) BPK/EtOH at 543 K and 10 MPa, (b) BPK/CyHx at 573 K and 6 MPa, and (c) APK/EtOH at 543 K and 9 MPa.

(a) TA Measurement. Figure 1 shows the TA spectra after photoexcitation of BP/EtOH, BP/CyHx, and AP/EtOH at several temperatures (See also Figure 1S). TA spectrum of BP/MeOH is similar to that of BP/EtOH. Photoreaction schemes of BP and AP in these solvents have been studied well.^{13,43,44} After photoexcitation of BP and AP, benzophenone ketyl radical (BPK) and acetophenone ketyl radical (APK) are produced by the abstraction of a hydrogen atom from the solvent, respectively. The TA spectra at the high temperature were very similar to the reported absorption spectra of BPK and APK under ambient conditions⁴³ but slightly blue-shifted. These TA spectra indicate that the same photochemical reactions of BP and AP occur under the supercritical condition as those under the ambient conditions. From the decay rates of the TA signals, the half-lifetimes of BPK and APK under this experimental condition are estimated to be at most 100 μ s. These half-lifetimes depend on the initial concentrations of radicals, or, on the intensity of excitation pulses, because the radical disappearance is dominated to the recombination of second-order reaction process.⁴⁴ Because we have used much weaker excitation laser intensity for the TG measurement than for the TA spectral measurement, the lifetimes of BPK and APK in the TG measurement are expected to be much longer.

We examined the lifetimes of the radicals under the same condition as the TG measurement. Figure 2 shows the time profiles of the transient absorption signals probed at 543.5 nm after the photoexcitation of BP/EtOH and BP/CyHx. The decay of each absorption signal is relatively slower even under the supercritical conditions; BPK survives about 7 ms (half-lifetimes) under high temperature and high-pressure conditions. For APK, a probe light for the APK absorption (400–450 nm) was not available, and the lifetime could not be determined. However, in the following section, we will show that the lifetime is long enough to be measured for diffusion process.

(b) TG Measurement and Analysis. Typical TG signals are shown in Figure 3 for BP/EtOH from ambient to supercritical conditions. The signal rises quickly after the photoexcitation and decays near to the baseline and shows a rise-and-decay profile. The faster part corresponds to the thermal grating signal, and the slower part corresponds to the diffusion of the parent molecule and the radical. Based on the discussion in a liquid phase reported previously,^{12–14} we attribute the parent molecule and the radical to BP and BPK, respectively, because the signals due to the solvent molecule and the solvent radical are expected to be much weaker. For other sample solutions, the temporal

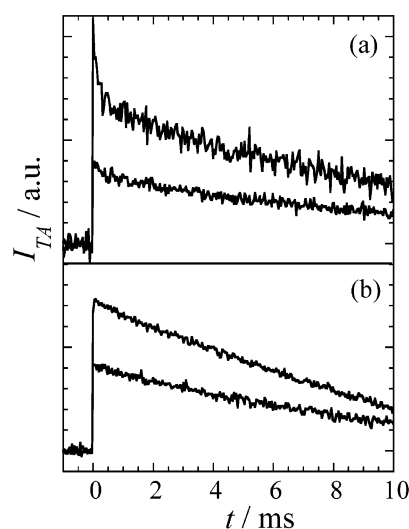


Figure 2. Time profiles of the transient absorption of (a) BPK/EtOH at 543 K and 25 MPa (upper) and at 543 K and 10 MPa (lower), (b) BPK/CyHx at 573 K and 25 MPa (upper) and at 573 K and 5 MPa (lower).

