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# Excitation Wavelength Dependence of Pyrene Fluorescence in Supercritical Carbon Dioxide. Evidence for a Supercritical Solvent-Assisted Solute–Solute Clustering Mechanism

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Supercritical fluids, with their very unique properties, have recently attracted much attention.[1,2] The most important properties of a supercritical fluid are its tunable low densities between those of a gas and a normal liquid and its local density effect (or solute–solvent clustering).[1-3] In addition, a very special property of a supercritical fluid, which we believe has the same origin as the local density effect, is its ability as a special medium to assist solute–solute clustering. Some evidence has been presented for such clustering in several systems,[4] with support from theoretical calculations.[5] However, while the issue of solute–solute clustering in supercritical fluids is of great theoretical and practical importance, it remains controversial at best even for a classical system like pyrene.[6,7] The initial proposal[6] of pyrene–pyrene clustering in supercritical fluids based on the observation of unusually efficient pyrene excimer formation was later dismissed primarily on the basis of a time-resolved fluorescence study,[7,8] in which an agreement between the rate constants of pyrene diffusion and excimer formation was observed. However, since the widely discussed solute–solute clustering[4-6] is principally a ground-state phenomenon, time-resolved fluorescence probing of diffusion processes can hardly prove or disprove such clustering. Here, we report an absorption and emission study of pyrene in supercritical $CO_2$ over a wide density range. The unusual excitation wavelength dependence of pyrene fluorescence is best accounted for by a solvent($CO_2$)-assisted pyrene–pyrene clustering mechanism.

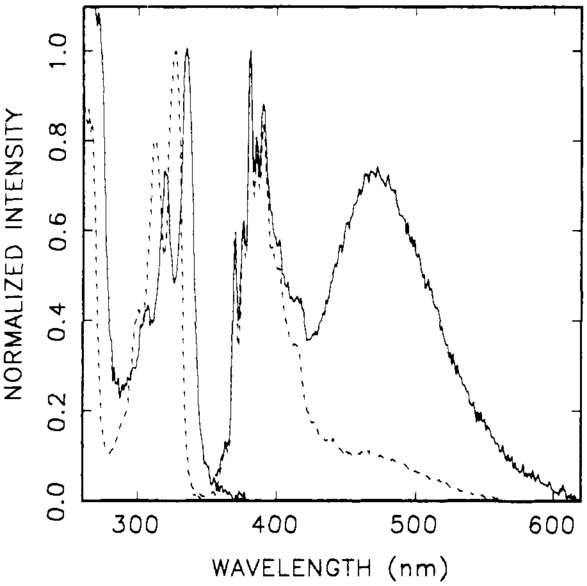

**Figure 1.** Corrected fluorescence (solid line, $\lambda_{ex}$ = 335 nm; dashed line, $\lambda_{ex}$ = 314 nm) and fluorescence excitation (solid line, $\lambda_{em}$ = 470 nm; dashed line, $\lambda_{em}$ = 390 nm) spectra of pyrene in $CO_2$ ($\rho$ = 3 mol/L) at 45 °C.

Fluorescence, fluorescence excitation, and absorption spectra of pyrene[9] (Aldrich 99%, recrystallized from hexane) in supercritical $CO_2$ (Air Products, 99.9999%) were measured as a function of $CO_2$ density in a home-built high-pressure optical cell. The emission measurements were carried out on a SPEX Fluorolog-2 photon-counting spectrometer using a small-angle (~22.5°) front surface excitation geometry in order to avoid self-absorption. At 45 °C, the observed pyrene fluorescence spectra in $CO_2$ at low densities ($\rho_r < 1$) always consist of both the monomer and excimer emission bands, and their relative intensities are strongly excitation wavelength dependent. As shown in Figure 1, the contribution of the excimer fluorescence is much larger with 335 nm excitation than with 314 nm excitation. Excitation spectra recorded at emission wavelengths of 390 and 470 nm, corresponding to predominantly monomer and excimer emissions, respectively, have almost the same structures, but the spectrum for the excimer is ~7-nm red-shifted from the spectrum for the monomer (Figure 1). Although the amount of pyrene initially added to the optical cell is equivalent to a concentration of $2 \times 10^{-5}$ M, the actually observed pyrene concentrations at low $CO_2$ densities are determined by pyrene solubilities. At 45 °C and a $CO_2$ density of 3 mol/L, a pyrene concentration of ~$6 \times 10^{-7}$ M (Figure 2) can be estimated from the maximum absorbance using a molar absorptivity of 50 000 cm$^{-1}$ M$^{-1}$ determined in cyclohexane solution.[10]

Excimer fluorescence was also observed at densities close to the critical density $CO_2$ (10.63 mol/L). At higher $CO_2$ densities ($\rho_r > 1$), however, the contribution of the excimer fluorescence decreases with increasing density. The excimer band nearly vanishes at a $CO_2$ density of 11.5 mol/L ($\rho_r$ = 1.1), as does the excitation wavelength dependence.

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[8] Some steady-state emission results were also presented in ref 7 in support of the claim that the fluorescence spectra of pyrene in supercritical $CO_2$, $C_2H_4$, and $CHF_3$ are excitation wavelength independent for pyrene concentrations of 10 and 100 μM. By examining the significant difference between the excitation spectra of pyrene in $CO_2$ at the two different concentrations,[7a] one may logically conclude that at least the spectrum at the higher pyrene concentration (100 μM) is significantly distorted as a result of severe inner filter effect.

[9] For a general review of pyrene photophsics, see: Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970.

[10] This value is close to the literature value, see: Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*, 2nd ed.; Academic Press: New York, 1971.

