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Diffusion of Photochemically Generated Intermediate Radicals in Water−Ethanol Mixed Solvents

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Diffusion processes of intermediate radicals created by the photoinduced hydrogen abstraction reactions of benzoquinone (BQ) and acetophenone (AP) in ethanol−water mixed solvents are studied by using the transient grating (TG) method. The electrically neutral radicals and the anion radicals are created selectively by adding sodium hydroxide (NaOH) or sulfuric acid (H_2SO_4) to the solutions. The intermediate species and the chemical stability of the radicals were monitored by the transient absorption and time-resolved EPR methods. The diffusion constants (D) of the radicals and the parent molecules are determined simultaneously. D of the anion radicals are similar to those of the neutral radicals in any mixtures of the solvents. D of the neutral and anion radicals (D_R) are much smaller than those of the parent molecule (D_P) in ethanol ($D_P/D_R \sim 2.8$ for BQ and $D_P/D_R \sim 2.1$ for AP in ethanol), while D_P become closer to D_R with increasing water content in the solvent ($D_P/D_R \sim 1.3$ for BQ and QP in 90% water solution). The temperature dependence of D was also investigated. A possible origin of this water effect is discussed from the point of view of hydrophobic hydration.

1. Introduction

Recently we have been investigating unique diffusional processes of organic transient radicals in solution by the transient grating (TG) technique. We have found that the diffusion constants (D) of the radicals created by the hydrogen abstraction of ketones, quinones, and azaromatic compounds are smaller than those of the parent molecules of nearly the same size and the same shape in organic solvents.[1−7] It was found that the differences in D between the radicals and the parent molecules become larger with increasing solvent viscosities,[2] decreasing solute sizes,[3] and decreasing temperature.[4] The difference in D does not depend on the solvent properties, such as the polarity, the dipole moment, and the protic (or aprotic) character of the solvent except the viscosity.[2] The slow radical diffusion was explained in terms of a strong solute−solvent interaction.

In this paper, we study the effect of water on the translational diffusion of transient radicals. Water is a unique solvent in many senses. One of the most remarkable properties of water is the strong and steric solvent structure formed by the hydrogen-bonding network. In particular, the solvent structures play a very important role in the hydrophobic case. If the solute molecule is strongly hydrophobic, the water network around the hydrophobic solute tends to be stronger than that of the bulk phase. It is called the hydrophobic hydration. In 1938, Butler et al. found that the dissolution entropy changes of nonpolar solutes are negative and heat capacity changes are very large.[8] In 1945, Frank and Evans interpreted this observation by the iceberg hydration model, which is the basic model of the hydrophobic hydration.[9] In 1959, Kauzmann proposed the concept of the hydrophobic interaction,[10] and since ∼1970, Ben-Naim has developed the concept of hydrophobic hydration.[11] After that, many observations[12−14] and calculations[15] of hydrophobic hydration have been reported. The solvent structure of water has been elucidated by X-ray diffraction,[16] neutron diffraction,[17] and several calculations.[18] The hydrogen bond of the water molecule can extend to four directions, and the solvent structure is tetrahedral like that of diamond.[18,19]

Because of this structure, the diffusion in water is different from that in organic solvents.[19] The diffusion processes of stable molecules in aqueous solution have been reported by many groups so far.[20] Generally, the products $D\eta$ (η: viscosity of solvent) in aqueous solutions are smaller than that in the organic solutions. These observations have been interpreted on the basis of several theories by the hydrodynamic model. Simply, D is calculated by the Stokes−Einstein (SE) equation,[20]

$$D_{SE} = \frac{k_B T}{f\pi r\eta} \tag{1}$$

where r and T are the radius of the solute and the temperature, respectively, f is a constant which depends on the boundary condition between the solute−solvent molecules; $f = 4$ (slip) to 6 (stick). However, in many organic solutions, f should be much smaller than 4 (slip) to reproduce the experimental values of D by eq 1.

While f in an organic solvent becomes smaller with increasing η (decreasing T), Tominaga et al. found that f in water is nearly 6 and rather insensitive to the temperature.[21] This fact suggests that the hydrodynamic description with the stick boundary condition is more appropriate in water than in organic solvents. Tominaga et al. explained this observation by two factors: (1) The molecular size of water is smaller than that of organic solvents, so the continuous fluid approximation of the hydrodynamic theory becomes reasonable. (2) Hydrogen bonding of water becomes stronger so that friction between solute and solvent increases with decreasing T; it prevents the breakdown of hydrodynamic theory (in an organic solvent, the friction becomes much smaller than that of hydrodynamic theory with decreasing T).[21] Moreover, although the solute and solvent hydrogen bonding generally decreases the diffusion constant in protic solvents, D in water, which is one of the protic solvents, does not decrease.[22]

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In order to examine the diffusion behavior in the hydrogen bond network, the diffusion constants of neutral radicals, anion radicals, and parent molecules are measured in mixed solutions of ethanol and water. Ethanol is miscible with water in any proportion, and a water−ethanol mixture is one of the typical mixed solutions. The properties of these mixed solvents such as thermodynamic character,[23] structure,[24] and viscosity[25] have been already reported.

We found that the difference in D between the radicals and the parent molecules becomes smaller with increasing water concentration in the solution. This feature is discussed in terms of the solution structure of the mixture. We think that the difference in D between the radicals and the parent molecules decreases because of the hydrophobic hydration around the solutes.

