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Evidence for Enhanced Bimolecular Reactions in Supercritical CO_2 at Near-Critical Densities from a Time-Resolved Study of Fluorescence Quenching of 9,10-Bis(phenylethynyl)anthracene by Carbon Tetrabromide

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Abstract: The quenching of 9,10-bis(phenylethynyl)anthracene (BPEA) fluorescence by carbon tetrabromide (CBr_4) is investigated in supercritical carbon dioxide as a function of densities. Fluorescence lifetimes of BPEA at different CBr_4 concentrations are determined using the time-correlated single photon counting method. While the fluorescence decays adhere closely to single-exponential functions and the CBr_4 concentration dependence follows the Stern−Volmer relationship, the quenching of fluorescence lifetime is unusually efficient at near-critical densities. The results are in support of a solute−solute clustering mechanism in which the enhanced bimolecular reactions are attributed to a higher local quencher concentration than the bulk under near-critical solvent conditions.

Introduction

Supercritical fluids as unique solvent systems have been studied extensively.[1−3] There is considerable interest in the understanding of so-called clustering effects in supercritical fluid systems. The presence of solute−solvent clustering, a phenomenon in which the local density of solvent molecules about a solute molecule is greater than the bulk, has been widely recognized.[4−19] However, still unsettled is the issue concerning the existence of solute−solute clustering, namely that the local concentration of solute molecules is higher than the bulk in supercritical fluids under certain conditions.[20] The clustering may result in unusually efficient intermolecular reactions.

The precursor for the concept of solute−solute clustering in supercritical fluids is the observation of entrainer effects. It was found that the presence of a small amount of liquid cosolvent can dramatically increase the solubility of solids in supercritical fluids,[22] and that there are preferred interactions between the solute and cosolvent molecules.[7a] In a steady-state fluorescence study of excited state complexes, Eckert and coworkers observed[5a,23] unusually efficient formation of pyrene excimer and naphthalene−triethylamine exciplex in supercritical CO_2 and ethylene, and attributed the phenomenon to enhanced interactions of the solute molecules. The proposal has been supported by subsequent observations of enhanced solute−solute interactions in several other systems[24,25] and by results from theoretical calculations.[15,18,19,26,27] However, there are also other experimental studies that seem to indicate no unusual behavior

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(20) In principle, there are two aspects in the definition of the solute−solute clustering phenomenon: (1) increasing intensity of solute−solute interactions and (2) increasing number of interactions due to a higher local concentration of solute molecules. We believe that local solute concentration augmentation in supercritical fluids is a more realistic possibility.[21]

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in solute–solute interactions in supercritical fluids.[28–31] Recently, we have shown[21] that the excimer formation of pyrene in supercritical CO_2 is indeed unusual, in support of the proposal of Eckert and co-workers. The experimentally determined relative fluorescence yields of pyrene monomer Φ_{FM} and excimer Φ_{FD} in supercritical CO_2 can hardly be accounted for in the context of the classical photophysical mechanism. The ratios Φ_{FD}/Φ_{FM} are abnormally large at near-critical densities, and the augmentation is more significant at temperatures closer to the critical temperature of CO_2.[21] The unusual behavior in the density dependence of pyrene excimer formation in supercritical CO_2 is further confirmed by a comparative fluorescence study of the pyrene intermolecular excimer with intramolecular excimers in 1,3-di(1-pyrenyl)propane and 1,3-di(2-naphthyl)propane.[32] The Φ_{FD}/Φ_{FM} ratios in the intramolecular systems are only weakly density dependent, showing no augmentation at near-critical densities.[32] It is likely that the enhanced intermolecular excimer formation is due to a higher local monomer concentration in the vicinity of an excited monomer molecule (solute–solute clustering).[20,21] However, systems that form emissive excited state complexes are intrinsically more complex probes because of the involvement of two excited states. Arguments can always be made to find some rather remote possibilities to explain the observed unusual enhancement of intermolecular complex formation at near-critical densities. Therefore, simple bimolecular reactions are more desirable probes in the investigation of solute–solute clustering in supercritical fluids. Based on such a consideration, we have been studying fluorescence quenching of polyaromatic molecules by carbon tetrabromide (CBr_4) in supercritical CO_2. It is known from results in room-temperature solutions[33] that fluorescence intensities and lifetimes of polyaromatic compounds such as anthracenes and perylene are effectively quenched by carbon tetrachloride (CCl_4) and CBr_4 without the formation of emissive excited state complexes. Unlike CCl_4, the fluorescence quenching by CBr_4 is excitation wavelength independent.[33,34] Thus, the arene–CBr_4 systems are ideal probes in the investigation of solute–solute clustering in supercritical fluids. Here we report a time-resolved study of 9,10-bis(phenylethynyl)anthracene (BPEA) fluorescence quenching by CBr_4 in supercritical CO_2 as a function of density. The results show unambiguously that there is indeed enhanced fluorescence quenching at near-critical densities, which could be attributed to higher local quencher concentrations under the near-critical solvent conditions.

