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Sean G. Mueller

Jay R. Werber

Muthanna H. Al-Dahhan
Missouri University of Science and Technology, aldahhanm@mst.edu

Milorad P. Dudukovic

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RESEARCH NOTES

Using a Fiber-Optic Probe for the Measurement of Volumetric Expansion of Liquids

Sean G. Mueller, Jay R. Werber, Muthanna H. Al-Dahhan, and Milorad P. Dudukovic*

Chemical Reaction Engineering Laboratory, Department of Energy, Environmental and Chemical Engineering,
Washington University in St. Louis, 1 Brookings Drive, Urbauer Hall, Campus Box 1198,
St. Louis, Missouri 63130

A fiber-optic probe is developed for the fast, in-situ measurement of volumetric expansion of multiphase and multicomponent systems. An experiment with the binary mixtures of CO_2−toluene and CO_2−ethanol was conducted to demonstrate the usefulness of the fiber-optic probe in accurately tracking the isothermal volumetric expansion as a function of pressure. In the 1-L autoclave that has been used, the probe was shown to detect the liquid level height within a precision of 0.35% of the total height of the vessel. The results for the volumetric expansion of toluene and ethanol with CO_2 correlate well with those found in the literature. The probe itself can be used up to pressures of 140 barg and temperatures of 120 °C.

1. Introduction

Supercritical fluids have been the focus of many studies in green engineering. Dense-phase carbon dioxide has received much attention because of its environmental and economic benefits, such as replacement of harsh solvents, enhanced product selectivities, ease of product separation, and pressure tunability.[1−3] To utilize these benefits efficiently in dense-phase reactors, a detailed knowledge of the phase behavior of multicomponent and multiphase systems is needed. The magnitude of the volumetric expansion of solvents with CO_2 is important to many industrial applications, such as catalytic reactions and the gas−antisolvent process.[4−7]

While many equations of state, such as the Peng−Robinson equation,[8] are able to estimate fluid properties at high pressure, they require empirical mixing rules that must be optimized using experimental data. On the experimental front, the most commonly applied methods for the measurement of volumetric expansion are densitometry (coupled with sampling)[9,10] or the use of some type of view cell,[3,5,10−12] such as a Jerguson cell, that is separate from the reactor. These measurements can be expensive and time-intensive.

We present a simple, fiber-optic probe for the fast, in situ, and direct measurement of volumetric expansion within a high-pressure vessel.

2. Experimental Section

2.1. Materials. High-performance liquid chromatography (HPLC)-grade toluene and ethanol (Fischer Scientific) and liquid CO_2 (CeeKay) were used for the expansion experiments.

2.2. Apparatus. The experimental setup is shown in Figure 1. An HPLC pump (Waters 515) delivers CO_2 to the 3-in. inner diameter (ID), 1-L autoclave (Autoclave Engineers). Pressure was controlled via a Tescom 4000 back-pressure regulator and Validyne pressure transducers. Temperature control was achieved using Omegalux heating tape wrapped around the autoclave, an Omega thermocouple inserted into the vessel's thermowell, and an Omega CN132 temperature controller. The outside of the autoclave, including the heating tape, was then surrounded by 1-in.-thick insulation to minimize temperature gradients through the vessel.

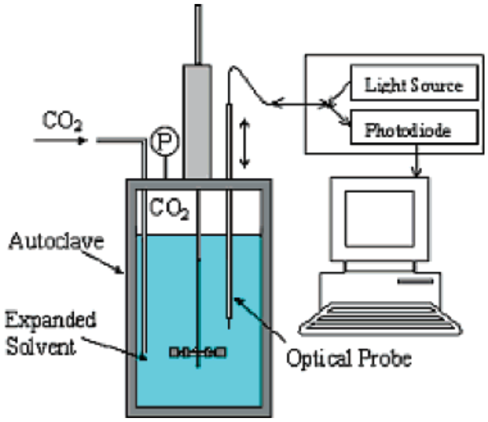

Figure 1. Experimental setup for the autoclave and fiber-optic probe.

