

LOCAL DENSITY AUGMENTATION AROUND EXCIPLEX IN SUPERCRITICAL CARBON DIOXIDE AS REVEALED BY TRANSIENT ABSORPTION AND FLUORESCENCE LIFETIME MEASUREMENTS

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The pressure dependence of the decay of exciplex formed between acetophenone (AP) and *N,N,N',N'*-tetramethylbenzidine (TMB), and anthracene (A) and *N,N*-dimethylaniline (DMA) was studied in supercritical carbon dioxide by transient absorption and fluorescence techniques. Both the exciplexes showed similar trend in decay rate constant measured at various pressures of supercritical carbon dioxide. The results showed local density augmentation around exciplex in low-pressure (8.8-11 MPa) region. In the high-pressure (11-17.5 MPa) region, decay rate constant could be well explained by Kirkwood equation. However, in the low-pressure region, exciplex was more stable than predicted by Kirkwood analysis, which has been interpreted as a result of local density augmentation around the exciplex. At a measured pressure and temperature, solvent aggregation around the A-DMA exciplex was greater than that around the AP-TMB exciplex. The difference in the solvent aggregation also known as local density augmentation around the exciplex has been attributed to the nature of exciplex species.

INTRODUCTION

Local density augmentation in near-critical region of fluids has attracted much attention as a phenomenon specific to the solvent state. A lot has been studied about the local density augmentation around long-lived solutes. However, the local density augmentation around short-lived species such as reaction intermediate has been hardly investigated. We clarified local density augmentation around exciplex in supercritical carbon dioxide (SC-CO₂) by lifetime analysis of exciplex. The acetophenone (AP) *N,N,N',N'*-tetramethylbenzidine (TMB) exciplex was investigated by a transient absorption technique [1], and anthracene (A) and *N,N*-dimethylaniline (DMA) was investigated by fluorescence lifetime analysis [2]. Though structure dependence of local density augmentation is interesting, the pressure range of these data was different, and the data is not enough to compare.

In this paper, we investigate the photochemical reaction between AP and TMB, and A and DMA in wide pressure range (8.8-17.5 MPa), and compare the results. The local density augmentation estimated by Kirkwood analysis [3] of the decay rate of exciplex provides information on the polarity change around the exciplex. It is expected that the decay rate of the exciplex will change, for the reason that the local density around solute molecules in SC-CO₂ is higher than the bulk density in near-critical region.

EXPERIMENTAL

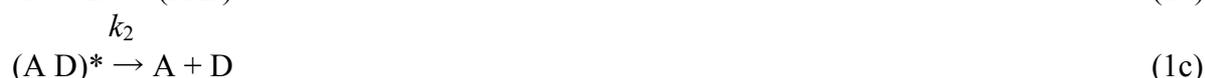
Detector, light source, and timing generator of the transient absorption measurement system were the same as in the previous study [1]. In brief, the unit consisted of a spectrometer (Chromex C5094), streak camera (Hamamatsu Photonics C4880) as detector,

Nd:YAG laser (Spectra-Physics GCR-130; 355 nm; 90 mJ; pulse width 5-6 ns) as excitation source, Xe flash lamp (Tokyo Instruments XF-80; 60 W) as monitoring source, two digital delay generators (Stanford Research DG-535) and simple frequency divider as digital delay line, and optical cell. The details of fluorescence lifetime measurement have been described in previous paper [2]. The difference from transient absorption measurements was no use of Xe flash lamp.

Concentrations of AP and TMB were fixed at 5×10^{-2} M and 5×10^{-4} M, respectively. Concentration of anthracene and DMA were taken at 5×10^{-4} M and 0.016 M, respectively. Reactants were loaded into the cell at atmospheric pressure, after closing the cell, air from the cell was removed by flowing carbon dioxide gas before finally introducing carbon dioxide at an adjusted pressure. Temperature of the cell was kept at 40 °C for all the measurements. Pressure was varied in the range of 8.8 to 17.5 MPa.

