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Thermal Lensing in a Supercritical Water Medium

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A pulsed, two-beam, thermal lensing experiment was performed to determine the concentration of aqueous solutes above the critical point of water. Despite a very significant mirage effect due to thermal gradients in the cell and absorption by water itself, the thermal lensing signal strength for aqueous benzoic acid in supercritical water was found to be linear with concentration in the sub-millimolar range. Although thermal lensing experiments in aqueous media are notoriously insensitive, the sharp density gradient near the critical point considerably improves the signal intensity. In this study a short-pulse pump 266 nm YAG laser and continuous low-power probe Ar ion beam were both focused into a supercritical water cell, giving a lensing signal whose strength could be maximized by changing the overlap of the two beams.

Introduction

Supercritical water (SCW) has been receiving renewed interest recently due in large part to two factors: use of SCW oxidation for the remediation of environmental organic pollutants[1] and the potential use of SCW coolant in Generation IV nuclear reactors.[2] Solutes in SCW can be oxidized by free-radical or ion-initiated mechanisms in which the reactive species involved depends on the fluid density. To date, the oxidation kinetics of degradation for a variety of aromatic and aliphatic compounds have been reported.[3] However, the analytical measurement methods used in these studies, such as gas chromatography[4−7] and gas chromatography/mass spectrometry,[6,8] often require acquisition of a grab sample from the effluent of the supercritical water reactor, which must be cooled and depressurized prior to analysis.

The use of in situ analytical techniques facilitates the study of the kinetics and mechanisms of oxidation reactions in SCW. Spectroscopic methods that have previously been employed include UV/vis,[9−11] infrared,[12,13] and Raman spectroscopy.[13] However, as a result of the high pressures and temperatures necessary for SCW conditions (above the critical point of water of 22.4 MPa and 374 °C), direct optical spectroscopic analysis of analytes is difficult. It is necessary to construct sample cells capable of surviving these extreme conditions that also allow transmission of the optical signal.[14,15] Optical windows must be thick and of small diameter. The seating of the windows, and the optical properties of the window materials, change as the water is heated and pressurized making alignment especially difficult.

Limiting factors for in situ studies include the sensitivity of the instrumentation and applicability of the wavelengths available. For example, UV/vis spectroscopy is usable down to a ppm level and applicable to a wide range of organic compounds, but many compounds only absorb in the deep UV portion of this spectrum. Absorption measurements in this region require special window materials, and for supercritical measurements these materials also must have small temperature and pressure coefficients. In addition, as the windows have to be of small diameter, absorption measurements are difficult to achieve using a conventional light source.

In contrast, thermal lensing (also called thermal deflection) is a laser-based, ultrasensitive, UV−vis absorption technique. It has been used to measure and monitor the concentration of analytes absorbing in the visible and ultraviolet region at the 10^{-7} absorbance unit level and is more readily employed in a harsh environment. In a crossed beam arrangement, either pulsed or continuous-wave lasers can be used as the pump beam, and a stable continuous laser can be used for the probe beam. For these experiments, the aperature size necessary can be quite small.[16−18]

Theoretically, the thermal lens signal would be enhanced in supercritical water over the normal signal expected from UV−vis absorbance. The enhancement of the thermal lens depends on several factors and is proportional to the following[19]

$$\text{thermal lens signal} \sim |\,(dn/dT)|_p\, \Phi_0/(\lambda_p \kappa) \qquad (1)$$

where dn/dT is the constant pressure temperature dependence of the refractive index, Φ_0 is the pump laser power, κ is the sample thermal conductivity, and λ_p is the wavelength of the probe laser. On the basis of this equation, it can be seen that the lens signal will be greatest for solvents that have low thermal conductivities, such as organics, but exhibit less sensitivity in aqueous solution where the thermal conductivity is higher.