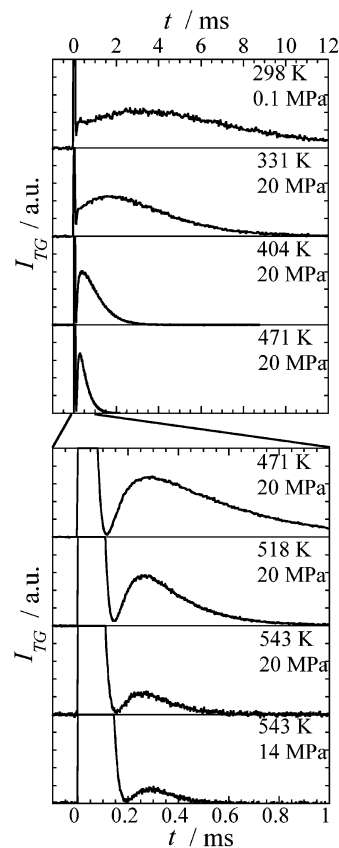


Figure 3. Time profiles of the TG signals of BP/EtOH solution ($q^2 = 0.37 \mu\text{m}^{-2}$) at several temperatures and pressures. After the thermal grating (the fastest and the largest decay), population gratings of the parent molecule (BP) and the radical (BPK) are observed as a slower rise and decay, respectively. The population grating of the parent molecule is nearly buried in the thermal grating at the higher temperature.

profiles of TG signals are similar. We observed a much weaker signal after the slower decay, which cannot be recognized without magnification in this figure. We think that this very weak signal is due to a product of the succeeding radical reactions and neglected this contribution in the following discussion.

The intensity of a TG signal (I_{TG}) is expressed^{8,45} as

$$I_{\text{TG}} \propto (\Delta n)^2 + (\Delta k)^2 \quad (1)$$

where Δn and Δk denote the peak-null difference of the refractive index and that of the absorption coefficient, respectively. In the present case, Δk is negligible because the parent molecules and radicals do not absorb the probe light we used (633 nm). Following the previous papers,^{12,13} the TG signals are expressed as

$$\begin{aligned} I_{\text{TG}}(t) &\propto \{\Delta n_{\text{th}}(t) + \Delta n_{\text{p}}(t) + \Delta n_{\text{r}}(t)\}^2 \\ &= \{\Delta n_{\text{th}}^0 \exp(-D_{\text{th}}q^2t) + \Delta n_{\text{p}}^0 \exp(-D_{\text{p}}q^2t) + \\ &\quad \Delta n_{\text{r}}^0 \exp(-D_{\text{r}}q^2t)\}^2 \quad (2) \end{aligned}$$

where q denotes the grating wavenumber which is determined by the pump wavelength and the angle between the pump pulses. We call the first term a thermal grating (Δn_{th}) and the other terms population gratings (Δn_{p} and Δn_{r}). The subscripts p and r indicate the contribution from the parent molecule and the radical, respectively. The superscript 0 means the amplitude at $t = 0$. Generally Δn_{th} is negative for the thermal expansion. Δn_{p} and Δn_{r} are negative and positive, respectively. We have to consider that radicals are intermediates with a short lifetime. If the disappearance of the radical is expressed as a single-exponential decay with a rate constant k_{r} , Δn_{r} should be modified as

$$\Delta n_{\text{r}}(t) = \Delta n_{\text{r}}^0 \exp\{-(D_{\text{r}}q^2 + k_{\text{r}})t\} \quad (3)$$

The grating wavenumber q was determined from the lifetime of the thermal grating τ_{th} and the thermal diffusivity D_{th} , according to the relationship $\tau_{\text{th}}^{-1} = D_{\text{th}}q^2$. We estimated τ_{th} from the fitting of the thermal grating by neglecting the population gratings.⁴⁶