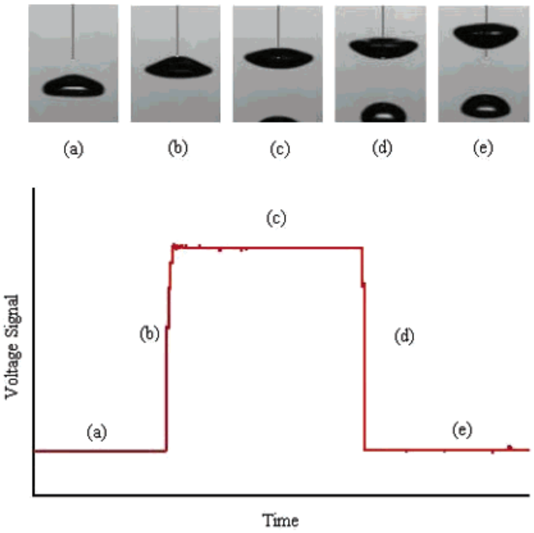

Figure 2. Characteristic step response of a bubble striking the probe tip. Steps (a) and (e) show the probe response in the liquid, (c) the response in the gas, and (b) and (d) the response of the tip entering and leaving gas/liquid interface.

2.3. The Fiber-Optic Probe. The fiber-optic probe measures the refractive index of the environment surrounding the tip of

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* To whom correspondence should be addressed. E-mail address: dudu@wustl.edu.

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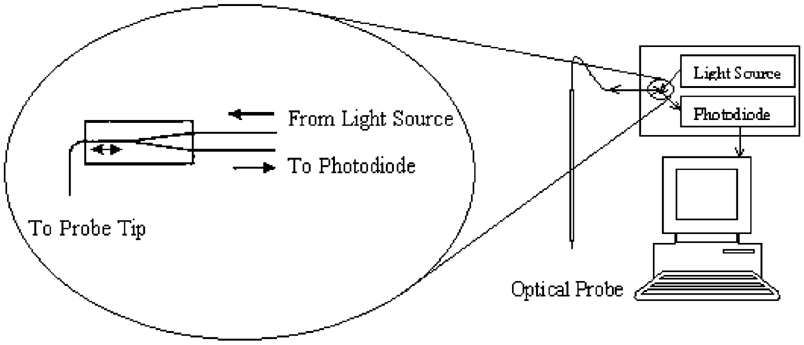

Figure 3. Fiber-optic coupling.

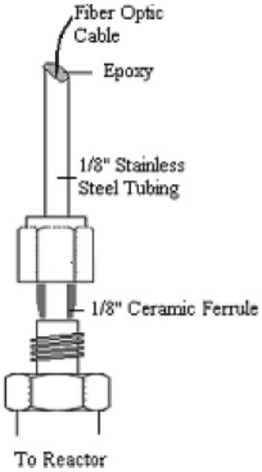

Figure 4. Probe insertion into autoclave.

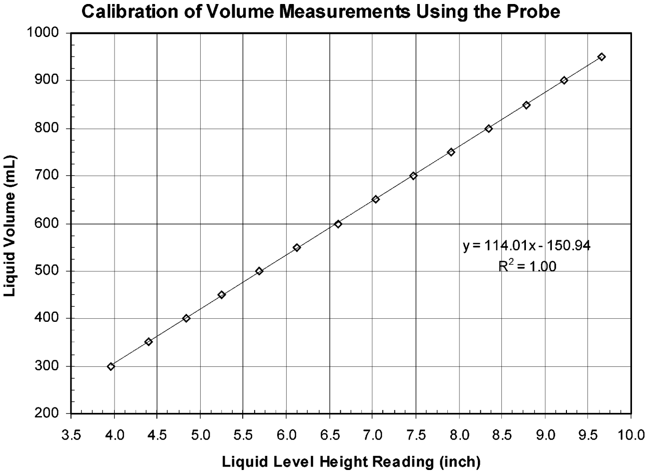

Figure 5. Height-to-volume calibration.