2. Experimental Section

The setup of the TG method has been reported elsewhere.[1−7,26] An excitation beam from an excimer laser [XeCl (308 nm); Lumonics Hyper-400] was split into two beams by a beam splitter. The repetition rate of the excitation pulse was 1−3 Hz, and the pulse width was about 20 ns. These beams crossed inside a quartz sample cell, and the interference pattern between these beams (optical grating) was created. The laser fluence at the crossing point was measured by a pyroelectric joulemeter (Molectron J3-09), and it was typically ~0.3 mJ/cm^2. The thermal energy released by the nonradiative relaxation raises the temperature of the sample, and it creates the thermal grating. The excited molecules partly react, and the concentrations of the reactant and products were modulated (species grating). A diffracted probe beam (the TG signal) was isolated from the excitation beams with a pinhole and a red-filter (Toshiba R-60) with a cut-off wavelength of 600 nm. The intensity of the TG signal is detected by a photomultiplier tube (Hamamatsu R-928) and recorded with a digital oscilloscope (Tektronix 2430A). The fringe spacing Λ was roughly estimated from the crossing angle θ and then calibrated by the decay of the thermal grating signal of a benzene solution.[26] The temperature of the sample solution was controlled (50 to −50 °C) by circulating temperature-regulated methanol around a cell holder with a temperature control system (Lauda RSD6D).

For a transient absorption (TA) measurement, the sample was excited by excimer laser light (5 mJ/cm^2) and probed by light from a 100 W Xe lamp. The probe light was monochromated with a Spex model 1704 and detected by a photomultiplier.

Time-resolved EPR spectra were measured by the JEOL EPR spectrometer (ES-FE3X) as reported previously.[27] The EPR and TA measurements were carried out at room temperature (~20 °C).

Spectroscopic grade ethanol, distilled water, and solute (benzoquinone, BQ; acetophenone, AP) were purchased from Nacalai tesque Co. BQ and AP were purified by recrystallization and vacuum sublimation, respectively. Typical concentrations of the solutes were ~10^{-2} M. Sample solutions were deoxygenated by the nitrogen bubbling method and circulated by a peristaltic pump (Atto SJ-1211).

The van der Waals volumes V_W of the molecules were obtained from the atomic increments method given by Edward.[28] The radii of the molecules, r, were calculated from V_W using a relation $r = (3V_W/4\pi)^{1/3}$.

3. Results

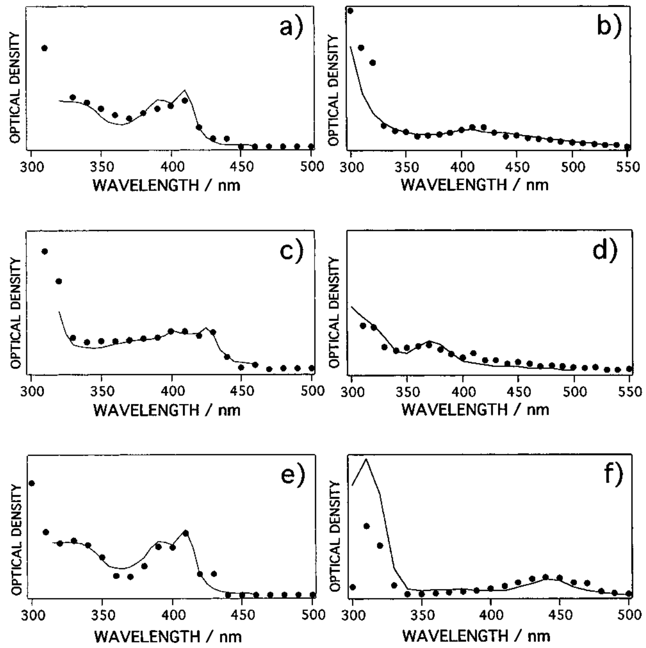

Figure 1. Transient absorption spectra at a 10 μs time delay after the excitation of (a) BQ in ethanol, (b) AP in ethanol, (c) BQ in E/W (1/9), (d) AP in E/W (1/9), (e) BQ + H_2SO_4 in E/W (1/9), and (f) AP + NaOH in E/W (1/9). Closed circles represent observed TA spectra in this study, and solid lines represent reported spectra of (a, e) the BQ anion radical in ethanol from ref 32, (b) the AP neutral radical in ethanol from ref 31, (c) the BQ neutral radical in ethanol from ref 32, (d) the AP neutral radical in water from ref 33, and (f) the AP anion radical in water from ref 33.

3.1. Photochemical Reactions. Before going into the TG experiment, we first examine the photochemistry of the solutes we used (benzoquinone (BQ) and acetophenone (AP)). On the basis of previous studies, the photochemical reactions of BQ and AP are described by the following scheme:[29]

$$\mathrm{M} \rightarrow {}^1\mathrm{M}^{**} \tag{a}$$

$${}^1\mathrm{M}^{**} \rightarrow {}^1\mathrm{M}^{*} \tag{b}$$

$${}^1\mathrm{M}^{*} \rightarrow {}^3\mathrm{M}^{*} \tag{c}$$

$${}^3\mathrm{M}^{*} + \mathrm{AH} \rightarrow \mathrm{MH}^\bullet + \mathrm{A}^\bullet \tag{d}$$

$$2\mathrm{MH}^\bullet \rightarrow (\mathrm{MH})_2 \text{ or } \mathrm{M} + \mathrm{MH}_2 \tag{e}$$

Here M stands for BQ or AP and AH is the hydrogen-donating solvent, in this case ethanol. The lowest excited triplet (T_1) state is created by the intersystem crossing from the lowest excited singlet (S_1) state by UV irradiation within an excitation laser pulse width (processes (a)−(c)). The benzosemiquinone radical (BQH$^\bullet$) or the AP ketyl radical (APH$^\bullet$) is created from the T_1 state by hydrogen abstraction from the solvent (process (d)). The recombination reaction of the two radicals is a dominant subsequent reaction (process (e)).