As is shown in Figure 3, the decay of the thermal grating becomes slower and those of population gratings become much faster as the temperature increases. We attempted to fit the signal with multiexponential functions based on eq 2.^{13,14,47} Indeed, at the lower temperature (to 418 K), we could determine D_{th} , D_{p} , and D_{r} from the lifetimes of the respective contributions simultaneously. However, at the higher temperatures, these lifetimes were not determined uniquely by this fitting procedure. In particular, the lifetime of the population grating of the parent molecule τ_{p} ($\equiv (D_{\text{p}}q^2)^{-1}$) had a lot of ambiguity. Therefore, we focused the evaluation of only the lifetime of the population grating of the radical τ_{r} ($\equiv (D_{\text{r}}q^2 + k_{\text{r}})^{-1}$) by fixing the value of τ_{p} . Only a few data of diffusion coefficients have been reported at the present experimental conditions because of the technical difficulty with treating the high temperature and high-pressure fluids. The diffusion coefficients of BP and AP have not been reported in supercritical alcohols and CyHx. However, the diffusion coefficients of aromatic hydrocarbons in supercritical alcohols and CyHx have been reported by Sun and Chen.⁴⁸ We assume that diffusion coefficient of BP (D_{BP}) is the same as that of phenanthrene (PN; D_{PN}), and that of AP (D_{AP}) as that of mesitylene (MS; D_{MS}), because they resemble each other in their molecular weights and molecular volumes.⁴⁹ In fact, in a lower temperature range (to 418 K), we could analyze the TG signal with three exponentials and found that D_{BP} and D_{AP} are similar to D_{PN} and D_{MS} , respectively (Figure 4). The difference between D_{BP} and D_{PN} is at most 30% and the average deviation is around 10%, which would not affect τ_{r}

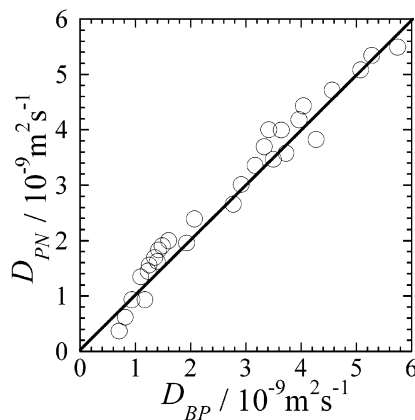


Figure 4. Comparison of the diffusion coefficients of BP in EtOH estimated by the TG signal with those of PN in ref 48.

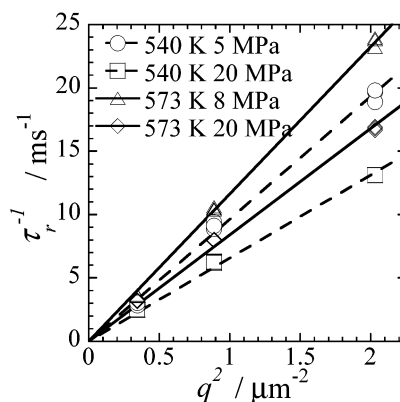


Figure 5. Decay rates of the population gratings due to the radical diffusion against q^2 at the higher temperatures for BPK/CyHx.

seriously. D_{PN} and D_{MS} are estimated from the equation suggested by Sun and Chen with a revision.⁵⁰ In this way, we could fit the TG signals almost uniquely.

By plotting of τ_{r}^{-1} against q^2 , we can evaluate D_{r} and k_{r} in eq 3 from the slope and the intercept at $q = 0$, respectively. Figure 5 shows an example of the plot of τ_{r}^{-1} against q^2 for BPK/CyHx under the supercritical conditions. In this case, the intercept is almost zero. In other words, a disappearance rate of the radical (k_{r}) is negligible. For other sample solutions, we obtained the same results. The small k_{r} is consistent with the TA measurement because the decay rate of the TA spectra for BPK/EtOH and BPK/CyHx is small enough.

4. Discussion

(a) Viscosity Dependence. Figure 6 shows D of BPK/EtOH, BPK/MeOH, APK/EtOH, and BPK/CyHx plotted against $T\eta^{-1}$. According to the Stokes–Einstein (SE) relationship, D is given by

$$D = \frac{k_{\text{B}}T}{C\pi r\eta} \quad (4)$$

where C , k_{B} , r , and η denote a constant determined by the boundary condition, the Boltzmann constant, the radius of the solute, and the viscosity of the solution, respectively. The plots also include D_{s} (D_{PN} or D_{MS}) for the comparison.