Reports of the use of thermal lensing in supercritical CO_2 describe a large enhancement in the signal strength.[20,21] Because the coefficient of thermal expansion of a fluid diverges at the critical point, the index of refraction change with temperature should be very large, and thus the analytical sensitivity of

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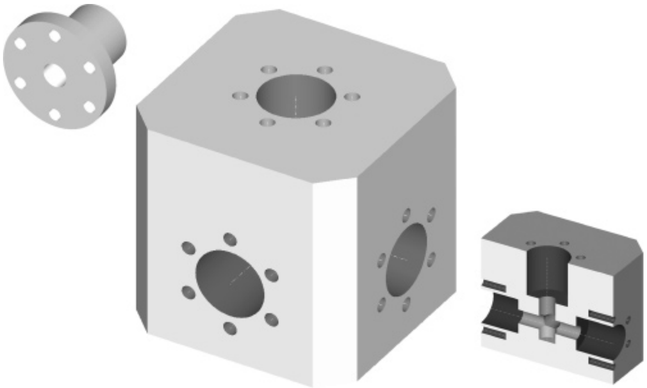

Figure 1. Supercritical fluid water cell with port cap and small cutaway view.

thermo-optical absorbance measurements should be enhanced when the solvent is near its critical point, either as a subcritical liquid or supercritical fluid.[20]

Therefore, although the thermal lens effect in normal water at room temperature is quite small, thermal lensing in aqueous solutions near the critical point is worth investigating as a large dn/dT near the critical point would significantly enhance the signal. Moreover, at the critical point, the thermal conductivity decreases dramatically, further enhancing the signal. Because of these two effects, thermal lensing may be a viable tool for monitoring a particular analyte through its absorption spectrum in supercritical aqueous solutions.

In this study, we explore the use of thermal lensing as an in situ optical technique for the determination of benzoic acid in SCW. Additionally, we provide details of the construction of a high-temperature, high-pressure cell, suitable for conducting optical experiments in SCW.

Experimental

The supercritical water cell (SCWC) was machined from a solid block of 316 stainless steel (see Figure 1). The ports in each of the four sides and top are 3.17 cm in diameter and 2.86 cm deep (the top port is 4.11 cm deep). The ports are connected by 1.27 cm diameter through-holes, giving an internal volume of ~12 mL. Although the arrangement of the five windows in the cell provided for great versatility, in the present experiments only two windows on opposite sides were used. The windows were composed of 2.54 cm diameter, 1.27 cm thick sapphire, and were sealed with gold gaskets. Brass spacers were used on the opposite side to allow maximal flexibility with respect to sealing the windows.

The SCWC was heated using five separate cartridge heaters. The temperature of the cell was measured by a thermocouple and controlled to within one degree by adjusting the current to the heaters by employing a Suprex Corporation model 050−20 heater controller. The solution was pumped into the cell through a stainless steel line preheated to the desired temperature using an ISCO model 260D syringe pump with a Series D pump controller.

The thermal lensing setup employed the 266 nm pulsed output from a Nd:YAG laser (Quanta-Ray model DCR 2A-10) as the pump laser. The beam profile of this laser was a non-Gaussian, donut-like shape. The probe laser was a Lexel model 95 Ar-ion laser in single mode. The detector consisted of a photomultiplier tube (Hamamatsu 928) enclosed in a metal housing with a pinhole (~0.5 mm) input aperture. The pump and probe laser beams were focused through the front sapphire window into the benzoic acid solution in the center of the cell. After passing out the back window, the UV beam was blocked using a filter, and only the 514 nm green probe beam was allowed down the rest of the path to the detector. A schematic of our setup is given in Figure 2.

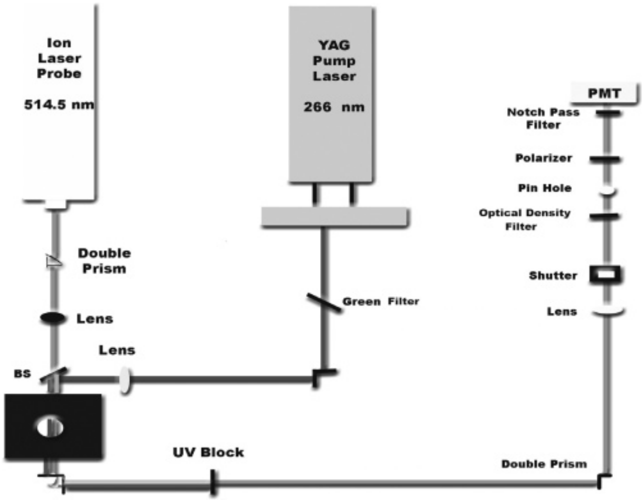

Figure 2. Schematic of the thermal lensing setup used in this study.

