LETTER

Spectroscopic determination of the critical temperatures and pressures of H\textsubscript{2}O, CO\textsubscript{2}, and C\textsubscript{2}H\textsubscript{5}OH

Chizu Sekiguchi, Nobuo Hirano, Atsushi Okamoto and Noriyoshi Tsuchiya

Graduate School of Environmental Studies, Tohoku University, 6-6-20 Aramaki-aza-Aoba, Aoba, Sendai 980-8579, Japan

The transmittance of 500-800 nm light was shown to change significantly at the critical points of three pure fluids. Spectroscopic measurements of H\textsubscript{2}O, CO\textsubscript{2}, and C\textsubscript{2}H\textsubscript{5}OH were made in a visible-type autoclave at high temperature and pressure. Each fluid showed significantly decreased transmittance as its critical point was approached; transmittance reached a local minimum at the critical temperature and pressure. The experimentally determined critical temperature and pressure of H\textsubscript{2}O are 374 °C and 22.07-22.09 MPa, respectively, similar to reference values of 374.15 °C and 22.12 MPa; C\textsubscript{2}H\textsubscript{5}OH showed values of 243 °C and 6.30-6.31 MPa (versus reference values of 241 ± 7 and 6.14 MPa); and CO\textsubscript{2} showed values of 32 °C and 7.36-7.43 MPa (versus reference values of 31.04 ± 0.2 °C and 7.37 ± 0.04 MPa). The good agreement between the experimental results and the reference values indicates that the spectroscopic method used here could be applied to other fluids, including mixed geofluids.

Keywords: Critical point, Supercritical fluid, Spectroscopic measurement, Hydrothermal experiment, Geofluids

INTRODUCTION

The physicochemical states of geofluids such as CO\textsubscript{2} and H\textsubscript{2}O are divided into three phases (solid, liquid, and vapor), and the boundary between the vapor and liquid phases is termed the saturation vapor pressure curve. This curve terminates at a critical point, which has a defined critical temperature (\(T_c\)) and pressure (\(P_c\)). This point marks the conditions under which the density of the liquid and the vapor phases are equal; fluids under conditions of higher temperature and pressure are then said to be in a supercritical state.

Supercritical fluids have characteristic chemical reactivity, solubility, and/or ionic product properties; they have been identified during super-deep drilling and within fluid inclusions in both ancient and currently active geothermal areas (Doi et al., 1998; Ikeuchi et al., 1998; Bandó et al., 2003; Arnórsson et al., 2007). Supercritical geofluids are not unusual within the interior of the earth, and they play important roles in a variety of geological processes, including earthquakes, volcanism, and hydrothermal ore formation (Fournier, 1999; Scambelluri and Philippot, 2001; Liebscher, 2010).

Examination of the hot and compressed conditions encountered in areas such as deep-sea hydrothermal vents has led to the development of various complicated reactions that attempt to model supercritical fluids (Bischoff and Rosenbauer, 1988; Foustoukos and Seyfried, 2007). Comprehension of the behavior of supercritical fluids is important to our understanding of the processes of fluid-rock interactions in and around submarine hydrothermal vents and/or the interior of the earth. Various thermodynamic constraints and equations of state have been identified for specific geofluids such as pure H\textsubscript{2}O (Belonoshko and Saxena, 1991; Wagner and Prüß, 2002), the H\textsubscript{2}O-CO\textsubscript{2} binary system (Takenouchi and Kennedy, 1964; Diamond, 2001; Duan and Zhang, 2006), and the H\textsubscript{2}O-CO\textsubscript{2}-NaCl ternary system (Duan et al., 1995, 1996; Schmidt and Bodnar, 2000); however, the critical point of a multicomponent geofluid cannot be directly determined using the equation of state for a specific other fluid system.

Molecules within a supercritical fluid are heterogeneously distributed, forming both densely and sparsely packed areas within the fluid. This significant heterogeneity of density is caused by a divergence in density at the critical point, which affects the extension of the saturation vapor pressure curve (Nishikawa et al., 1996; Morita et al., 2000). The density fluctuations that occur within supercritical fluids also cause various chemical reactions during dissolution (Tsuchiya and Hirano, 2007).
determined $T_c$ and $P_c$ values for H$_2$O-CO$_2$ and H$_2$O-CO$_2$-NaCl fluids by directly observing the disappearance and appearance of menisci within the fluids. This research was the first attempt to determine the critical points of fluids via direct measurement through transparent windows installed in an autoclave; however, this approach also showed some inherent difficulties. The uncertainty of observing the disappearance and appearance of menisci was a notable drawback; the uncertainty was due to the emergence of critical opalescence within the fluid as it neared its critical point. Critical opalescence occurs owing to light scattering within a fluid that is at or close to its critical point; it is a result of the heterogeneous distribution of molecules, which causes local variations of refractive index and Rayleigh scattering. However, supercritical H$_2$O is transparent and does not have a meniscus. The fluid appears darker during cooling toward the critical point; consequently, the reappearance of the meniscus can be observed with the naked eye under relatively dark conditions and used to indicate the state of the fluid.

