



Heat capacities of supercritical fluid mixtures: Comparing experimental measurements with Monte Carlo molecular simulations for carbon dioxide-methanol mixtures



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ABSTRACT

Accurate thermophysical properties of supercritical fluid mixtures are important to today's practicing scientists and engineers as they endeavor to correctly capture the unique attributes of these high pressure fluids in chemical processes and energy systems. Isobaric heat capacity, pertinent to many heat exchange calculations and thermodynamic variable manipulations, was measured for carbon dioxide-methanol mixtures using a flow calorimeter over a wide range of compositions (5–30 mol% methanol), temperatures (60–150 °C), and pressures (90–300 bar). Heat capacity predictions from Monte Carlo molecular simulations were compared to experimental measurements at each state point. The average absolute difference between simulation predictions and measurements was slightly larger than +4%. Maximum deviations occurred in the near critical region for each mixture composition. In addition to providing new experimental data, this study validates the utility of molecular simulations as a predictive tool for this mixture in this experimentally challenging region of phase space, though more work is required to accurately calculate fluid properties in regions proximate the mixture critical point.

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1. Introduction

In order to design, construct, and operate equipment for supercritical fluid processing and to determine and optimize process operating conditions, accurate thermophysical property values are required. Experimental measurements support almost all other property estimation methods, either through direct measurement with one or more experimental techniques or experimentally validated calculations using thermodynamic relationships. By repeating measurements in multiple laboratories, each with its own method and rigorous uncertainty assessment, a foundation is laid for credible property estimation.

To satisfy the process simulation and modeling requirements of practicing chemical engineers, highly accurate, multiparameter EOSs are needed for about 1000 pure substances and their mixtures [1]. A good example is supercritical carbon dioxide-methanol

binary mixtures. This mixture has many industrial applications due to the enhanced solvation behavior of supercritical carbon dioxide (scCO₂) with methanol added as a polar co-solvent. For instance, with the addition of methanol, scCO₂ has been used to extract soy isoflavones [2], high value pharmaceutical compounds from microalgae [3], and divalent metal ions from fly ash [4]. For the scCO₂-methanol binary mixtures, parameters for the multiparameter GERG (Groupe Européen de Recherches Gazières) EOS have been fit to existing experimental measurements [5]. But, like many other empirical EOSs, the accuracy of the GERG EOS is unknown outside the range of experimental data utilized for fitting the parameters. More specifically, in the critical region of scCO₂-methanol mixtures, only sparse thermodynamic data are available for regression of EOS parameters. This limitation motivated us to undertake a study of scCO₂-methanol mixtures using both experimental measurements and molecular simulation to provide predictions and better understanding of intermolecular interactions affecting fluid properties.

This study aims to provide an alternative to developing empirical, multiparameter EOSs by coupling selective experimental measurements with molecular simulation estimates of the isobaric heat capacity (C_p) in the near critical and supercritical region for scCO₂-methanol binary mixtures. By comparing the C_p values

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from experimental measurements, molecular simulations, and the GERG EOS, we assessed the potential of classical molecular simulations for improving the accuracy of EOS models. With the advent of inexpensive computational power, the feasibility of using molecular simulations for this purpose can be tested. However, since classical molecular simulations rely on empirical parameters and other assumptions, such as pairwise additivity and lack of polarizability, experimental measurements were used to validate their accuracy. In this work, we present the results of such experimental C_p measurements for scCO₂-methanol mixtures performed using a custom-designed supercritical flow apparatus described in our previous work [6].

2. Monte Carlo molecular simulation theory

In this work, the Metropolis Monte Carlo algorithm was employed to simulate the behavior of the system by deciding molecular movements and system volume changes. Intramolecular and intermolecular interactions are represented using force fields that employ Lennard Jones, Coulomb, and harmonic potentials [7]. Computational methods utilize data generated by molecular simulations to estimate thermodynamic properties, including C_p . The total C_p can be decomposed into residual isobaric heat capacity (C_p^{res}) and ideal gas heat capacity (C_p°). Classical molecular simulations can only estimate C_p^{res} [8,9]. C_p° accounts for energy contributions from both intramolecular interactions from the vibration, torsion, and rotation of molecular bonds, and the kinetic energy of translating molecules. Since intramolecular energy cannot be accurately captured by classical molecular simulations, C_p° is calculated from approximations fitted to highly accurate experimental results.

There are several different methods available for calculating C_p^{res} from molecular simulations. Of these methods, the fluctuation method applied to molecular simulations run in the NPT ensemble, as developed by Lagache et al., has been most extensively used [9–11]. For methane, the fluctuation method has successfully estimated the C_p^{res} along isotherms of 21.1 °C and 104.4 °C [9] and to trace isoenthalps over a wide range of pressures [8] to within the statistical uncertainty of experimental results.