RESULTS AND DISCUSSION

In both systems, exciplex formation and decay by laser flash occurs according to the following reaction scheme [4]:



where A represents electron acceptor (AP or anthracene), and D represents electron donor (TMB or DMA). Under the assumption of pseudo first order kinetics, the time dependence of exciplex concentration can be written as following:

$$[(A D)^*] = [A^*]_0 \left(\frac{k_1'}{k_2 - k_1'} \right) (e^{-k_1't} - e^{-k_2t}), \quad (2)$$

where k_1' is given as $k_1[D]$ and $[A^*]_0$ is the concentration of excited state at the end of the laser pulse. The k_1' and k_2 were determined by fitting Equation (2) to the absorption or emission time profiles.

In AP-TMB system, exciplex (AP TMB)* in SC-CO₂ at 10 MPa absorbed clearly in the 350 to 550 nm region (Figure 1). The maximum absorbance at each pressure was used for each respective experiment. In all the measurements, peak shape was found to be invariant with pressure. Reaction rate constants were obtained from analysis of time profile of peak intensity by fitting with Equation (2). The k_1 decreases with increasing pressure, which was caused by viscosity increase [1].

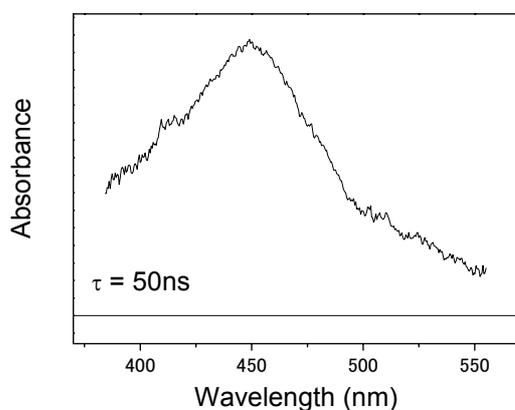


Figure 1 : Absorption spectrum of exciplex of AP-TMB system at 40 °C and 10 MPa.

Pressure dependence of the decay rate constant k_2 of exciplex (AP TMB)* decreased with increasing pressures, which probably can be attributed to the increase in the permittivity of the reaction medium. Since the exciplex has a dipole moment, it should be stabilized in a

solvent environment that has higher permittivity. The viscosity of the reaction medium cannot explain the decrease in the rate constant, since the exciplex decay is a monomolecular reaction. The kinetic controlled reaction rate constant k_2 can be related to the dipole moment by the theory of Kirkwood [3]:

$$\log(k_2/k_0) = -\frac{N_A}{4\pi\epsilon_0 RT} \left(\frac{\epsilon-1}{2\epsilon+1} \right) \left(\frac{\mu^2}{r^3} - \frac{\mu^{\ddagger 2}}{r^{\ddagger 3}} \right) \quad (3)$$

where N_A is Avogadro number, ϵ_0 is the vacuum permittivity, μ and r are the electric dipole moment and radius of the reactant (AP TMB)*. In Equation (3), μ^{\ddagger} and r^{\ddagger} are the electric dipole moment and radius of the transition state, k_0 is the reaction rate constant for the case of no dipole moment change, and ϵ is the relative permittivity. This change in slope can be attributed solely due to changes in the exciplex since the local concentration enhancement was found not to occur. In low-pressure region, experimental results located lower than Kirkwood equation, which means the exciplex stabilized by local density augmentation.

In A-DMA system, exciplex (A DMA)* in SC-CO₂ at 10 MPa showed emission over 350 to 550 nm range (Figure 3). Peak shape was similar for all pressures, and the maximum point at each pressure was used for each respective experiment.

In our previous study, it was shown that the main reaction of the decay of the exciplex is nonradiative reaction [2]. Since the decay of the exciplex is a monomolecular reaction, reaction rate constant k_2 was obtained from exponential decay fitting of transient data after 30 ns.

The dependence of $\log(k_2/k_0)$ versus $(\epsilon-1)/(2\epsilon+1)$ determined in this work was shown in Figure 4, which showed a similar trend to that of transient absorption analysis for AP-TMB exciplex, in which the local density augmentation around exciplex in SC-CO₂ occurred. This shows that solvent aggregation around the anthracene-DMA exciplex was greater than that around the AP-TMB exciplex.