Experimental Section

Materials. 9,10-Bis(phenylethynyl)anthracene (Aldrich, 97%) and carbon tetrabromide (Aldrich, 99%) were used without further purification. Hexane and THF (Burdick & Jackson, spectrophotometry grade) were used as received. Carbon dioxide (Air Products, 99.9999%) was checked for oxygen content by comparing fluorescence quantum yields of pyrene before and after a rigorous deoxygenation procedure in which the carbon dioxide was repeatedly passed through oxygen traps (Alltech Associates, Inc.). Because the results indicated no oxygen quenching, the carbon dioxide was used without further purification.

Measurements. Absorption spectra were recorded on a computer-controlled Shimadzu UVPC-2101 spectrophotometer. Steady state fluorescence spectra were obtained on a Spex Fluorolog-2 photon-counting emission spectrometer equipped with a 450 W Xe lamp and a Hamamatsu R928 photomultiplier tube. All fluorescence spectra were corrected for nonlinear instrumental response of the spectrometer using predetermined correction factors. Excitation and emission slits were 0.25 mm (1 nm resolution) and 1.25 mm (5 nm resolution), respectively. Fresh solutions were used in all measurements to minimize the effect of possible photochemical reactions.

Fluorescence decays were measured using a time-correlated single photon counting apparatus. The excitation source was a Hamamatsu SLDH041 light pulser at 414 nm. The detector consisted of a Philips X2020 photomultiplier tube in a thermoelectronically cooled housing (Products for Research Inc.). The photomultiplier tube was operated at 2 kV using an EG&G 556 high-voltage power supply. The detector electronics from EG&G include two 9307 discriminators, a 457 biased time-to-amplitude converter, and a 916A multichannel analyzer. The time resolution of the setup as measured by the half width of the instrument response function was ~0.9 ns. The fluorescence decays were detected by use of either a 435- or a 495-nm color-glass sharp-cut filter from Schott. Fluorescence lifetimes were determined from observed decay curves and instrument response functions using a standard deconvolution method. A home-developed least-squares program was used. The instrument was calibrated with a carefully deoxygenated benzene solution of 9,10-diphenylanthracene.

The high-pressure setup for spectroscopic studies in supercritical CO_2 is similar to the one reported previously.[35] The system pressure was generated by a Teflon-packed syringe pump (High Pressure Equipment Company, 87-6-5) and monitored by a precision pressure gauge (Dresser Industries, Heise-901A). The calibrated accuracy of the pressure gauge is better than ±1 psia at 1100 psia. The system temperature was controlled and monitored by an RTD temperature controller (Omega, 4200A) coupled with a pair of cartridge heaters (Gaumer, 150W) inserted into the optical cell body. Absorption and fluorescence measurements were carried out using a cubic shape high-pressure optical cell made from stainless steel. The cell chamber (calibrated volume 1.87 mL) consists of four channels which open at the four side walls of the cell. Three of the channels are for accommodating optical windows and the fourth one is for cell cleaning. The three quartz windows (12.7 mm diameter and 5 mm thick) were sealed using Teflon O-rings. The optical paths of the cell for absorption (180°) and fluorescence (90°) measurements are 30.5 (calibrated) and 7.5 mm, respectively.