We investigate this reaction scheme and also the chemical stability of the radicals in ethanol + water mixed solution by the transient absorption (TA) and time-resolved EPR methods. The TA spectrum at a 10 μs time delay after the excitation of BQ and AP in ethanol and in a ethanol (10% (v/v)) + water (90% (v/v)) mixed solution (E/W (1/9)) is shown in Figure 1. In pure ethanol (Figure 1a,b), the observed spectra are similar to the reported spectra of BQH$^\bullet$ and APH$^\bullet$,[30−32] and it is reasonable to assign these species to BQH$^\bullet$ and APH$^\bullet$. The TA spectrum of AP in E/W (1/9) is also similar to the reported spectrum of APH$^\bullet$ in an aqueous solution (Figure 1d).[33]

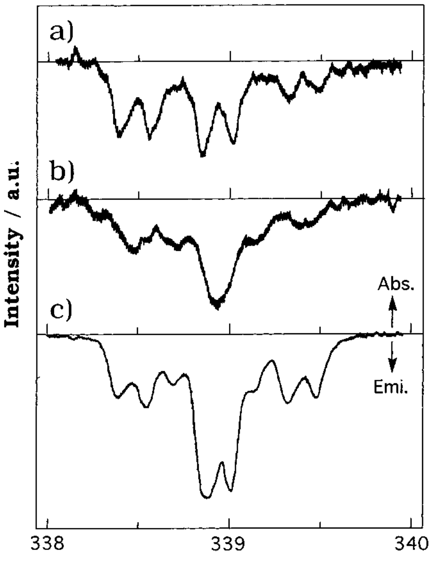

Figure 2. Time-resolved EPR spectra at a 1 μs time delay after the excitation of BQ (a) in ethanol, (b) in E/W (1/9), and (c) in E/W (5/5).

Therefore, APH$^\bullet$ should be created dominantly in ethanol and E/W (1/9). Although, the neutral radical (MH$^\bullet$) and the anion radical (M$^{\bullet-}$) are in equilibrium,[32−34]

$$MH^\bullet \rightleftarrows M^{\bullet-} + H^+ \qquad (f)$$

$$MH^\bullet + OH^- \rightleftarrows M^{\bullet-} \qquad (g)$$

the pK_a of APH$^\bullet$ was reported to be 9.9 [33] and the relatively large pK_a makes APH$^\bullet$ dominant even in aqueous solution. On the other hand, the TA spectrum of BQ in E/W (1/9) is similar to the reported spectrum of BQ anion radical (BQ$^{\bullet-}$) in an aqueous solution (Figure 1c).[32] Therefore, we assign the chemical species in water-rich solution to BQ$^{\bullet-}$. Since pK_a of BQH$^\bullet$ is 4.0,[32] BQ$^{\bullet-}$ is created dominantly in an aqueous solution (pH = 7). On the other hand, as the autoprotolysis constant of ethanol is much smaller than that of water, BQH$^\bullet$ is created dominantly in pure ethanol.

Considering the chemical equilibria (f) and (g), one can create the anion radical or the neutral radical selectively by controlling the pH of the solution. The TA spectra of BQ in E/W (1/9) with H_2SO_4 (0.1 M) and AP in E/W (1/9) with NaOH (0.1 M) are shown in Figure 1e,f, and each spectrum is very similar to the reported spectra of BQH$^\bullet$ [32] and AP$^{\bullet-}$,[33] respectively.

The time profiles of all the TA signals can be expressed well by second-order kinetics, and the half-life period is ~10 ms at a fluence of ~1 mJ/cm^2 for photoexcitation.

Since the TA spectra of BQH$^\bullet$ and BQ$^{\bullet-}$ are rather similar, it is difficult to distinguish which species are dominantly created in mixed solvents. To identify the chemical species more clearly, we use the time-resolved EPR technique. The EPR spectra of BQH$^\bullet$ and BQ$^{\bullet-}$ have been reported, and the spectral shapes of both species are quite different.[35] Figure 2 shows the observed EPR spectra of BQ at a 1 μs time delay after the excitation (a) in ethanol, (b) in E/W (1/9), and (c) in E/W (5/5). The shapes of the obtained EPR spectra of three systems are quite different, and it was found that BQH$^\bullet$ and BQ$^{\bullet-}$ are created in ethanol and E/W (1/9), respectively.[35] This fact is consistent with the conclusion from the TA measurement. The equilibrium processes (f) and (g) should be very fast (the equilibrium should be complete within 1 μs). The EPR spectrum of BQ in E/W (5/5) can be analyzed by the superposition of the spectra (a) and (b). It suggests that both species of BQH$^\bullet$ and BQ$^{\bullet-}$ exist in E/W (5/5).

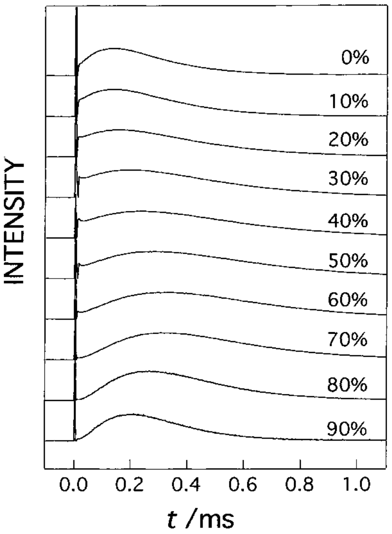

Figure 3. Time profile of the TG signal after the photoexcitation of benzoquinone in ethanol−water mixed solvents at room temperature (~20 °C). Volume % of water is indicated in the figure.