A synchronized electronic shutter was used to prevent saturation of the photomultiplier tube. The output of the photomultiplier tube was amplified and sent to a LeCroy model 9310 oscilloscope. The time base on the scope determined the number of data points collected. The thermal lens signal was averaged by the oscilloscope (typically 100 scans at a frequency of 10 Hz), and the final signal was digitized by a Labview program (ScopeExplorer) and was output as an ASCII file.

ACS certified benzoic acid was obtained from Fisher Scientific and was used without further purification. This particular chemical was used in these experiments as it readily dissolves in water, is nontoxic, and is thermally stable. Initial experiments in this study examined the extent of acid decomposition under supercritical conditions; in practice, we did not observe any significant decrease in thermal lens signal intensity (assumed directly proportional to benzoic acid concentration) for over a period of 1 h.

Benzoic acid has a room temperature and pressure extinction coefficient of approximately 800 L $\mathrm{mol^{-1}\ cm^{-1}}$ at 266 nm. Initial solution concentrations were established by both weighing out the solid acid and by spectrophotometric measurement. After thermal lensing experiments on individual solutions were completed, the cell contents were pumped out and the solution absorption at 266 nm again was measured to verify that there was minimal degradation of this acid.

Problems with steering of the probe beam occurred when the cell solution was very near the critical point, with this beam moving by as much as 2−3 cm as measured at a distance of 30 cm from the exit window of the cell. This movement was believed to be due to the apparent large changes in the index of refraction associated with small fluctuations in the temperature and pressure as well as perhaps that the pump and probe laser beams were not propagating normally to the two window surfaces. To minimize the steering effect, all experiments were conducted at 400 °C and 22.4 MPa, and it was necessary to allow the cell to equilibrate for approximately 15−20 min following any change in the pressure or temperature of the cell.

To change benzoic acid concentrations, the cell was completely depressurized and heated pure water was rinsed through it three times. Then the new benzoic acid solution was heated

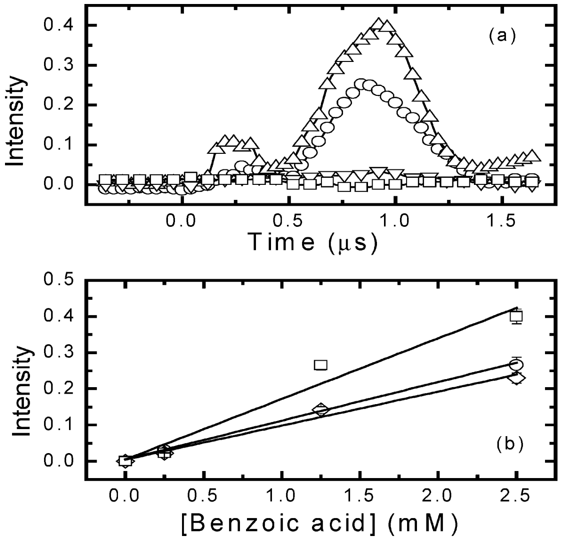

Figure 3. (a) Thermal lens signal for benzoic acid in supercritical water (400 °C, 22.4 MPa) for (△) 2.50×10^{-3} M, (○) 1.25×10^{-3} M, (▽) 2.5×10^{-4} M, and (□) 0.00 M (pure water). (b) Linearity of thermal lens signals; (□) single-point intensity of thermal lens at ~1 μs. These signal intensities are divided by 10^6 to scale with other integrated fits. Straight line fit gives slope of $(1.70 \pm 0.13) \times 10^{-4}$ M^{-1}, $R^2 = 0.966$. (◇), area of only major peak, straight line fit gives slope of $(9.63 \pm 0.49) \times 10^{-5}$ M^{-1}, $R^2 = 0.983$, and (O), integration of entire thermal lens signal as shown in (a), straight line fit gives slope of $(1.10 \pm 0.04) \times 10^{-4}$ M^{-1}, $R^2 = 0.992$.

and rinsed once through the cell. The cell then was refilled with the new benzoic acid solution and brought to the final supercritical temperature and pressure. By slightly retuning the optical lineup after supercritical conditions were reached, the thermal lens signal was successfully collected under supercritical conditions.