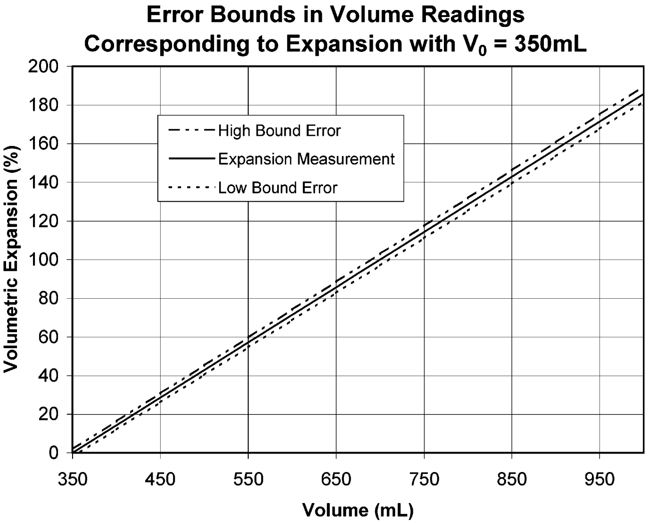

Figure 6. Error in expansion measurements due to volume.

the probe. The refractive indices of gases are vastly different from liquids; therefore, gas/liquid boundaries can be easily determined. As an example, the probe response to a bubble striking the probe tip is shown schematically in Figure 2.

Figure 3 shows a light source that sends a single wavelength of light (670 nm) to the probe. Depending upon the environment surrounding the probe tip, a percentage of the emitted light is reflected back through the fiber. The fiber-optic coupler sends the reflected light to a photodiode, which converts the quanta of light into a voltage signal for processing.

Figure 4 shows that the fiber-optic probe consists of a 200 micron multimode fiber (Thorlabs), which is glued inside of $^1/_8$-in. stainless steel tubing using a high-pressure/temperature epoxy.

The probe is sealed into the autoclave using a ceramic ferrule; because the ferrule does not swage onto the metal tubing, the probe can be moved vertically through the autoclave under high pressure without any leaks. To prevent the probe from blowing out of the autoclave, the probe is clamped into an actuating arm that controls the vertical movement.

2.4. Experimental Method. To measure volumetric expansion, a known quantity of solvent is placed in the autoclave at atmospheric pressure. Any air in the system is then purged by flushing the reactor with CO_2, and the system is brought to a constant temperature for the entire experiment. After the system reaches the desired temperature and the pressure in the reactor is 1 bar, a reading of the initial liquid level height in the vessel is recorded. (Note: The liquid in the autoclave is not stirred during the expansion measurements but is stirred during the time between measurements.) Next, the CO_2 pressure is increased, which causes the liquid phase to expand as a result of further dissolution of CO_2 into the liquid phase. As the liquid level in the autoclave begins to rise with increasing pressure, the probe is moved vertically through the autoclave to determine the location of the liquid level. The probe-detected position of the gas−liquid interface (hence, the liquid volume), as a function of pressure, is then recorded to determine the percent isothermal volumetric expansion (VE) as

$$\mathrm{VE} = \frac{V_{\mathrm{exp},T_0} - V_{0,T_0}}{V_{0,T_0}} \times 100 \qquad (1)$$

where the initial condition (V_{0,T_0}) is the volume of the liquid in the vessel at a 1 bar of CO_2 and temperature T_0.