It is evident that the diffusion of the radical is always slower than that of the stable molecules. In the lower $T\eta^{-1}$ range, D_{r} is almost proportional to $T\eta^{-1}$ as predicted by the SE relationship, which is consistent with the previous paper.^{13,17} On the

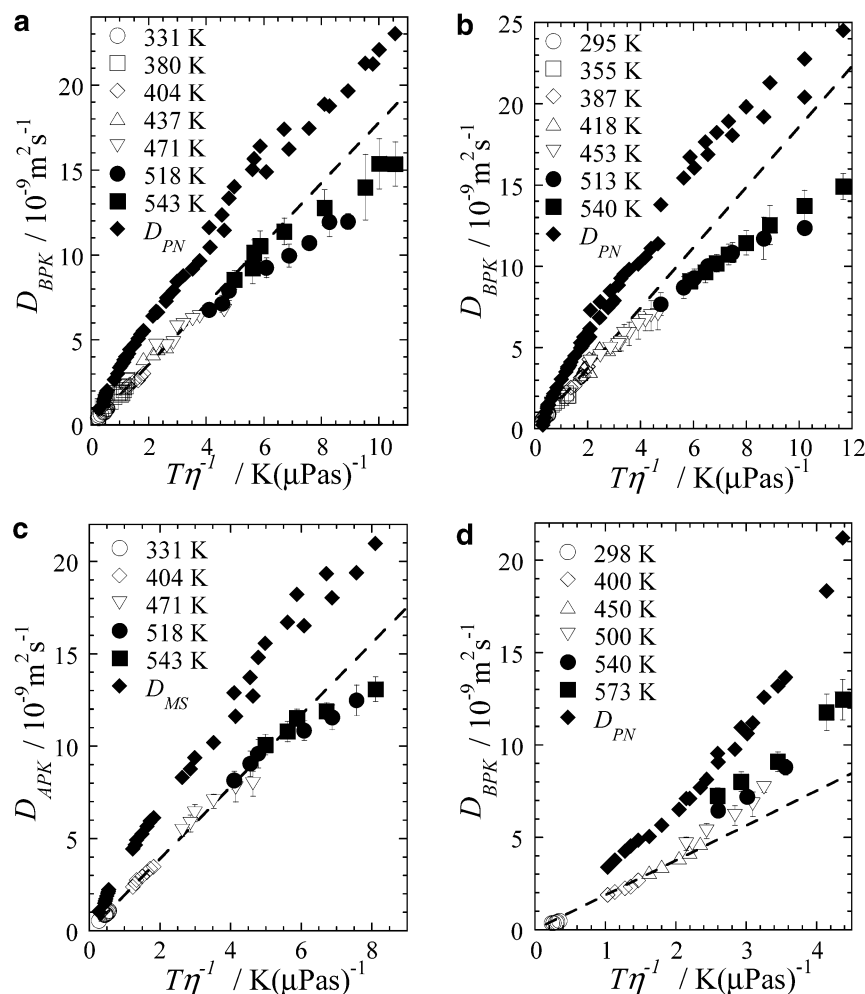


Figure 6. Plots of the diffusion coefficients against $T\eta^{-1}$ of (a) BPK in EtOH, (b) BPK in MeOH, (c) APK in EtOH, and (d) BPK in CyHx. The sequence of each symbol represents the diffusion coefficient at the same temperature. The upper sequence of filled diamond represents D_s (D_{PN} or D_{MS}). The dashed line is the optimized fitting line at the lower temperatures to the Stokes–Einstein relationship. Typical examples of the error bars are shown for the data near the critical temperature. The errors are estimated less than (a and b) 14% and (c and d) 10% of their values.

