Constant-Volume Heat Capacity of Mixed Supercritical Fluids and Molecular Interaction in the Systems

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Abstract: Constant-volume heat capacities of supercritical (SC) CO_2, SC CO_2-n-pentane, and SC CO_2-n-heptane mixtures were determined at 308.15 K in the pressure range from 6 to 12 MPa. It was found that there is a maximum in each heat capacity *vs* pressure curve. Intermolecular interaction in the fluids was studied.

Keywords: Constant-volume heat capacity, mixed supercritical fluids, molecular interaction .

Supercritical fluids (SCFs) have many features. For example, density, dielectric constant and solubility parameter can be altered between gas-like and liquid-like through modest manipulations of pressure and/or temperature. In recent years, different techniques have been used to study the molecular interactions in SCFs, such as UV[1], FTIR[2], fluorencence[3], and partial molar volume measurement[4]. It is known that solvent (SCF)-solute clusters exist in SCF mixtures in high compressible region[4]. Molecular simulations[5] showed that self-association of the molecules exists in pure SCFs (one component).

Constant-volume heat capacity (Cv) is directly related with internal energy, which can give information about molecular interaction, and the data for pure SC CO_2 have also been reported[6]. However, constant-volume heat capacity data of mixed SCFs near critical region were not found in a literature survey, although some constant-pressure heat (Cp) data were determined[7] . In this work, the heat capacities of SC CO_2, CO_2-n-pentane, and CO_2-n-heptane were determined, and molecular interactions in the systems were studied.

CO_2 with a purity of 99.995% was supplied by Beijing Analytical Instrument Factory. n-Pentane and n-heptane were A. R. grade produced by Beijing Chemical Plant. The apparatus used was built in this laboratory. It consisted mainly of a calorimeter vessel, a thermostat, an electric calibrator, a precision thermistor thermometer, and a high pressure system. The heat capacity of water was determined 5 times at 308.15 K and the maximum deviation from the value in the handbook[8] is less than 1%. We will not give more detailed description of the apparatus in this short paper.

Figure 1 illustrates the dependence of Cv of pure SC CO_2, SC CO_2-n-pentane, and SC CO_2-n-heptane on pressure at 308.15 K determined in this work. The concentration of n-pentane and n-heptane in the mixtures is 0.5 mol%. The Cv data of pure CO_2 reported by Amirkhanov *et al.*[6] are also given in the figure. The results of this work agree well

with those reported by other authors[6], which verifies the reliability of the apparatus.

Figure 2 shows the effect of pressure on the isothermal compressibility (K_T) which was calculated on the basis of the densities of the fluids determined in this work

The results in **Figure 1** show clearly that there is a maximum in each Cv *vs* pressure curve. There are also maxima in K_T *vs* pressure curves, as shown in **Figure 2**. It is very interesting to notice that the maxima of Cv and K_T occur at almost the same pressures. This is discussed qualitatively in the following.

There are clusters in SCFs and degree of clustering is a function of temperature and pressure[1-5]. Some of the clusters are broken when raising temperature. Breaking clusters is endothermal. The higher the degree of clustering, the more clusters are broken when raising temperature, and more energy is required. So the maxima in Cv curves occur. Thus, it can be concluded that the degree of clustering is largest when K_T is highest. **Figure 1** indicates that the maxima of the Cv curves for SC CO_2-n-pentane and SC CO_2-n-heptane are lower than that of pure CO_2. A very interesting conclusion can be obtained from this phenomenon: the clusters in the mixtures are more stable than that in pure CO_2.

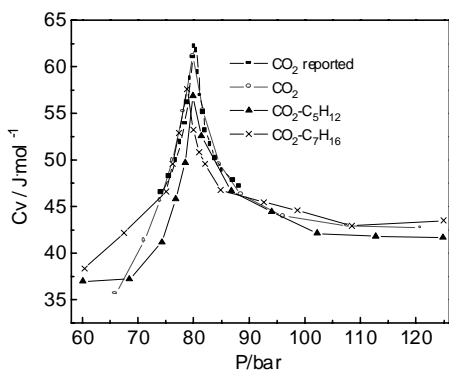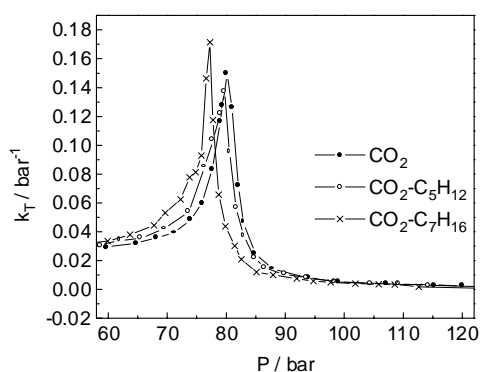
Figure 1   Dependence of Cv on pressure   **Figure 2**   Dependence of KT on pressure

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