3.2. TG Experiment.

The time profiles of the TG signals after the excitation of BQ in E/W (10/0−1/9) are shown in Figure 3. All signals consist of three components, a spikelike signal, a subsequent slow rise component, and slow decay. The TG signal of BQ in ethanol agrees well with that reported previously.[3] The spikelike signal which decays in a few microseconds originates from the thermal grating. After the thermal grating signal decays to the baseline completely, the slower components of the signal appear. The slower rise and decay components should be the species grating created by the photochemical reaction. In this reaction system, four chemical species (BQ, BQH$^\bullet$, ethanol, and hydroxyethyl radical) could contribute to the TG signal. However, since the absorption coefficients of ethanol and the hydroxyethyl radical[36] are smaller than those of BQ and BQH$^\bullet$ in the visible and near-UV regions,[30,32] only two species (BQ and BQH$^\bullet$) dominantly contribute to the species grating (Figure 3).

Similar signals were observed for AP. Because the absorption coefficients of AP and APH$^\bullet$ [31,33,34] are larger than those of ethanol and the hydroxyethyl radical, the species grating mainly comes from the AP and APH$^\bullet$ contributions.

The analysis of the TG signal has been described elsewhere.[1−7,26] In these systems, the solute molecules (BQ, BQH$^\bullet$, BQ$^{\bullet-}$, AP, APH$^\bullet$, and AP$^{\bullet-}$) do not have any absorption bands at the wavelength of the probe light (633 nm).[30−34,36] Hence, the square root of the TG signal should be proportional to only the refractive index change. The species grating decays by the mass diffusion process and the subsequent reaction process of the radicals, which is mainly the recombination of the radicals. The recombination of BQH$^\bullet$ and APH$^\bullet$ is reported as a diffusion-controlled process.[37] As the excitation laser fluence for the TG measurement is much weaker (~0.3 mJ/cm^2) than that for the TA experiment, the half-life period of the radicals should be much longer than that of the TA measurement (~10 ms). The concentrations of the radicals should be almost constant within the time range for the TG measurement (~1 ms). Therefore, it is reasonable that the decay profile of the species grating signals can be analyzed by only the diffusion process. The time profile of the TG signal is

TABLE 1: Diffusion Constants (*D*) of the Parent Molecules, Neutral Radicals, and Anion Radicals of Benzoquinone (BQ) and Acetophenone (AP) in Ethanol−Water Mixed Solutions at ∼20 °C

		diffusion constants (10^{-9} m^2 s^{-1})							
		BQ		BQ + H_2SO_4		AP		AP + NaOH	
water content (%)	viscosity[a] (cP)	parent	radical[b]	parent	radical[c]	parent	radical[d]	parent	radical[e]
0	1.20	1.6	0.57			1.3	0.61	1.3	0.45
10	1.61	1.2	0.44			0.89	0.44	1.0	0.39
20	2.01	0.85	0.34			0.72	0.38	0.75	0.34
30	2.37	0.72	0.36			0.55	0.33	0.61	0.31
40	2.67	0.64	0.32			0.48	0.28	0.61	0.31
50	2.87	0.58	0.32	0.58	0.31	0.42	0.27	0.43	0.29
60	2.91	0.56	0.35	0.60	0.37	0.39	0.26	0.38	0.22
70	2.71	0.62	0.42	0.65	0.39	0.42	0.30	0.41	0.28
80	2.18	0.77	0.50	0.79	0.48	0.49	0.40	0.49	0.32
90	1.54	0.76	0.61	0.76	0.57	0.55	0.46	0.57	0.45

[a] Reference 25 (at 20 °C). [b] Neutral radical and anion radical of BQ are created. [c] BQ neutral radical are created. [d] AP neutral radical are created. [e] AP anion radical are created.

given by[1−6,26]

$$I_{\mathrm{TG}}(t)^{1/2} = |\delta n_{\mathrm{th}}{}^{0} \exp(-D_{\mathrm{th}}\, q^2 t) - \delta n_{\mathrm{P}}{}^{0} \exp(-D_{\mathrm{P}}\, q^2 t) + \delta n_{\mathrm{R}}{}^{0} \exp(-D_{\mathrm{R}}\, q^2 t)| \quad (2)$$

where $\delta n_{\mathrm{th}}{}^0$, $\delta n_{\mathrm{P}}{}^0$, and $\delta n_{\mathrm{R}}{}^0$ are the initial refractive index changes of the thermal grating and the species gratings of parent molecules (BQ, AP) and radicals (BQH$^\bullet$, APH$^\bullet$), respectively. Generally, the refractive index change of the thermal grating is negative ($\delta n_{\mathrm{th}}{}^0 < 0$) and the refractive index change of the species grating of all species in this system is positive ($\delta n_{\mathrm{P}}{}^0$, $\delta n_{\mathrm{R}}{}^0 > 0$).[30−34,36] D_{th}, D_{P}, and D_{R} are the thermal diffusivity, the mass diffusion constants of the parent molecules, and the radicals, respectively, and q is the grating vector [$q = 2\pi/\Lambda$ (Λ, fringe length)].