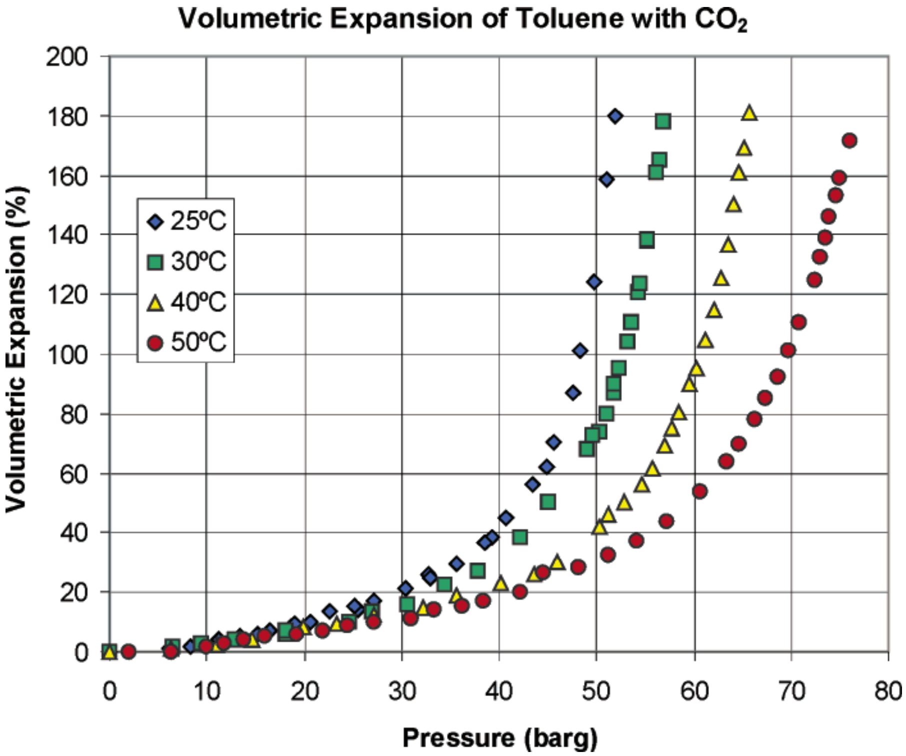

Figure 7. Volumetric expansion of toluene with CO_2 as a function of pressure.

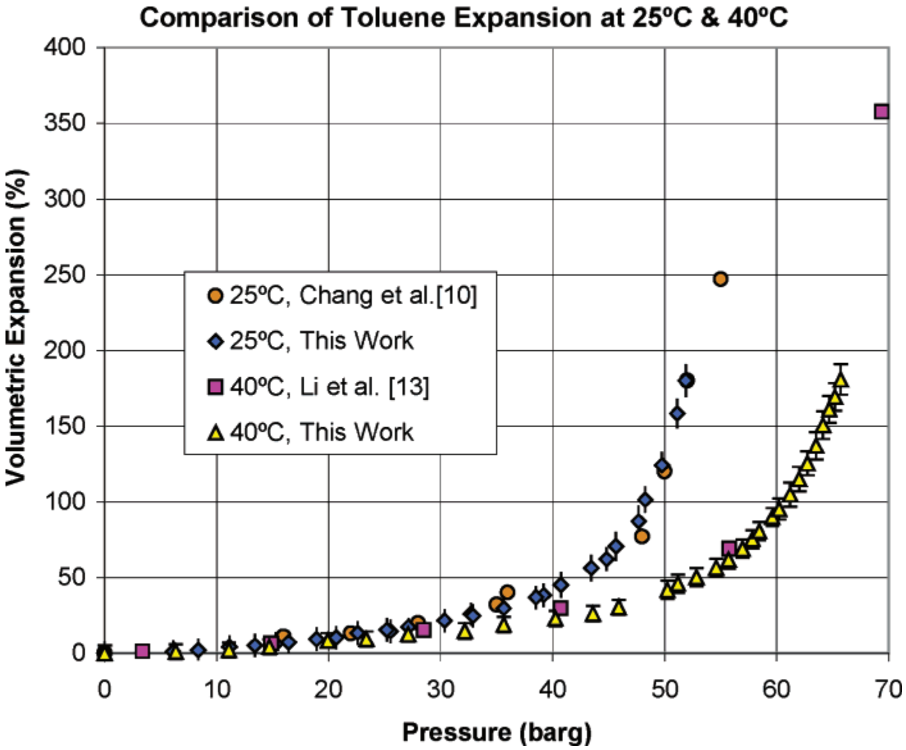

Figure 8. Comparison of toluene expansion with CO_2 from different studies.

2.5. Experimental Uncertainty in Volume, Pressure, and Temperature (*V, P, T*) Measurements. The probe was shown to detect the liquid level height within a precision of 0.35% of the total height of the vessel. This introduces an error no greater than ± 3.56 mL in any volume reading. Volume measurements in the vessel were calibrated in 50 mL increments, as shown in Figure 5.

Knowing this uncertainty in the volume determination, the error in the volumetric expansion readings, as defined in eq 1, is shown in Figure 6.