Results and Discussion

During our SCW experiments, the overlap point of the focused-pump and probe laser beams was altered by using the micrometer adjustment on the beamsplitter (BS) mount that reflected the 266 nm Nd:YAG laser beam into the cell. As the overlap point changed, the signal due to the thermal lens moved in time relative to the firing of the YAG laser. The detector trace appeared to change into a derivative signal and could be observed at up to several hundred nanoseconds after the firing of the pump laser. This type of signal has been previously observed in a pulsed expansion of acetylene.[22] The shape of the signal (see Figure 3a) and the delay in time can be attributed to the deflection of the probe beam by the shock wave formed by the absorption of the 266 nm pump beam by the analyte. A similar shock wave deflection has been seen by other researchers.[23] A possible explanation for the presence of a second peak in Figure 3a is that the pump beam profile was donut shaped. For the highest concentration, shock waves due to both side of the ring might be observable. The speed of sound decreases to very small values when approaching the critical point and is difficult to measure for water. For example, at 380 °C and 22.4 MPa the speed of sound is roughly 410 m/s,[24] and at this speed of sound, a shock wave would move roughly 0.41 mm in 10^{-6} seconds. The thermal lensing can be seen at the shock wavefront, 1 μs after the pump pulse, if the pump−probe beam overlap is changed by a fraction of a millimeter. At 400 °C the speed would be slightly higher and detection of the wavefront by thermal lensing at 1 μs would require the overlap to change slightly more.

Figure 3a shows the tunability of the thermal lensing signal for a 2.5 mM aqueous benzoic acid solution at 400 °C and 22.4 MPa. Here the time-dependent thermal deflection signal is maximal approximately 1 μs after the firing of the Nd:YAG pump laser. The signal also was collected at the same supercritical temperature and pressure conditions for two other benzoic acid concentrations and for pure water.

The analysis of these signals was attempted in several different ways. By plotting the maximum height of the thermal deflection signal at ~1 μs against the benzoic acid concentration, a reasonable linear relationship was seen (see Figure 3b and values given in the caption). An improved linear relationship was obtained if the integrated area of the major peak was used. By fitting this thermal lens signal to a single Gaussian waveform, the second linear plot in Figure 3b was obtained. Although the magnitudes of the slope and intercept values are slightly different, considerable improvement in the linearity of the signal (as based on R^2 values) was obtained. However, the best linear relationship was obtained when the total area of the thermal lens was integrated by using a sum of three Gaussians. It is important to note that this latter area determination was bounded by the time base settings on the LeCroy digitizing oscilloscope used in these experiments, and that the reported slope value in Figure 3b was based upon a fixed zero intercept. The weighted linear-least-squares error value for this fit is 8.32×10^{-3}, and based on this uncertainty one can readily determine the minimum concentration (3σ) of benzoic acid that could be measured by this thermal lensing technique as $\sim 2.5 \times 10^{-6}$ M.

The thermal lens signal is proportional to the gradient in the index of refraction with temperature. To gain some insight into the general applicability of this technique for SCW solutions, one can look at this gradient near the critical point. Within a few degrees of the critical point, the change in density with temperature is large, and in the supercritical fluid region is similar to that in a gas. Thus in a pressure region not less than 5MPa from the supercritical pressure, and within 25 °C of the critical temperature, there should be a significant enhancement in the thermal lensing signal allowing this technique to be used.

Conclusions

A thermal lens signal for dilute benzoic acid solutions was gathered at three concentrations under supercritical water temperatures and pressures. This signal is attributed to a changing index of refraction from the shock wave resulting from the absorption of the 266 nm pump beam by the benzoic acid. Extremely good linear correlations for these signals were obtained with acid concentration over the range 0.25 to 2.5 mM with single signal peak intensity or integrated peak area. On the basis of total integrated signal area, a theoretical lower limit of detection of ~2.5 μM was predicted using this methodology.

By varying the crossing point of the beams, the thermal deflection signal could be moved in time relative to the firing of the pump laser. In practice, under the supercritical conditions, the thermal deflection signal can be detected at delays as long as 1−2 μs after the pump laser fires. It is interesting to note that this delay in the signal relative to the pump firing could prove useful for kinetic studies involving a noisy pump source such as a pulsed linear accelerator. By delaying the thermal lens signal to a time far removed from the firing of the accelerator and the pump laser, the background radiofrequency noise should be diminished.

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