As the heat conduction process is generally much faster than the mass diffusion ($D_{\mathrm{th}} \gg D_{\mathrm{P}}, D_{\mathrm{R}}$), it is obvious that the spikelike component of the TG signals is the thermal grating signal. D_{th} from the TG signal agrees well with the calculated one from $D_{\mathrm{th}} = \lambda_\omega / C_{\mathrm{P}}\rho$ (λ_ω, thermal conductivity; C_{P}, heat capacity, ρ, density).[38] It is important to note that the signal drops to the baseline once. This suggests that the dominant component of the species grating (the slower decay component) has a positive change of the refractive index. On the other hand, the slowly rising component has a negative change of the refractive index. Comparing the sign of the refractive index in eq 2 ($\delta n_{\mathrm{P}}{}^0$, $\delta n_{\mathrm{R}}{}^0 > 0$) with the TG signals (Figure 3), we assigned the slowly rising component and decay component of the TG signal as due to the species grating of the parent molecules and the radicals, respectively. We fitted the species grating component of the TG signals with a double-exponential function and determined D_{P} and D_{R} (Table 1). As the result of the fitting, it was found that the magnitude of $\delta n_{\mathrm{R}}{}^0$ is larger than that of $\delta n_{\mathrm{P}}{}^0$. This is consistent with the fact that the absorption bands of the radicals are located at longer wavelength than those of the parent molecules. It is easily predicted that the refractive index changes at the wavelength of the probe light (633 nm) of the radicals are larger than that of the parent molecules by the Kramers−Kronig relation.

The TG signals of BQ in E/W (5/5−1/9) + H_2SO_4 (0.1 M) and AP in E/W (10/0−1/9) + NaOH (0.1 M) are similar to the TG signal shown in Figure 3. *D* of BQH$^\bullet$ and AP$^{\bullet-}$ in several mixed solvents are determined by the same analytical method (Table 1). It is noteworthy that, although the TG signals of BQ in E/W (5/5) can be fitted by a double exponential function, the Time-resolved EPR spectra (Figure 3) clearly indicate the presence of three species (BQ, BQH$^\bullet$, and BQ$^{\bullet-}$). This fact suggests that the *D* values of BQH$^\bullet$ and BQ$^{\bullet-}$ are similar in ethanol + water. This observation is consistent with the similar diffusion constants of anion radicals and neutral radicals created from ketones in ethanol.[7] The *D* values of the anion radicals and those of the neutral radicals of AP are also very close in the mixture of ethanol and water. The intensities of the TG signals in pure water are much smaller than that in the water−ethanol mixed solution, because the efficiency of the hydrogen abstraction from the water molecule may be smaller than that from the ethanol molecule.

A main source of the experimental error in *D* comes from the fitting error of the double-exponential function.[2b] Recently, Donkers and Leaist have reported *D* of BQ and AP in ethanol determined by the Tayler dispersion (TD) method as 1.44 and 1.26 × 10^{-9} m^2 s^{-1}, respectively.[39] Our values from the TG method are close to their values from the TD method within 10%. The fitting errors for the *D* values of the radicals should be smaller than those of the parent molecules (≤10%).

4. Discussion

4.1. Comparison of *D* Values of the Parent Molecules and Radicals. *D* is plotted against the concentration of water (%) in ethanol in Figure 4. Figure 4a shows that the *D* of a mixture of BQH$^\bullet$ and BQ$^{\bullet-}$ (open squares) are quite similar to *D* of BQH$^\bullet$ (open circles). Figure 4b shows that the *D* values of APH$^\bullet$ (white squares) are quite similar to *D* of AP$^{\bullet-}$ (white circles). Therefore, the *D* values of the neutral radicals and the anion radicals are quite close each other in all the mixed solutions.

We compare the obtained *D* with the SE equation (eq 1) and the empirical equation proposed by Evans et al.,[40]

$$D_{\mathrm{EV}} = \frac{T \exp(a/r + b)}{\eta^{(c/r+d)}} \qquad (3)$$

where *a b*, *c*, and *d* are constants, which are determined as $a = 5.9734$ Å, $b = -7.3401$, $c = -0.863\,65$ Å, and $d = 1.0741$. Generally, *D* values of neutral molecules in organic solvents can be reproduced well by D_{EV}.[40] In a series of our previous studies, we have shown that *D* values of parent molecules agree very well with D_{EV}.[4,5,7] On the other hand, *D* values of the neutral or anion radicals are close to D_{SE} with the stick

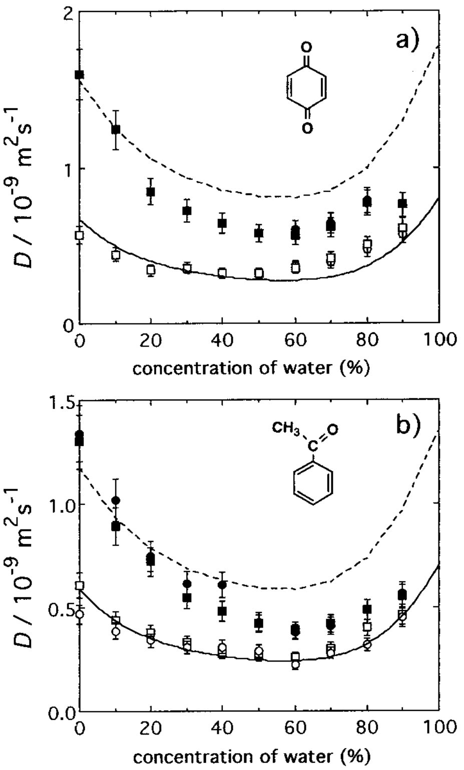

Figure 4. Water concentration dependence of D of the parent molecules (■) and the radicals (□) of BQ (a) and AP (b), D of the parent molecules (●) and the radicals (○) of BQ + 0.1 M H_2SO_4 (a) and AP + 0.1 M NaOH (b). The broken line and the solid line are values of D calculated by eqs 1 and 3, respectively.