The observation of geofluids through transparent windows in a pressure vessel can be used in the determination of the critical values of multicomponent fluids. Here, we present a new technique for the determination of the critical point of a multicomponent fluid via observation of its optical properties as it approaches its critical point.

**EXPERIMENTAL**

**Experimental apparatus and fluids**

Spectroscopic measurements under conditions of high temperature and pressure were undertaken using a visible-type autoclave (SE800S–SW1/8 NPS60SW–1MV, Taiatsu Techno). The experimental configuration is outlined in Figure 1. The maximum temperature and pressure of this apparatus are 500 °C and 40 MPa. Conditions inside the inner autoclave were measured using a thermocouple and a pressure gauge installed within the autoclave. They respectively measured temperature within ±0.5 °C and pressure within ±0.2%.

Fluids within the autoclave were observed through transparent sapphire windows installed on both sides. The windows were 25.5 mm in diameter and 13 mm thick. The autoclave had an internal diameter of 15 mm and a capacity of 12.5 cm$^3$; its main body comprised a Hastelloy C-22 alloy (58 wt% Ni, 22 wt% Cr, 13 wt% Mo, 4 wt% Fe, and 3 wt% W). The autoclave also had outer quartz windows that protected the sapphire windows from the thermal stresses associated with rapid temperature changes. The autoclave wall contained six cylindrical cartridge-type heaters.

The spectroscopic behaviors of H$_2$O and CO$_2$ were measured by considering them as simple geofluids. The behavior of an organic fluid, ethanol (C$_2$H$_5$OH), was also determined for comparison. A 50% (6.25 cm$^3$) filling ratio within the autoclave was used for H$_2$O and C$_2$H$_5$OH; CO$_2$ was introduced to the system via a delivery pump (PU-2080–CO$_2$, JASCO) that injected liquid CO$_2$ into the autoclave at a constant pressure. When the filling ratio of the internal fluid was around 50%, its temperature and pressure were increased along the saturation vapor curve; the resulting disappearance of the meniscus was observed. The exact filling ratio of liquid CO$_2$ was uncertain because direct measurement of flow rates during analysis was difficult; however, a suitable filling ratio could be achieved by using a similar fluid level to that shown by H$_2$O.

**Spectroscopic measurements**

Spectroscopic measurements were taken using incident light from a halogen lamp; the lamp provided illumination over a broad range of wavelengths with a smooth profile over the range 500–800 nm. The detector was placed on the opposite side of the autoclave. A multichannel spectrometer (USB2000+, Ocean Optics) was used to analyze the light transmitted through the fluid within the autoclave during both heating and cooling. Measurements were taken over the wavelength range 500–800 nm at 0.35 nm intervals. The experimental regime involved heating the flu-
id to a preset temperature, holding it for 10 min at that temperature to ensure thermal equilibrium, and then conducting spectroscopic measurements for 1 min. The fluid was then heated by 1 °C and then similarly held for 10 min and measured. Cooling followed a similar regime: a 1 °C change, a 10 min rest, and then measurement for 1 min.

Analyses were conducted using individual exposures of 100 ms, with a total of 600 measurements; therefore, each data point consists of 1 min of spectroscopic measurements. A baseline for these spectral data was obtained by measuring the background emission from the halogen lamp. The raw spectra ($I$) for each fluid sample were normalized by spectra ($I_o$) obtained using a blank sample at the same temperature to give transmittance ($I/I_o$).

RESULTS AND DISCUSSION

Figure 2 shows the transmittance of H$_2$O over the wavelength range 500–800 nm at 370, 373, 374, 375, and 380 °C. Spectroscopic measurements taken at 1 °C steps allowed identification of the minimum intensity of transmitted light. Transmittance in arbitrary units decreased during heating from 370 °C to 373 °C, reaching a minimum at 374 °C, before greatly increasing at 375 °C (Fig. 2a). The transmittance at 720–740 nm consistently remained relatively low at every tested temperature. This absorption in the near-infrared region corresponds to a combination of fundamental -OH vibrations in molecular H$_2$O. Additional absorption bands of pure water have been observed in previous works at visible wavelengths (514, 550, 605, and 662 nm) (Pope and Fry, 1997). However, such absorption was not observed here.

The meniscus between the vapor and liquid phases disappeared above 374 °C. When supercritical H$_2$O was cooled to the critical temperature (from 375 to 374 °C) after heating, the transmittance dropped sharply (Fig. 2b), before increasing with further cooling (373–370 °C). The transmittance dropped at the estimated critical temperature during both heating (Fig. 2a) and cooling (Fig. 2b).

Figure 3 shows the variation of transmittance of 500–800 nm light through CO$_2$ at 27, 31, 32, 33, and 37 °C. Higher transmittance was recorded during heating from 27 °C to 31 °C; a great decrease occurred with subsequent further heating to the critical temperature (32 °C) (Fig. 3a). The passing of the critical temperature was associated with an increase in transmittance through the CO$_2$: the spectra showed the lowest intensity around the critical temperature. This behavior during heating was similar to that of H$_2$O (Fig. 2a).

