

A new approach to correlating isothermal densities of supercritical CO₂ mixed fluids

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The study on physical and chemical properties of supercritical CO₂ (SC CO₂) is an important topic for CO₂ capture, storage and sequestration in the earth environment science. SC CO₂ has been used with effective organic co-solvents in many fields and most application systems are mixtures [1]. The thermodynamic properties and chemical activities of CO₂ mixed fluids are significantly different from that of pure CO₂ in the critical regions.

Our previous work demonstrated that phase behavior and molecular interaction of CO₂ mixtures in the critical region [2-6]. The strong clustering occurred in the fluid critical region and so the densities, isothermal compressibility and excess volume of fluids were very sensitive to pressure while the density vs pressure curves of the mixed fluids are far from linear. It is desirable to correlate experimental density data with pressure using a linear equation.

In this communication, we report our new finding. A simple linear equation is proposed to correlate the isothermal densities of fluid mixtures in or near the critical region. The model has been tested in the systems of CO₂+pentane, CO₂+acetone, CO₂+pentane+acetone mixtures with different compositions [7]. It is indicated that the model can correlate the data well, although the model is very simple. This is also interesting to practical applications. For example, densities of mixed fluids are often required in industrial processes and environmental application, and the data of the mixed fluids at high pressure are scarce. Using the linear correlation, we can get the data at the desired pressures by using only two data.

We are grateful to Program for New Century Excellent Talents in University (NCET-07-0769) and NSFC-40503008.

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Chromatographic pre-concentration of Hg from dilute aqueous solutions for isotopic measurement by MC-ICP-MS

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Previous studies have demonstrated both mass-dependent fractionation (MDF) and mass-independent fractionation (MIF) of Hg isotopes in environment and the potential for their application in biochemistry and geochemistry. Though understanding the Hg isotopic distribution in the aquatic system is critical for evaluating the mobility, toxicity, transformation, and biogeochemical cycle of Hg in nature, little has been reported for Hg isotope geochemistry in natural dilute aqueous environment. The main difficulty in measuring Hg isotopes in water samples is that Hg is present at very low concentration (several ng/L). Several liters of water are required to have sufficient Hg for an isotopic analysis (40 ng).

We have developed a new ion-exchange protocol for the direct pre-concentration of Hg from freshwater samples. The protocol is validated by testing both synthetic de-ionized (DI) water (n=22) and Hg-free river water solutions (n=20) of varying concentrations, and by assessing the effect of Hg recovery and organic complexants on the reproducibility of measured isotopic ratios. The results showed recovery of 101%±6 in the final Hg eluates. Finally, isotopic measurements of 17 spiked synthetic and natural samples gave $\delta^{202}\text{Hg}$ values of 0.00‰ ± 0.12, showing no isotopic fractionation during pre-concentration when compared with the Hg spike reference solution.

The pre-concentration protocol was applied to 16 natural water samples with Hg concentrations ranging from 0.9ng/L to 15600 ng/L. The result showed a total variation of 2.4‰ for $\delta^{202}\text{Hg}$ and evident MDF and MIF of Hg isotopes. Our study demonstrates that further research is required to fully understand the behavior of Hg isotopes in aqueous environment.