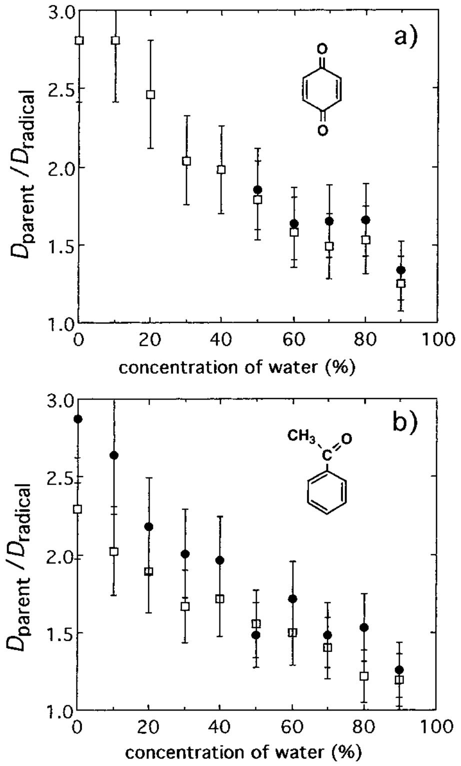

Figure 5. (a) Water concentration dependence of the ratio of parent molecule's D to radical's D of BQ (□) and BQ + 0.1 M H_2SO_4 (●) and (b) the ratio of D of the radicals of AP (□) and AP + 0.1 M NaOH (●).

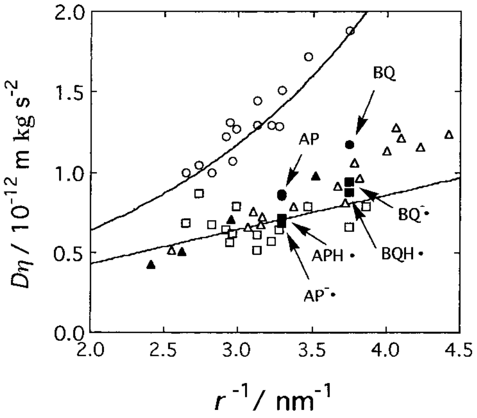

Figure 6. Solute size dependence of $D\eta$ of the parent molecules (●) and the radicals (■) in E/W (1/9) solution. The reported values by the TG method (refs 2 and 3) of the parent molecules (○) and the radicals (□) in ethanol are also plotted. The literature values of several molecules (△) (ref 20) and the tetraalkylammonium ions (▲) (ref 14c) in water are also plotted. The broken line and the solid line are values of D calculated by eqs 1 and 3, respectively.

boundary.[1-4,7] D_{SE} and D_{EV} in several solutions are also shown in Figure 4. D of the radicals are close to D_{SE} in all the solutions. D of the parent molecules are close to D_{EV} in ethanol-rich solutions but smaller than D_{EV} in the water-rich region. The difference becomes larger with increasing content of water in solution, and D becomes closer to D_{SE}.

Figure 5 shows the ratio D between the parent molecules and the radicals against the concentration of water in ethanol. The ratios of both systems decrease linearly with increasing concentration of water. The difference in D between the parent molecules and the radicals became smaller by addition of water. In our previous research, the slow diffusion of radicals was observed regardless of the solvent property (the polarity, the dipole moment, and the protic character, etc.).[2] Only in aqueous solution are the diffusion processes of the radicals similar to those of the parent molecules. The possible origin of this fact is considered in later sections.

Figure 6 shows $D\eta$ against $1/r$ of the parent molecule (open circles) and the radicals (open squares) in ethanol and those of stable molecules in water (open triangles) reported previously.[20] The curved and straight lines are calculated ones of $D_{SE}\eta$ and $D_{EV}\eta$, respectively. It is evident that $D_P\eta$ and $D_R\eta$ agree with $D_{SE}\eta$ and $D_{EV}\eta$, respectively, in ethanol. On the other hand, $D_P\eta$ in water are close to $D_{SE}\eta$ rather than $D_{EV}\eta$. The agreement with $D_{SE}\eta$ could indicate that the water molecules can be treated as a continuous fluid. $D\eta$ of BQ, AP (closed circles), and the radicals ($BQH^\bullet$, $BQ^{\bullet-}$, $APH^\bullet$and $AP^{\bullet-}$) (closed squares) in E/W (1/9) are also plotted in Figure 6. $D\eta$ of both the radicals and the parent molecules are close to D_{SE} rather than D_{EV}.