With V_{0,T_0} typically being near 350 mL, the error in the expansion measurements (in units of %) increases from ±2.2% at smaller volumes to ±3.8% at full volume (1000 mL). Thus, at larger pressures (larger V, compared to V_0), the uncertainty

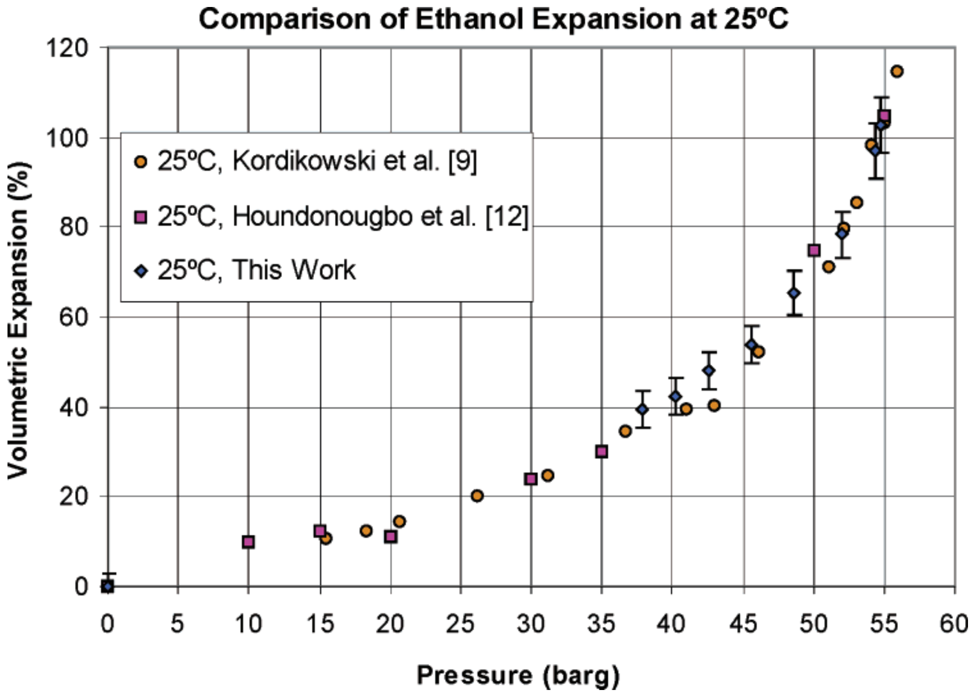

Figure 9. Comparison of ethanol expansion with CO_2 from different studies.

in the measurement would be greater than that at lower pressures.

Pressure measurements were taken with a transducer with a range of 0−220.63 barg at a span of 0−10 V. Therefore, we ideally expect an increase of 0.3125 V for every 6.89 barg. It was determined that the actual voltage reading is within ±0.03 V of the ideal reading, which is a difference of ∼0.69 barg. Therefore, one can assume that the pressure measurements could deviate by as much as ±0.7 barg.

Temperature was monitored in the vessel using a thermocouple that was calibrated against two different mercury thermometers at temperatures in the range of 20−50 °C. It was determined that the thermocouple never deviated from the mercury thermometers more than ±0.4 °C. Because the autoclave was insulated and well-mixed between readings, it is assumed that the temperature throughout the vessel is constant.

3. Results and Discussion

To demonstrate the usefulness of the optical probe, toluene was isothermally expanded with CO_2 at multiple temperatures; the results are shown in Figure 7.

A sharp increase in isothermal expansion is observed as the pressure increases and more and more CO_2 diffuses into the liquid phase. Also, note that isobaric volumetric expansion decreases as the temperature increases. The data for toluene at 25 and 40 °C are compared with the literature values in Figure 8.

For toluene, it is evident that the data obtained using the fiber-optic probe agrees well with the results reported in the literature.[10,13] Our results for ethanol expansion with CO_2 are compared to other literature results in Figure 9. Note that three different methods for determining volumetric expansion are compared: densitometry coupled with sampling,[9] visual measurement by the use of a view cell,[12] and our fiber-optic probe technique. Results of all three techniques agree well with each other.

4. Conclusions

The experiments with CO_2−toluene and CO_2−ethanol illustrate that the dynamic fiber-optic probe is a simple, fast tool for quantifying the volumetric expansion of solvents in a high-pressure vessel that requires no view window or sampling. Because the probe simply designates whether it is in the presence of a liquid or gas, no complex calibration is required. The probe is relatively inexpensive and can be used to quickly determine the in situ volumetric expansion in complex systems with multiple components and multiple phases with reasonable accuracy.

Acknowledgment

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