other hand, D_{PN} and D_{MS} do not follow the SE relationship and obey an empirical relationship like^{3,51–55}

$$D = AT\eta^{-p} \quad (5)$$

where A and p are empirical parameters. In the higher $T\eta^{-1}$ range, we can see that D of BPK and APK are no longer proportional to $T\eta^{-1}$. The $T\eta^{-1}$ dependence in alcohols is different from that in CyHx. For alcohols, D_r becomes smaller than the prediction of the SE relationship at the larger value of $T\eta^{-1}$. Meanwhile D_r becomes larger in CyHx. It is also to be noted that D_r in CyHx is not a smooth function of $T\eta^{-1}$; that is, even at the same value of $T\eta^{-1}$, D_r is different at different temperatures. This is reproduced in several experimental runs. This is considered not to be due to estimation errors of viscosity because D_{PN} looks smooth, which is evaluated from the function independent of viscosity.^{48,50} This phenomenon is hardly understandable in the framework of the SE theory.

The SE relationship is successful in describing the diffusion of relatively large solutes in the liquid phase. It often holds for D of relatively smaller solutes. From the hydrodynamic theory, the constant C should take a value between 4 and 6. However, the value of C often lies outside this limitation, if C is calculated from experimental values of D , T , η , and van der Waals radius r_{vdw} .^{3,55,56} In this sense, the value of C is an empirical factor related to the solute–solvent attractive interactions. Here we

evaluate the value of C in this way. r_{vdw} of BP and AP are estimated as 3.43 and 3.04 Å, respectively.⁴⁹ For BPK and APK, we assumed that r_{vdw} are same as those of their parent molecules.⁵⁷ We also postulated that these radii are invariant regardless of the solvent species and density. The obtained values of C are around 7 in the lower $T\eta^{-1}$ range, irrespective of the solvents. This suggests that the solute–solvent interaction is stronger than or as strong as those between some diols or triols and EtOH.^{55,56} Compared with the radicals, the values of C for BP and AP are around 4 in the density region where we can determine D_r and D_p simultaneously. The values of C are similar to those of other organic molecules.

The SE relationship does not hold in the medium-density region (corresponding to high $T\eta^{-1}$ range), which is general behavior for various solutes. In this density region, eq 5 is often used for evaluating the diffusion coefficient. At the temperature higher than 450 K, the power of the viscosity in eq 5 (the parameter p) for BPK/EtOH, BPK/MeOH, and APK/EtOH are 0.82, 0.75, and 0.75, respectively. We compare our results with the diffusion coefficients of various solutes in supercritical CO₂ which are investigated intensively. We evaluated the values of p for the various solutes in supercritical CO₂ by eq 5.⁵⁸ The results are summarized in Table 2. As is shown in the table, the values of p lie between 0.74 and 0.85 regardless of the solute size or nature except for benzene (0.63). Interestingly, the p values are similar to the values for the radical diffusion in

TABLE 2: Parameter p in Eq 5 for the Solute Diffusion in Supercritical CO₂ in Ref 30

solute	$r_{vdW}/\text{\AA}$ (ref 49)	p
acetone	2.49	0.85
benzene	2.68	0.63
2-butanone	2.69	0.80
2-pentanone	2.87	0.77
3-pentanone	2.87	0.83
phenol	2.76	0.79
α -tocopherol	4.84	0.81
β -carotene	5.23	0.75
vitamine K ₃	3.32	0.74
ubiquinone-10	6.08	0.74

alcohols, although the solvent properties of these alcohols are quite different from those of CO₂.

However, the p value of BPK in CyHx is apparently different from those in alcohols or in CO₂. As expected from Figure 6d, the value of p is 1.51 for BPK/CyHx at 450 K and higher temperatures. The value of p larger than 1 has never been reported so far.^{3,15,29,30,51,52,54} Furthermore, according to the previous studies, the value of p is often determined only by nature of the solute, and independent of the solvents.^{29,51–55} Therefore, the value of p may change if there is a drastic change of the solute size due to, for example, the complex formation or the decomposition at high temperature. However, the TA spectra in Figure 1 do not show such changes. In the next section, we will examine the reason the solvent affects the parameter p .