In the preparation of samples for fluorescence measurements in supercritical CO_2, hexane solutions of BPEA and CBr_4 were added to the high-pressure optical cell. The cell was purged with a slow stream of nitrogen gas to remove the solvent hexane. A procedure of repeatedly filling-and-discharging with low-pressure CO_2 gas (<100 psia) was used to eliminate trace amounts of oxygen trapped in the optical cell chamber. The cell was then sealed and thermostated at the desired temperature before CO_2 was introduced. The CBr_4 concentrations were determined spectroscopically using a calibration curve based on absorption in the wavelength region of 250–320 nm.

Experimental viscosity values of supercritical CO_2 are available at selected temperatures and pressures.[36] Interpolation for obtaining the values under our experimental conditions was made using the empirical equation due to Jossi, Stiel, and Thodos,[37]

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$$[(\eta - \eta^0)\xi_T + 1]^{1/4} = a_0 + a_1\varrho_r + a_2\varrho_r^2 + a_3\varrho_r^3 + a_4\varrho_r^4 \quad (1)$$

$$\xi_T = (T_c/M^3P_c^4)^{1/6} \quad (2)$$

where η and η° are viscosities of the fluid and low-pressure gas, respectively; P_c and T_c are the critical parameters; M is the fluid molecular weight, and ρ_r is reduced density. The parameters a_i in eq 1 generalized for nonpolar fluids are available in the literature.[37] However, in order to be more accurate specifically for CO_2 under our experimental conditions, the parameters were obtained from the experimental viscosity data through a least-squares regression. For CO_2 in the temperature range of 35 to 57 °C and pressures up to 400 bar,[37] the parameters are $a_0 = 0.9975$, $a_1 = 0.2061$, $a_2 = 0.6998$, $a_3 = -0.5258$, and $a_4 = 0.1372$.[21]

Results and Discussion

Fluorescence Quenching in Solution. Absorption and fluorescence spectra of BPEA in hexane are shown in Figure 1. The absorption is independent of CBr_4 concentration in the range used in this study (up to 5×10^{-2} M). As the CBr_4 concentration increases, the intensity of BPEA fluorescence decreases, but the spectral profile remains unchanged (Figure 1). There is no evidence for any emission contribution from BPEA−CBr_4 exciplexes. The observed fluorescence spectra are excitation wavelength independent. The quenching of BPEA fluorescence intensities by CBr_4 follows the linear Stern−Volmer relationship,

$$\Phi_F{}^\circ/\Phi_F = 1 + K_{SV}[CBr_4] \quad (3)$$

where $K_{SV} = k_q\tau_F{}^\circ$, with k_q and $\tau_F{}^\circ$ being quenching rate constant and the fluorescence lifetime of BPEA, respectively. As shown in Figure 2, the quenching is also excitation wavelength independent.

Fluorescence decays of BPEA in room-temperature solutions were fitted to a mono-exponential equation by deconvoluting from corresponding instrument response functions. The lifetimes are 3.62 ns in hexane and 3.56 ns in THF, which are in agreement with those reported in the literature.[38] The fluorescence lifetimes of BPEA were also determined as a function of CBr_4 concentration in hexane. As the CBr_4 concentration increases, the lifetime becomes shorter. The quenching also follows the linear Stern−Volmer relationship,

$$\tau_F{}^\circ/\tau_F = 1 + k_q\tau_F{}^\circ[CBr_4] \quad (4)$$

As shown in Figure 2, the results from quenchings of fluorescence intensity and lifetime are similar. A linear least-squares regression of the results yields a K_{SV} value of 31 M^{-1}. With the BPEA fluorescence lifetime of 3.62 ns in hexane, the quenching rate constant k_q is 8.6×10^9 M^{-1} s^{-1}. The k_q value can be compared to the diffusion rate constant of the BPEA−CBr_4 pair in hexane. In terms of hydrodynamic theories, diffusion rate constants in solution can be represented approximately by the Smoluchowski equation,

$$k_{SE} = (4 \times 10^{-3})\pi N(r_{BPEA} + r_{CBr_4})(D_{BPEA} + D_{CBr_4}) \quad (5)$$

where r_{BPEA} and r_{CBr_4} are molecular radii of BPEA and the quencher CBr_4, respectively. In a stick boundary condition the diffusion coefficients D_i can be expressed as follows,