The fluctuation method estimates C_p^{res} from Monte Carlo (MC) molecular simulations through fluctuations in volume, intermolecular potential energy, and configurational enthalpy. Eq. (1) was used to obtain averages of thermodynamic properties, denoted as $\langle X \rangle$, in the NPT ensemble [12],

$$X = \frac{\sum_i X_i \exp(-\beta(U_i + PV_i))}{\sum_i \exp(-\beta(U_i + PV_i))} \quad (1)$$

where the sum is over all configurations sampled during the equilibrium run, U represents the configurational energy, V is the volume of the system, P is the pressure of the simulation, and $\beta = 1/k_B T$, where k_B is Boltzmann's constant and T is the absolute system temperature. The fluctuation formula, Eq. (2), is used to find thermodynamic derivative properties [9].

$$\frac{\partial X}{\partial \beta} = \langle X \rangle \langle \hat{H} \rangle - \langle X \hat{H} \rangle \quad (2)$$

The configurational enthalpy (\hat{H}) is estimated as $U^{ext} + U^{int} + PV$, where U^{ext} represents the intermolecular energy contributions from interactions between different molecules and U^{int} represents the intramolecular energy contributions from molecular bond rotations, torsions, and vibrations (i.e. as described by the classical force field used). Eq. (3) represents the application of the fluctuation formula to C_p^{res} calculations.

$$C_p^{res} = \langle H^{res} \rangle \langle \hat{H} \rangle - \langle H^{res} \hat{H} \rangle \quad (3)$$

Expressing the residual enthalpy (H^{res}) as $U^{ext} + PV$, Eq. (4) is obtained for $C_p^{res,N}$, which represents the C_p^{res} on a basis of N molecules [9].

$$C_p^{res,N} = \frac{1}{k_B T^2} (\langle U^{ext} \hat{H} \rangle - \langle U^{ext} \rangle \langle \hat{H} \rangle) + \frac{P}{k_B T^2} (\langle V \hat{H} \rangle - \langle V \rangle \langle \hat{H} \rangle) - N k_B \quad (4)$$

3. Methods

3.1. Experimental measurements

Carbon dioxide of at least 99.99% purity and methanol of at least 99.9% purity, supplied by Airgas and Sigma respectively, were used in this study without further purification. The experimental apparatus and method have been detailed elsewhere [6]. A brief description follows. Isobaric heat capacity is measured via the flow calorimetric method, characterized by Eq. (5), where a small amount of thermal energy ($\dot{q} \sim 2$ W) induces an increase in temperature ($\Delta T \sim 3$ °C) of the passing fluid ($\dot{m} \sim 13$ g/min).

$$C_p(T, P, x) \equiv \left(\frac{\partial H}{\partial T} \right)_{P,x} \sim \frac{\dot{q}}{\dot{m} \Delta T} \Big|_{\text{low} \Delta P} \quad (5)$$

Together, measurements of the heat rate, the induced temperature rise, and the fluid mass flow rate account for a basic uncertainty of approximately 1% of the experimentally determined heat capacity value. Assignment of each heat capacity to a specific temperature, pressure, and composition contributes additional uncertainty. The temperature measurements were made with a thermocouple calibrated to ± 0.1 °C, and the pressure measurements were made with a pressure transducer accurate to ± 0.4 bar. Systematic uncertainty in mixture composition, on average $\pm 0.7\%$ of the methanol mole fraction, was estimated from the uncertainties in the differential mass measurement of the methanol reservoir (± 0.04 g), the stopwatch timing (± 0.05 s), and the mixture mass flow rate (± 0.05 g/min) measured by a Coriolis mass flow meter. Using estimates for $\left(\frac{\partial C_p}{\partial T} \right)_{P,x}$, $\left(\frac{\partial C_p}{\partial P} \right)_{T,x}$, and $\left(\frac{\partial C_p}{\partial x} \right)_{T,P}$, and the uncertainty of each state point assignment, the typical uncertainty contribution to a heat capacity measurement is calculated to be approximately 0.4% of the experimentally measured C_p value. This contribution to the total measurement uncertainty becomes very significant near a mixture's critical point, tripling in value in this study, where the fluid mixture's heat capacity is extremely sensitive to variations in temperature, pressure, and composition. In summary, the typical overall measurement uncertainty is approximately $\pm 1.4\%$ but can reach $\pm 3\%$ close to the critical locus of the mixture.

In addition to using high-quality measurement devices and high purity fluids, high accuracy in flow calorimetry is attained by limiting heat loss, pressure drop, and fluid inhomogeneity within the measurement cell. Placing the vacuum jacketed calorimeter within a thermal bath at the experimental measurement temperature helps eliminate heat loss. To verify the calorimeter operated with negligible heat loss, heat capacity measurements were repeated at the same temperature and pressure while varying the induced temperature rise at a constant mass flow rate. No significant change was found in the measured heat capacity values, indicating insignificant heat loss from the calorimeter. A small fluid pressure drop through the calorimeter (~ 0.05 bar) was achieved by operating at low flow rates and utilizing a short length of wide diameter measurement tubing (0.4 m length and 5.15 mm ID). Finally, the calorimeter's heating element, a wound piece of Ni-Cr wire directly placed in

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