(b) Temperature Dependence. The temperature dependence of the diffusion coefficient is often expressed by^{3,14,52,56}

$$D/T = D_0 \exp(-E_D/k_B T) \quad (6)$$

where E_D denotes the activation energy of the diffusion.⁵⁹ For the viscosity, a similar equation is given as

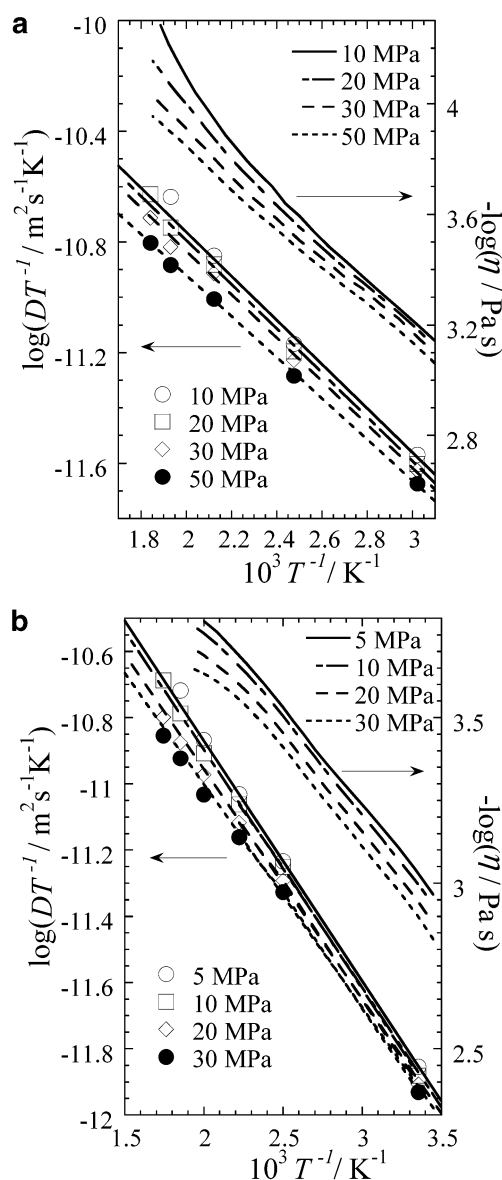
$$\eta = \eta_0 \exp(E_\eta/k_B T) \quad (7)$$

where E_η denotes the activation energy of the solvent viscosity.⁵⁹ If the SE relationship holds strictly, E_η should be the same as E_D . However, these activation energies are different from each other in most cases.^{14,56,60–62} If eq 5 holds, E_D is proportional to E_η as

$$E_D = pE_\eta \quad (8)$$

Figure 7 shows the logarithms of D/T and η^{-1} plotted against T^{-1} in the same scale for BPK/EtOH and BPK/CyHx, respectively. The results for BPK/MeOH and APK/EtOH are similar to that for BPK/EtOH (see Figure 2S). Interestingly, the Arrhenius equation nearly holds over the wide density region (e.g., at 10 MPa of EtOH from 783 to 468 kg m⁻³), although some deviation is observed at higher temperatures. Using the data to 471 K (where the SE relationship almost holds, see Figure 6), we evaluated the activation energy by eq 6. The results are summarized in Table 3, together with the results of the fit of the self-diffusion coefficients⁶³ and viscosities^{39,41} of the pure solvents. For alcohols, the temperature dependence of D_r is similar to that of viscosity and the self-diffusion. On the other hand, the activation energy D_r for CyHx is slightly larger than E_η , although E_D for the self-diffusion is close to E_η .