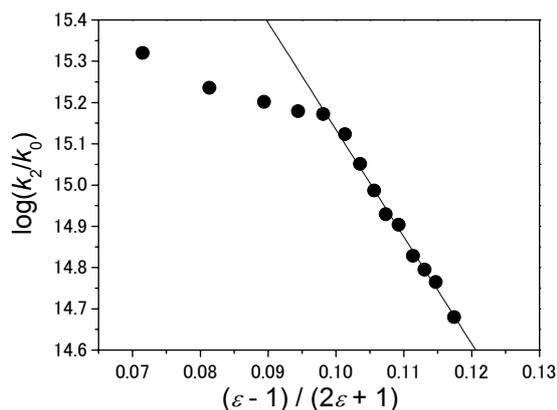


Figure 2 : Plot of $\ln(k_2/k_0)$ against $(\epsilon-1)/(2\epsilon+1)$. Circles: Experimental results; solid line: Kirkwood equation.

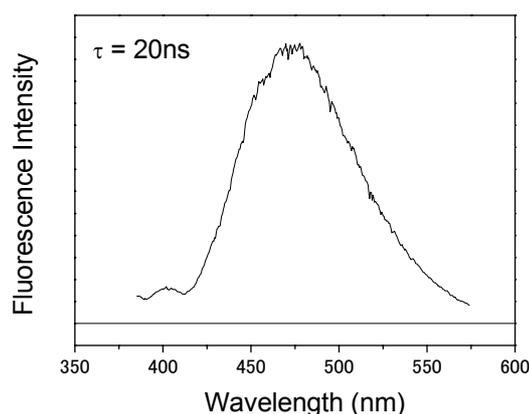


Figure 3 : Fluorescence spectrum of anthracene-DMA exciplex at 40 °C and 10 MPa.

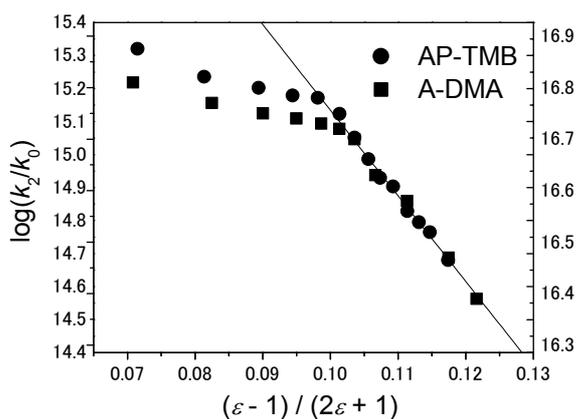


Figure 4 : Plot of $\ln(k_2/k_0)$ against $(\varepsilon-1)/(2\varepsilon+1)$. Circles: experimental results of AP-TMB ; squares: experimental results of A-DMA; solid line: Kirkwood equation. Left scale: AP-TMB; right scale: A-DMA.

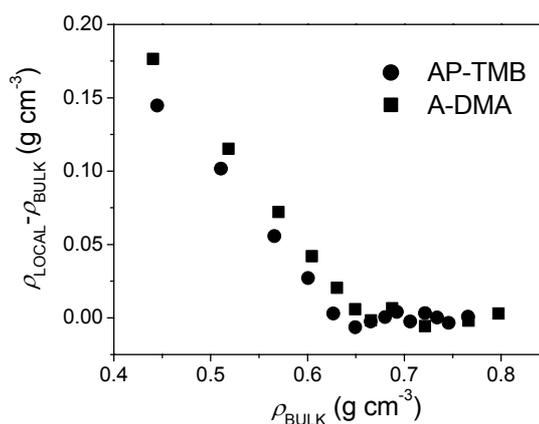


Figure 5 : Excess density in each density. Circles: AP-TMB; squares: A-DMA.

From Figure 4, we calculated excess density in each bulk density (Figure 5). It was clear that excess density in A-DMA system was higher than that in AP-TMB system. It has been reported that local density augmentation around the anthracene molecule is much greater than that for benzene in SC-CO₂ [5]. This could be an additional factor in the familiarity of A-DMA exciplex to CO₂ molecule is larger than AP-TMB exciplex.

CONCLUSION

Local density augmentation around exciplex was measured in AP-TMB system and A-DMA system by time-resolved techniques. In both system, exciplex shows local density augmentation in near-critical region. The enhancement of local density around A-DMA exciplex is larger than AP-TMB exciplex, which should reflect the familiarity of the elements to CO₂ molecule.

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