$$D_i = kT/6\pi\eta r_i \quad (6)$$

where η is solvent viscosity. From eqs 5 and 6, a diffusion rate constant of 2.5×10^{10} M^{-1} s^{-1} can be calculated for the BPEA−CBr_4 pair in hexane, which is larger than the observed fluorescence quenching rate constant. It is known[39] that in applications of the hydrodynamic Smoluchowski equation to molecular diffusion, corrections are often required. A factor f can be used to account for the difference between the Smoluchowski and observed diffusion rate constants,

$$k_d = fk_{SE} \quad (7)$$

For BPEA−CBr_4 in hexane, $f = k_q/k_{SE} = 0.34$ is obtained if the fluorescence quenching is assumed to be diffusion controlled ($k_d = k_q$).

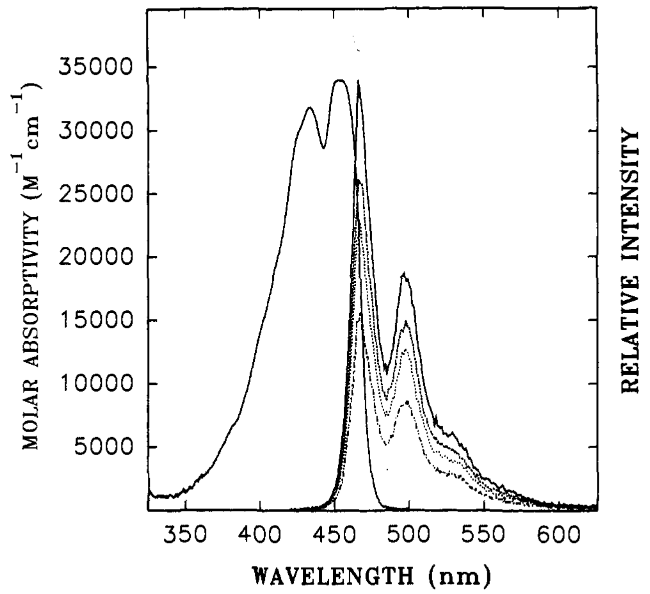

Figure 1. The absorption spectrum of BPEA in room-temperature hexane and fluorescence spectra at CBr_4 concentrations of 0 (—), 1.3×10^{-2} (- - -) 2.0×10^{-2} (···), and 3.5×10^{-2} M (-···-).

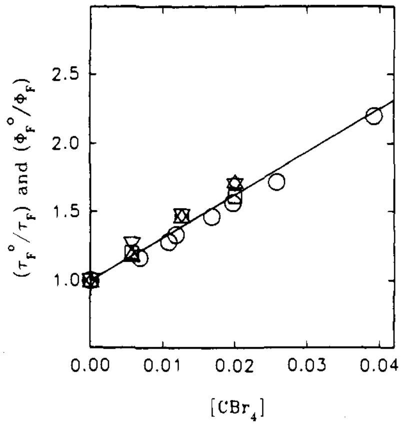

Figure 2. Stern−Volmer plots for BPEA fluorescence lifetime quenching $\tau_F{}^\circ/\tau_F$ (○) and quantum yield quenching $\Phi_F{}^\circ/\Phi_F$ at different excitation wavelengths (410 nm, △; 430 nm, □; 452 nm, ▽) by CBr_4 in room-temperature hexane. The line is from a linear least-squares regression, with a slope of 31 M^{-1}.

Fluorescence Quenching in Supercritical CO_2. For a quantitative investigation of BPEA fluorescence quenching by CBr_4 in supercritical CO_2, CBr_4 solubilities in CO_2 were determined as a function of CO_2 density. At 35 °C and a CO_2 reduced density of 1.0, the solubility of CBr_4 in CO_2 is approximately 3×10^{-2} M, which is much larger than the

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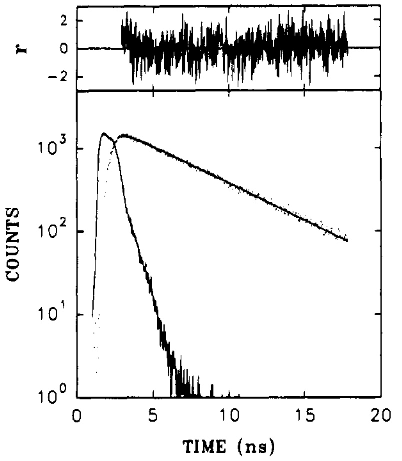

Figure 3. The fluorescence decay of BPEA in CO_2 at a reduced density of 1.18 at 35 °C. The instrument response function was obtained under the same experimental conditions using a 400 nm band pass filter (10 nm half width) for detection. Shown in the inset is the fitting residual, $r = (I_{EXP} - I_{CALC})/I_{EXP}^{1/2}$.