What causes the difference for the activation energy in alcohols from that in CyHx? The absolute values of E_D has not been well interpreted despite several attempts.^{14,60,61,64} However, according to the previous works, E_D is related to the sizes and interactions of the solute and the solvent: E_D becomes larger

**Figure 7.** Plots of the logarithm of D_{BPK}/T in EtOH (a), and in CyHx (b) against the inverse of temperature. The logarithm of the inverse of pure solvent viscosity is shown together in the same scale.**TABLE 3: Summary of the Activation Enthalpy of the Diffusion of the Radicals, That of Self-Diffusion of Solvent, and That of Solvent Viscosity**

$E_D, E_\eta/\text{kJ mol}^{-1}$	P/MPa							
	5	10	20	25	30	40	50	
BPK/EtOH (to 471 K)	15	15			15	14	14	
APK/EtOH (to 471 K)	16	15			15	14	14	
BPK/MeOH (to 453 K)	11	10	10				10	
BPK/CyHx (to 450 K)	14	14	13		13			
self-diffusion (from ref 63)								
EtOH (290–437 K)	15	15			15	14	14	
MeOH (292–453 K)	11	11	11				10	
CyHx (313–383 K)	12	12	12		12			
viscosity (all data to 460 K, from ref 39 and 41)								
EtOH	15	14			14		14	
MeOH	12	11	11				11	
CyHx	11	11	11		11			

for the solute with a larger radius,^{14,52,56,61} the solvent with a larger radius,^{14,52,65} the stronger solute–solvent attractive interaction,^{56,62} and the stronger solvent–solvent attractive interaction.⁶⁵ As is shown in Table 3, E_D of BPK in CyHx is larger than that of self-diffusion of CyHx; that is, E_D increases by

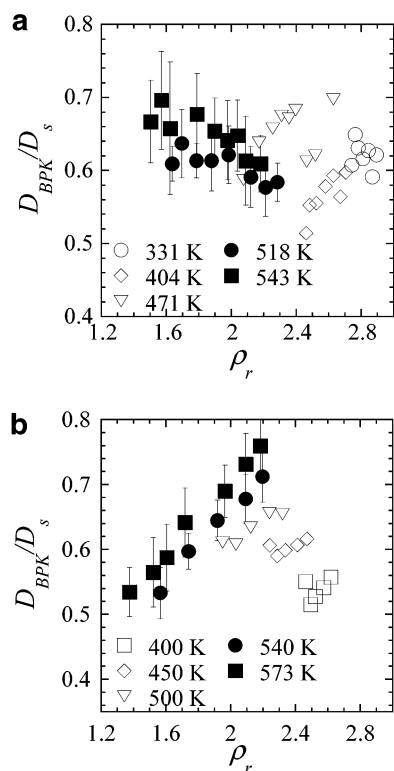


Figure 8. Plots of the ratios D_r/D_s (corresponding to D_{BPK}/D_{PN}) against the density. Below 418 K, the ratios D_r/D_p (corresponding to D_{BPK}/D_{BP}) are plotted instead of D_r/D_s . (a) BPK/EtOH and (b) BPK/CyHx. Typical examples of the error bars are shown for the data near the critical temperature.

changing the solute molecule from CyHx to BP. Roughly speaking, there are two possible reasons for the increase of E_D : the effect of the size and/or the solute–solvent attractive interaction. According to ref 61, E_D of Bu_4Sn , of which diameter is estimated as 7.4 Å, is evaluated as 11 kJ mol⁻¹, which is smaller than that of BPK. Therefore, we believe that the larger E_D of BPK than that of self-diffusion is not due to the molecular size difference but probably due to the stronger attractive solute–solvent interaction than solvent–solvent interaction.

It is also to be noted that CyHx viscosity at the higher pressure and the higher temperature deviates from the Arrhenius plot in a different way from the viscosity of these alcohols; that is, the temperature dependence of the viscosity becomes small. This causes that the parameter p of eq 5 exceeds unity at the higher temperature. The temperature dependence of the viscosity is smaller than that of D_r in CyHx at higher temperatures as is shown in Figure 7b; that is, $E_\eta < E_D$. According to eq 8, it is easily understandable that $p > 1$.