The transmittance of CO$_2$ during cooling was high above 33 °C, and decreased greatly around the critical temperature.
Spectroscopic determination of the critical temperatures and pressures

Figure 4. Transmittance spectra of C\(_2\)H\(_5\)OH with respect to wavelength during (a) heating and (b) cooling.

Figure 5. Relationship between temperature and transmittance through H\(_2\)O during heating.

Figure 6. Relationship between temperature and transmittance through CO\(_2\) during heating.

Figure 7. Relationship between temperature and transmittance through C\(_2\)H\(_5\)OH during heating.

temperature (Fig. 3b). It then increased with further cooling (31–27 °C). Transmittance was lowest around the critical point, with similar results obtained during heating (Fig. 3a) and cooling (Fig. 3b).

Figure 4 shows the transmittance through C\(_2\)H\(_5\)OH at 238, 242, 243, 244, and 248 °C. It increased with heating from 238 °C to 242 °C, before sharply decreasing at 243 °C. Transmittance then increased with further heating to 244 °C. Cooling resulted in similar changes (Fig. 4b), with transmittance reaching a minimum at 243 °C, the critical temperature. The absorption around 720–740 nm that was observed during both heating and cooling corresponds to a combination of fundamental –OH vibrations.

The spectra of the pure fluids all show that transmittance was lowest close to or at the critical temperature of the fluid. Therefore, the critical temperature of a fluid can be determined by identifying this local minimum of transmittance.

Figure 5 shows the relationship between temperature and transmittance at 600, 650, and 700 nm for H\(_2\)O during heating (i.e., data from Fig. 2a). For each wavelength, transmittance was lowest at 374 °C, which is the experimentally determined critical temperature of H\(_2\)O. The critical pressure was determined to be the pressure at the observed minimum transmittance. Further heating beyond the critical point (374 °C) resulted in sharp increases of transmittance at 600, 650, and 700 nm.

Figure 6 shows the relationship between temperature and transmittance at 600, 650, and 700 nm for CO\(_2\) during heating (i.e., the data from Fig. 3a). Minimum transmittance was observed at 32 °C, the experimentally determined critical temperature. The critical pressure was determined to be the pressure at this measured critical
temperature.

Figure 7 shows the relationship between temperature and transmittance at 600, 650 and 700 nm for C$_2$H$_5$OH during the heating shown in Fig. 4a. Each wavelength showed lowest transmittance at 243 °C, the experimentally determined critical temperature. The critical pressure was determined to be the pressure at 243 °C.

Table 1 summarizes the critical temperatures and pressures of pure H$_2$O, CO$_2$, and C$_2$H$_5$OH determined here. Reference values from previous studies are also listed. The values determined here agree well with the reference values, with differences in critical temperature of ~0.15, 0.96, and 0.4–2.0 °C for H$_2$O, CO$_2$, and C$_2$H$_5$OH, respectively; even smaller differences were found for pressure. The good agreement between the present values and reference values suggests that the method proposed here could be useful in assessing the geochemical behavior of fluids during water–rock interactions within the interior of the earth.

The spectra of the three fluids reported here show similar characteristics, indicating that these geofluids have similar spectroscopic characteristics and behaviors during heating and cooling. Therefore, this finding suggests that spectroscopic measurements can be used to determine the critical points of multicomponent geofluids. Future research may be able to develop qualitative methods of experimentally analyzing such geofluids.

The temperature and pressure conditions of the fluids analyzed here were shifted along the saturation vapor curve during heating. These conditions change along the density fluctuation ridge that forms an extension of the saturation vapor curve at temperatures and/or pressures above the critical point. We suggest that the lower transmittance around these critical points is caused by scattering by the clustering of molecules. This clustering is the result of significant fluctuations in fluid density at the critical point.

**CONCLUSIONS**

Spectroscopic measurements of H$_2$O, CO$_2$, and C$_2$H$_5$OH fluids at wavelengths of 500–800 nm under subcritical and supercritical conditions were taken to determine the critical points of the fluids. Transmittance markedly decreased around the critical point of each fluid, indicating that the spectroscopic method presented here could be used to determine the critical temperature and pressure of other fluids.

The critical temperatures and pressures experimentally determined here do not differ significantly from previously published reference data. Further research is needed to understand the optical properties of molecules to enable the spectroscopic characteristics of these fluids under subcritical and supercritical conditions to be determined and, thereby, aid the development of new methods to assess the critical temperatures and pressures of multicomponent geofluids.

**ACKNOWLEDGMENTS**

The authors thank Drs. A. Kizaki and T. Watanabe of Tohoku University for helpful comments during the course of this study. This work was partly supported by Grants-in-Aid for Scientific Research (No. 23656558 and No. 25000009 to NT) from the Japan Society for the Promotion of Science. The authors also thank the reviewers for valuable suggestions to improve our manuscript.

**REFERENCES**


Spectroscopic determination of the critical temperatures and pressures


Lemmon, E.W., McLinden, M.O., Friend, D.G. (2005) Thermo-


Manuscript received June 20, 2013
Manuscript accepted October 31, 2013
Published online December 6, 2013
Manuscript handled by Keiji Shinoda