4.2. Temperature Dependence of *D* in Ethanol and in Water. The temperature dependence of D is examined in ethanol and in water for studying the diffusion processes in these solvents. In many cases, the temperature dependence of D of neutral stable molecules can be expressed by the following Arrhenius-type equation:[20]

$$D = D_0 \exp\left(-\frac{E_D}{k_B T}\right) \tag{4}$$

Here E_D is the diffusion activation energy and D_0 is the pre-exponential factor. We plotted log D against $1/T$ (Arrhenius plot) in Figure 7 for the samples in ethanol. Although both Arrhenius plots in ethanol show a good linear relationship, the difference in the activation energy is notable. In a previous

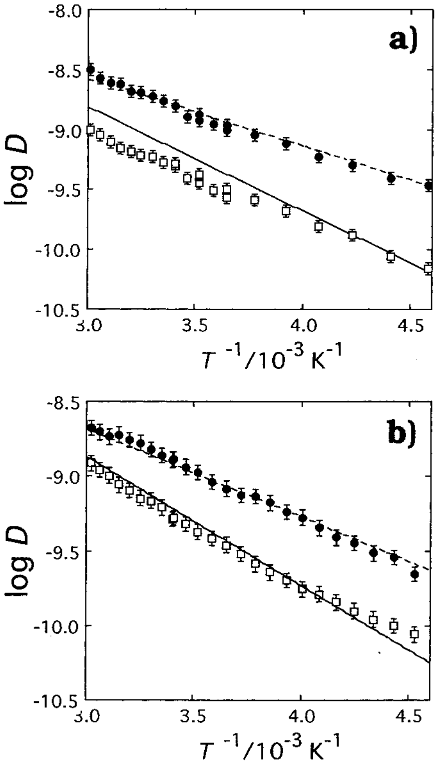

Figure 7. (a) Temperature dependence (Arrhenius plots) of D of BQ and (b) AP in ethanol (50 to −50 °C). Closed circles and open squares indicate D of the parent molecules and the radicals, respectively.

paper,[4] the different activation energies between the radicals and parent molecules in ethanol and 2-propanol are explained as follows.

If the temperature dependence of the viscosity is written as[41]

$$\eta = \eta_0 T \exp\left(\frac{E_\eta}{k_B T}\right) \qquad (5)$$

where E_η is the activation energy of viscosity and η_0 is the pre-exponential factor ($E_\eta = 3.96$ kcal/mol in ethanol),[42] we obtain $E_D = E_\eta$ from the hydrodynamic theory (eqs 1, 4, and 5). On the other hand, if D is well expressed by eq 3, E_D is given by

$$E_D = E_\eta\left(\frac{c}{r} + d\right) \qquad (6)$$

In this case, since c is negative (−0.863 65 Å), E_D is slightly smaller than E_η and depends on the molecular size. Indeed, if we plot D_{SE} and D_{EV} (Figure 7), it is evident that the temperature dependence of D of the radicals is expressed well with D_{SE}, while those of the parent molecules are close to D_{EV} with eq 6.

On the other hand, the Arrhenius plots of D of the radicals and the parent molecules in water (+10% ethanol) (Figure 8) are not linear and they resemble each other. We also plot D_{SE} and D_{EV} in Figure 8. D of both the radicals and parent molecules are close to D_{SE} rather than D_{EV} which suggests that the temperature dependence of D is mainly determined by that of η. This nonlinearity of the Arrhenius plot of D in water has been reported by Tominaga et al. for stable molecules in water.[21] This nonlinearity was explained by the fact that the temperature dependence of the viscosity of water cannot be expressed by eq 5. Water is strongly hydrogen bonded and builds a steric structure. The hydrogen bonding becomes stronger with decreasing T. Therefore, the slope of the Arrhenius plot becomes steeper with decreasing T. Our results are similar to their results. This result suggests that the hydrodynamic approximation of diffusion is reasonable. We conclude that D of the radicals and the parent molecules are similar in a wide range of temperatures in water.

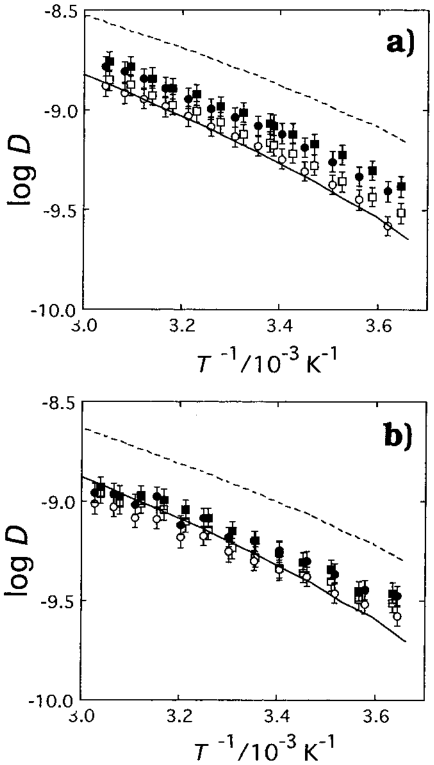

Figure 8. Temperature dependence (Arrhenius plots) of D in E/W (1/9) (50−0 °C) of the parent molecules (■) and the radicals (□) of BQ (a) and AP (b). D values of the parent molecules (●) and the radicals (○) of BQ + 0.1 M H_2SO_4 (a) and AP + 0.1 M NaOH (b) in ethanol−water mixed solutions are also shown. The broken line and the solid line represents the calculated D from eqs 1 and 3, respectively.

4.3. Similar D Values of the Radicals and Parent Molecules in Water.

In previous papers, we reported D of the radicals and the parent molecules in various organic solvents and found that D_R is always smaller than D_P.[1−7] In this study, we for the first time find a solvent in which D_R is similar to D_P. In this section, we consider a possible origin of the similarity of D_P and D_R. This unique property of water could be explained by the hydration.