Table 1. Fluorescence Lifetimes (ns) of BPEA in Supercritical CO_2 at Near-Critical Densities at 35 °C[a]

reduced density	$[CBr_4]$,[a] M 0	5.7×10^{-4}	1.5×10^{-3}	2.6×10^{-3}
1.03		4.45 (1.17)		
1.04				2.88 (1.22)
1.06	5.72 (1.31)		3.73 (1.11)	
1.09		4.52 (1.42)		
1.10			3.80 (1.14)	
1.11	5.65 (0.99)			3.05 (1.88)
1.15		4.55 (1.32)	3.86 (1.07)	
1.17				3.21 (1.16)
1.18	5.58 (0.99)			
1.19		4.59 (1.53)		
1.21			4.01 (1.07)	3.34 (1.28)
1.30	5.37 (1.08)			

[a] The χ^2 values from deconvolution using a least-squares method are shown in parentheses.

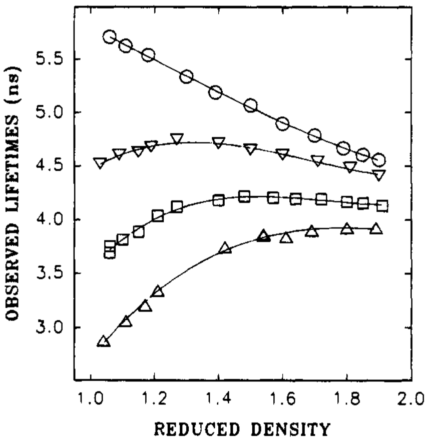

Figure 4. Observed fluorescence lifetimes of BPEA in supercritical CO_2 (35 °C) as a function of reduced density at CBr_4 concentrations of 0 (○), 5.7×10^{-4} (▽), 1.5×10^{-3} (□), and 2.6×10^{-3} M (△). The empirical curves are for interpolation of lifetime values at selected densities.

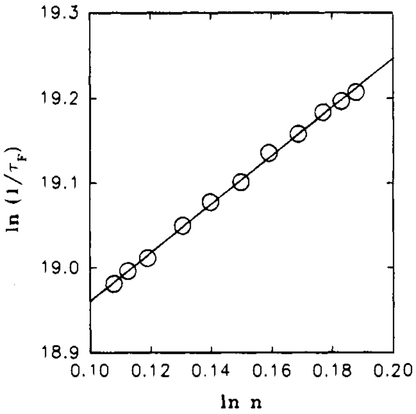

Figure 5. A plot of ln $(1/\tau_F)$ vs ln n for BPEA in CO_2 at 35 °C. The line is from a linear least-squares regression (slope = 2.86, intercept = 18.67, and correlation coefficient = 0.9993).

highest CBr_4 concentration used in this study. The CBr_4 solubilities are higher at higher CO_2 reduced densities.

Fluorescence decays of BPEA (~2×10^{-7} M) were obtained in supercritical CO_2 as a function of reduced density at 35 °C at different CBr_4 concentrations. The decay curves can be treated well using a single exponential function (Figure 3). There is no evidence for any deviations from single exponential decay behavior even in the near-critical density region at all CBr_4 concentrations (Table 1). It is thus concluded that the quenching of BPEA fluorescence lifetime by CBr_4 in supercritical CO_2 follows a simple dynamic process, which can be described by the Stern–Volmer relationship (eq 4). As shown in Figure 4, the observed fluorescence lifetimes depend not only on the CBr_4 concentration but also on the reduced density of CO_2. In the absence of CBr_4, the observed fluorescence lifetimes decrease with increasing CO_2 reduced densities, consistent with a known property that BPEA fluorescence lifetimes are dependent on the solvent refractive index n,