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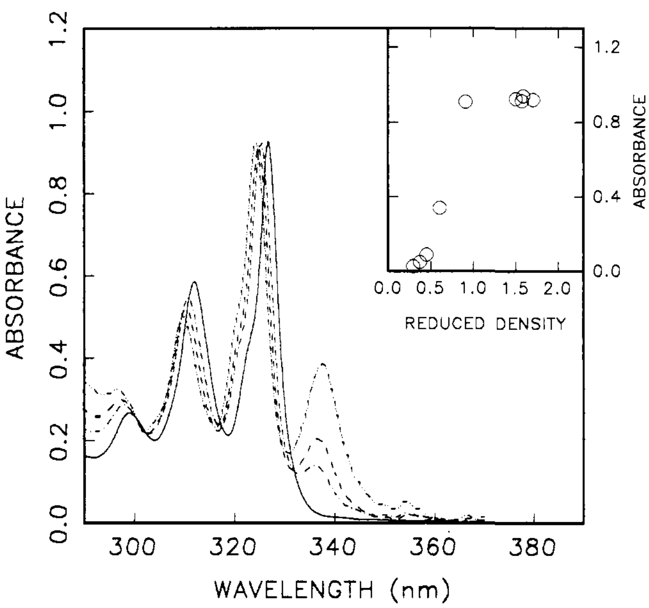

**Figure 2.** Absorption spectra of pyrene in $CO_2$ at 45 °C and densities of 3.1 (– ·· –, ×33), 3.9 (– – –, ×18.5), 4.8 (– · –, ×10.5), and 15.9 (—, ×1.0) mol/L. The numbers in the parentheses are factors used to put the spectra on the same scale. The insert is a plot of the maximum absorbance against $CO_2$ reduced density. The amount of pyrene added is equivalent to a concentration of $2 \times 10^{-5}$ M, and the absorbance is with respect to an optical path of 1.0 cm.

The absorption spectra of pyrene also depend on the $CO_2$ density, Figure 2. At low densities, there is an extra band at the red onset. As $CO_2$ density increases, the relative absorbance of the red-side band decreases, and the spectrum becomes more like the one observed in cyclohexane solution. This is in general agreement with the results of excitation measurements, namely that the observed spectra at low densities are superpositions of at least two absorptions.

Very similar results were also observed at 35 °C. Purification of the pyrene sample through recrystallization has no noticeable effect on the results.

The strong excimer emission of pyrene in supercritical $CO_2$ at pyrene concentrations as low as $6 \times 10^{-7}$ M and the characteristic excitation wavelength dependence are very interesting. While unusually efficient excimer formation was previously suggested,[6] no similar observations have been reported, presumably because previous studies[6-8] were carried out at high $CO_2$ densities. Our results are best accounted for by a supercritical solvent-assisted pyrene–pyrene clustering mechanism. The significant contribution of the excimer emission is probably due to a high pyrene local concentration in the immediate vicinity of an excited pyrene molecule, which is likely to be a direct result of the characteristic solvation properties of supercritical $CO_2$. It has been established that for a neat supercritical fluid in the near-critical region, density fluctuation becomes very large, resulting in the formation of fluid molecule clusters.[11] Significant microscopic solvation experienced by solute molecules in these clusters is apparently the underlying cause for the widely observed local density effects.[1-3] The existence of these clusters and their favorable solvation environment provide the necessary conditions for pyrene–pyrene clustering. Inclusion of two or more pyrene molecules in a loosely defined $CO_2$ cluster as a result of its favorable solvation environment probably makes the efficient excimer formation possible.

The pyrene–pyrene clustering discussed here does not refer to the formation of ground-state pyrene dimers, but rather to a high pyrene local concentration in solvent clusters. The red shift of the excimer excitation spectrum from the monomer spectrum indicates that there are at least two different solvent environments for pyrene molecules. Those molecules which are better solvated, corresponding to the red shift, are responsible for the efficient pyrene excimer formation. The excimer formation process is probably pseudostatic in nature, with no or very limited diffusion. Since pyrene molecules are close to each other in $CO_2$ clusters, some dimer formation might be possible. It might account for the broadness of the red-side absorption band at low $CO_2$ densities. However, judging from the different absorption and excitation spectra of pyrene dimers,[7a] we believe that the contribution of pyrene dimer to our observations should be small. The broad emission band ($\lambda_{max}$ = 470 nm) is likely dominated by pyrene excimer fluorescence.

A significant contribution of pyrene microcrystals to our observations is unlikely. The absorption and emission spectra of the pyrene solid generated by evaporating a concentrated hexane solution of pyrene onto a quartz surface are very different from the spectra shown in Figures 1 and 2. Special efforts were also made to avoid deposition of pyrene solid on the cell windows and to keep the cell walls from the exciting light. However, some perturbation from pyrene microcrystals can still be a possibility.

It is interesting that the pyrene–pyrene clustering was observed at low $CO_2$ densities. Solvatochromic studies have shown that the local density effect is the most pronounced at $\rho_r$ around 0.5 of a supercritical fluid.[2a] We have also observed[12] a characteristic dependence of the Py scale[13] ($I_1/I_3$) on $CO_2$ density, which is consistent with the solvatochromic results. The implication of these observations to the local density model deserves further attention.

The disappearance of the pyrene excimer emission at high $CO_2$ densities is probably caused by more than one factor. The most important is that the fluid at higher densities becomes more liquid-like, providing a solvent environment favoring a uniform distribution of pyrene molecules. Higher pyrene concentrations are required for the formation of excimer through diffusion.[6b,7a] The threshold pressure (or density) for the disappearance of excimer emission is somewhat temperature and pyrene concentration dependent. A more quantitative study is in progress.

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