(c) Density Dependence. In accordance with the analysis of the MD simulation on the local density effect on the diffusion,³¹ we evaluate the ratio of D_r to that of the parent molecule (D_{BP} or D_{AP}) or the molecule of similar size (D_s). Figure 8 shows these ratios for BPK/EtOH and BPK/CyHx. The results for BPK/MeOH and APK/EtOH are similar to that for BPK/EtOH (See Figure 3S). In the figure, we evaluate the ratio of D_r to D_{BP} and D_{AP} in the density region measured below 418 K, where we could determine the values from the fitting of the TG signals. Above 418 K, we show the ratio of D_r to D_s (D_{PN} or D_{MS}). The ratios are scattered around about 0.6. In the higher density region, the ratio slightly increases or does not change with a decrease of density because D_s (and D_{BP} and D_{AP}) obeys eq 5 and D_r obeys the SE relationship.¹³ In the lower density region, the behavior of the ratio is clearly different between alcohols

and CyHx. Figure 8a shows that the ratios in EtOH and MeOH are almost invariant within the errors. On the other hand, Figure 8b shows the decrease of the ratio in CyHx clearly. This is the same tendency as the case of LJ fluids, which suggests that the local density affects D_r ; that is, the difference of the friction on the radical from that on the parent molecule is enhanced in the medium-density region due to the local density enhancement. The temperature effect of the ratio is also explained by the attractive interaction; that is, the lower the temperature is, the more enhanced the local density effect is.

What makes the difference between these solvents? One possible source of the difference is the solute–solvent interaction which comes from the hydroxyl groups. If the hydrogen bonding is one of the reasons of the slow radical diffusion as is mentioned earlier in our papers^{13,14} and re-pointed out recently by others,²⁵ the anisotropic attractive interaction should be important for the intermolecular interaction between the radical and the solvent molecule. If the charge sensitivity is the origin of the slow diffusion as is pointed out by Morita and Kato,^{23,24} the local field should be very sensitive to the OH direction of the solvent molecules. In either case, the saturation of the local density effect is expected to occur in a relatively lower density region. Therefore, the local density effect could not be detected in alcoholic solvents in the density region we studied. On the other hand, the small D_r for BPK/CyHx cannot be explained by hydrogen bonding.^{13,14} Because the interaction with CyHx is relatively isotropic than that of alcohols, it is reasonable to think that the diffusion in CyHx resemble that in the LJ system. To clarify this point more, in particular for alcoholic solvents, it is desirable to study the density region which covers the near-gas and near-critical density. By the present experimental system, we cannot analyze the TG signal in lower-density region due to the overlapping of the thermal grating with the population grating. One possible approach is using the heterodyne detection to improve the S/N.

5. Conclusion

In this study, we performed the measurement of the diffusion coefficients of transient radicals BPK and APK generated by hydrogen abstraction from EtOH, MeOH, and CyHx. Regardless of solvents, we observed the slow diffusion of the radicals as is observed under the ambient conditions.^{12–14} We discussed the viscosity and temperature dependence of D_r and found that the behavior of the radical diffusion appears differently between CyHx and alcohols. In the medium-density region for BPK/CyHx, D_r is larger than the prediction from the SE relationship and the discontinuity is observed in the plot against $T\eta^{-1}$. These have not been observed for alcoholic solution in this study and for CO_2 solution in the previous works;^{3,15,29,30,51,52,54} the diffusion coefficients of the solutes in these solvents are smaller than those expected from the SE relationship at large $T\eta^{-1}$ values. We evaluate the temperature dependence of D_r , self-diffusion of the solvent, and solvent viscosity by using the Arrhenius equation. We found that the activation energy of the viscosity of the pure CyHx decreases with increasing temperature and pressure in contrast to the case of alcohols. This causes the different dependence of D_r on the viscosity for BPK/CyHx from that for alcohols. The density dependence of the ratio of the diffusion constant D_r/D_s for BPK/CyHx resembles the cases of the LJ fluids, suggesting that the effect of the local density enhancement is observed in this solvent. On the other hand, the ratio is insensitive to the density for alcoholic solution, which may reflect the anisotropy of the solute–solvent attractive interaction.

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Supporting Information Available: Full description of the material. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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