$$k_F = \Phi_F/\tau_F = n^x k_F^{\circ} \qquad (8)$$

where k_F° and k_F are fluorescence radiative rate constants in the gas phase and in the solvent, respectively. For BPEA, the fluorescence quantum yield Φ_F is unity,[38,40] so that the fluorescence radiative rate constants k_F can simply be calculated from the inverse of the observed fluorescence lifetimes. Shown in Figure 5 is a plot of ln $(1/\tau_F)$ vs ln n for results at different densities in supercritical CO_2. Linear least-squares regression yields x as the slope of 2.86, which is somewhat larger than the value obtained in room-temperature solutions.[38]

At a constant CBr_4 concentration, the observed fluorescence lifetimes change with CO_2 reduced densities in a characteristic fashion. The lifetime first increases with increasing CO_2 reduced density, and then levels off or decreases slightly at CO_2 reduced densities of ~1.4 and higher. For Stern–Volmer plots at individual reduced densities, the corresponding lifetime values were obtained by interpolation using the empirical curves shown in Figure 4. At the high reduced density of 1.90, a plot of τ_F°/τ_F vs $[CBr_4]$ yields a Stern–Volmer constant of 64 M^{-1} (Figure 6). With the τ_F° value of 4.6 ns at this particular reduced density, a quenching rate constant of 1.4×10^{10} M^{-1} s^{-1} is obtained, which is 18% of the Smoluchowski diffusion rate constant (7.9×10^{10} M^{-1} s^{-1}). The k_q/k_{SE} ratio is smaller than that in room-temperature hexane.

Linear Stern–Volmer plots are also obtained at other CO_2 reduced densities (Figure 6). The quenching rate constants are much larger at near-critical densities. The density dependence of the observed rate constants for BPEA fluorescence quenching by CBr_4 is very different from that of the Smoluchowski diffusion rate constants (Figure 7). A similar density dependence has also been observed in pyrene intermolecular excimer

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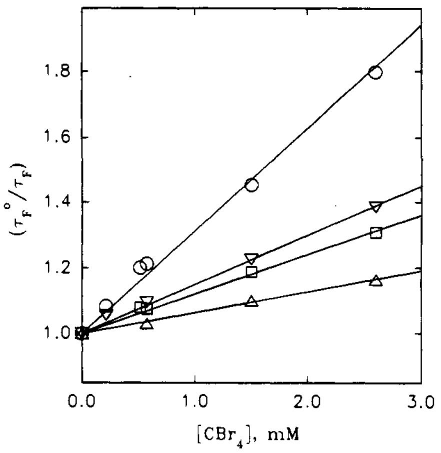

Figure 6. Stern–Volmer plots for BPEA fluorescence quenching by CBr_4 in supercritical CO_2 (35 °C) at reduced densities of 1.2 (○, 313), 1.43 (▽, 150), 1.52 (□, 120), and 1.9 (△, 64). The lines are from linear least-squares regressions, with the values of the slopes given in the corresponding parentheses.

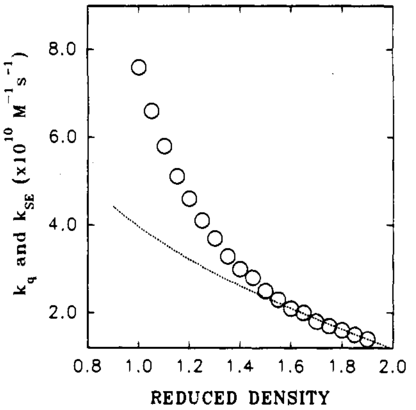

Figure 7. Observed quenching rate constants as a function of CO_2 reduced densities at 35 °C. The dashed line represents the density dependence of the Smoluchowski diffusion rate constants.