In the case of hydrophilic solutes (e.g. an ionic, polar, or hydrogen-bonded molecule), the hydrogen bonds of water are destroyed and/or complexlike hydration structures are constructed (hydrophilic hydration).[43] On the other hand, in the case of a hydrophobic solute, the solute molecules aggregate (hydrophobic bonded)[10] or the hydrogen bonds of water are reconstructed around the solute (hydrophobic hydration).[11−14] The hydrophobic hydration is sensitive not only to the polarity but also to the size and the shape of the solute molecules. The hydrophobic hydration has been observed for inert gas atoms, small alkanes, and also benzene.[12] Using X-ray diffraction, Nishikawa et al. reported that *tert*-butyl alcohol is solvated by hydrophobic hydration in spite of the hydrophilic part (−OH), while ethanol and propanol are not solvated by hydrophobic hydration.[13] Moreover, hydrophobic hydration was observed for tetraalkylammonium ions although they have a charge which could interact with water strongly.[14] These facts suggest that hydrophobic properties should be more effective than hydrophilic properties (hydrogen bonding or charge) of the solutes in the hydration mechanism. Tominaga et al. reported that the diffusion processes of toluene, ethylbenzene, hexafluorobenzene, *n*-butylbenzene, biphenyl, naphthalene, and ethylnaphthalene are very similar to that of benzene in water (D of these molecules are close to D_{SE} with stick boundary).[21] This fact suggests that these molecules are solvated by hydrophobic hydration as in the case of benzene. Therefore, it is very plausible that BQ and AP are solvated by a hydrophobic hydration in a water-rich solvent. Under this condition, D should be described by the SE equation with stick boundary ($f = 6$). Indeed, the D values of AP and BQ are close to D_{SE} rather than D_{EV}.

As we have reported recently, D of the transient radicals are close to D_{SE} with the stick boundary condition in many organic solutions.[1−4,7] The different D_R values compared to D_P in these organic solvents have been explained by an attractive interacton between the radicals and solvents, which was recently supported by a theoretical calculation by Morita and Kato.[44] We found, in this study, that the D values of the radicals in water-rich solutions are still close to D_{SE} with the stick boundary condition. This observation can be interpreted in two ways: the radicals diffuse under the influence of the attractive intermolecular interaction in aqueous solution as in the organic solvents or the diffusion is governed by hydrophobic hydration like that of the parent molecules. We think that hydrophobic hydration is more important in aqueous solution because even the tetraalkylammonium ion, which has an electric charge and should interact with solvent significantly, is solvated by the hydrophobic hydration.[14] We plot the reported D values of the tetraalkylammonium ions in Figure 6.[14c] D values of the radicals in water (+10% ethanol) are close to those of the tetraalkylammonium ions, and both D values are close to D_{SE} with the stick boundary (Figures 4 and 6). This fact may indicate that both species (radicals and tetraalkylammonium ions) are solvated by similar hydrophobic hydrations. The parent molecules, the radicals, and ions are surrounded by similar solvent structures of strong hydrophobic hydration, even if attractive interactions between the radicals and water exist or if Coulomb interactions between the ions and water exist. As the solvation structure of both the parent molecules and the radicals should be quite similar, D_P and D_R are close in water-rich solutions. Moreover, the weaker hydrogen-bonding effects in an aqueous solution reported by Tominaga et al.[21] have the same origin as the slow diffusion of radicals (the magnitude of the intermolecular interactions of hydrogen bonding may be similar to that of the radicals in ethanol).

The steric structure of water is gradually constructed by increasing the amount of water in ethanol as revealed by several means.[13,45] Therefore D of the parent molecules gradually changes from D_{EV} in ethanol to D_{SE} in water. On the other hand, D of the radicals can be expressed by D_{SE} in ethanol because of the attractive intermolecular interaction and also by D_{SE} in water because of the hydrophobic hydration. Therefore, D of the radicals are close to D in the entire region of the mixed solutions.

5. Conclusions

The diffusion constants (D) of the parent molecules, the neutral radicals, and anion radicals of benzoquinone and acetophenone in ethanol−water mixed solvents were measured by using the transient grating (TG) method. The neutral radicals and the anion radicals are created selectively by addition of the sodium hydroxide and sulfuric acid in water−ethanol mixed solution. D of the radicals are smaller than those of the parent molecules in ethanol as we have reported. D of the neutral radicals and the anion radicals are similar in any mixture of ethanol and water. We found that the difference between D_R and D_P becomes smaller with increasing water content in solution.

We compare the obtained D with those from the Stokes−Einstein equation (D_{SE}) and D proposed by Evans et al. (D_{EV}). D_R are close to D_{SE} in any solution we investigated. On the other hand, D_P are close to D_{EV} in ethanol and become smaller than D_{EV} and approach D_{SE} with increasing water content. In E/W (1/9) solution, D_R and D_P are similar and close to D_{SE}. We consider that both the parent molecules and the radicals are solvated by hydrophobic hydration. When the solvation structure of hydrophobic hydration is constructed, the special intermolecular interaction of radicals may be reduced by the strong solvent structures. Therefore, in the water-rich region, D_P values are close to D_R.

We also measured the temperature dependence of D. D of both radicals and parent molecules can be expressed by the Arrhenius type relationship with a single activation energy (E_D) in ethanol. E_D values of the radicals are close to the activation energies of viscosities (E_η), though the E_D values of the parent molecules are slightly smaller than E_η. These features can be explained in the expressions of D_{SE} and D_{EV}. On the other hand, the temperature dependence of D in water (+10% ethanol) cannot be expressed by a single activation energy. The temperature dependences of both the radicals and the parent molecules in water are reproduced well by that of D_{SE}. This result is also attributed to the hydrophobic hydration of the radicals and the parent molecules in water.

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