formation and the formation of intermolecular naphthalene–triethylamine[23] and anthracene–*N,N*-dimethylaniline[32] exciplexes. These results provide strong experimental evidence in support of a conclusion that solute–solute intermolecular reactions are indeed unusual in supercritical CO_2 at near-critical densities. It could be argued that the much more efficient quenching of BPEA fluorescence by CBr_4 at near-critical densities might be due to an unusual density dependence of the quenching rate constant, which could be very different from the density dependence of Smoluchowski diffusion rate constants. However, because of the known solute–solvent clustering effect, the local densities and, consequently, the microscopic viscosities should be larger than the corresponding bulk values. It is therefore hardly justifiable that diffusion could be more efficient under these conditions. If anything, molecular diffusion should be less efficient in the near-critical density region as a result of microviscosity effects. In several other systems, the Smoluchowski equation (or Debye equation when the two solute radii are equal) overestimates the diffusion-controlled rate constants in supercritical fluids by up to an order of magnitude.[29,41] Thus, it is more likely that the significantly enhanced fluorescence quenching is due to higher local concentrations of CBr_4 in the vicinity of an excited BPEA molecule at near-critical densities. By assuming that the local concentration $[CBr_4]_{LOCAL}$ is proportional to the bulk concentration $[CBr_4]$ with a proportionality constant $\alpha = [CBr_4]_{LOCAL}/[CBr_4]$, the Stern–Volmer relationship for BPEA fluorescence quenching by CBr_4 in supercritical CO_2 becomes

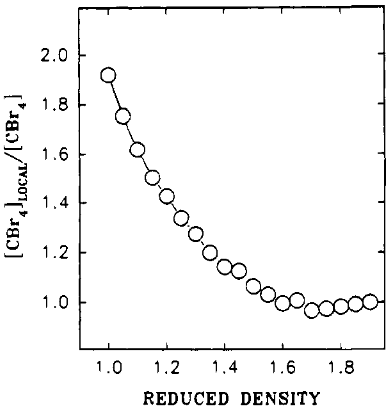

Figure 8. The local/bulk concentration ratios for the quenching of BPEA lifetime by CBr_4 in supercritical CO_2 at 35 °C.

$$\tau_F^{\circ}/\tau_F = 1 + k_q\tau_F^{\circ}[CBr_4]_{LOCAL} = 1 + k_q\tau_F^{\circ}\alpha[CBr_4] \quad (9)$$

By further assuming that the density dependence of k_q is the same as that of the Smoluchowski diffusion rate constants (namely that f is density independent), α values can be calculated as a function of CO_2 reduced density from the results shown in Figure 7. As shown in Figure 8, the CO_2 density dependence of α values is similar to those obtained from relative fluorescence quantum yields of pyrene intermolecular excimer formation, although the deviations from unity are smaller in this system than in pyrene.[21] Whether or not this can be used as evidence for a system-dependent conclusion remains a question for further experimental investigations.

Recently, there have been several studies[42–44] of bimolecular reactions in supercritical fluid systems, in which the cosolvent is a reactant. The observed bimolecular rate constants are abnormally large at lower pressures, which have been attributed to the effect of local composition enhancements under near-critical conditions.[42,43] The concept of local compositions is typically associated with the use of supercritical fluid–cosolvent systems.[7a,45,46] However, when the mole fraction of the cosolvent is very small, its modification to the microstructure of the supercritical fluid becomes insignificant. Then, the system can essentially be treated as a solute–solute/solvent problem, and the distinction between effects of local composition enhancements and solute–solute clustering may become trivial. In this regard, the results of fluorescence quenching reported here and those of bimolecular reactions in supercritical fluid–cosolvent systems[42,43] may be comparable. It seems unlikely that the physical state of the solute (solid or liquid) under the experimental conditions is an important factor in the observed solvent effects, though further experimental verifications may prove informative. Nevertheless, the fluorescence quencher CBr_4 used in this study is definitely a solute. The solvent effects on the bimolecular processes of excited BPEA and CBr_4 and on the pyrene excimer formation in near-critical fluids should be quite similar.

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In summary, the fluorescence quenching results for the simple BPEA$-$CBr$_4$ system show experimentally that there are indeed unusual enhancements in the efficiency of bimolecular reactions in supercritical CO$_2$ at near-critical densities. The enhancements are most likely due to effects of higher local quencher concentrations than the bulk in a near-critical solvent environment. In this context, the results can be used as evidence in support of a solute$-$solute clustering mechanism. Further experimental and theoretical investigations are required in order to understand the origin and structural details of the solute$-$solute clustering phenomenon in supercritical fluids.

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