Effect of Molecular Size of Solutes on Their Partial Molar Volumes in Supercritical n-Pentane

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Abstract: The densities of n-pentane, methane-n-pentane, propane-n-pentane, n-heptane-n-pentane, and n-decane-n-pentane binary mixtures were determined at 476.5K in the pressure range from 2 to 5 MPa. The partial molar volumes of the solutes in n-pentane were calculated using the density data. It was found that the partial molar volumes of methane and propane are positive , while those of n-heptane and n-decane are negative.

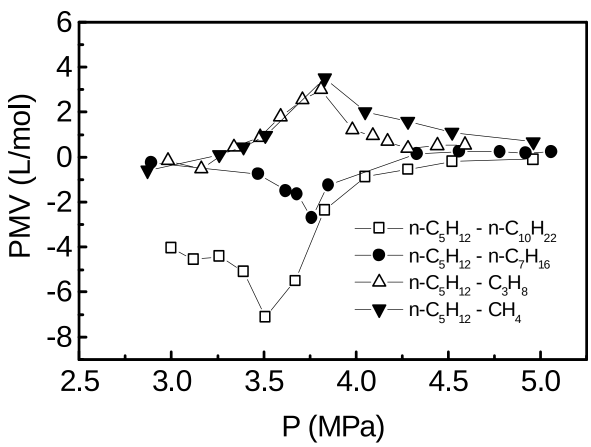
Keywords: Density, supercritical fluid, partial molar volume.

Supercritical fluids (SCFs) have many unique properties[1]. However, nearly all of the features are related with the aggregation or clustering of the molecules in the fluids. Some researchers have reported that the partial molar volumes (PMVs) of the solutes in dilute supercritical (SC) solutions are large negative values[1-4], which is different from common liquid solutions. Negative PMV of a solute in SC solution results from the fact that the local density of the solvent surrounding the solute is higher than the bulk density. This phenomenon is called as local density enhancement, or clustering[1]. Fluorescence spectroscopy showed that local density can be as high as 2.5 times of the bulk density[5]. This work studied PMVs of methane, propane, n-heptane and n-decane in SC n-pentane.

Purity of both methane and propane were 99.9% supplied by Beijing Analytical Instrument Factory. The n-pentane (99.9%), n-heptane (99.9%), and n-decane (99.9%) were produced by Beijing Chemical Plant. These chemicals were used without further purification. The apparatus and experimental procedures for determining the densities of the mixtures were similar to that described previously[6]. The PMV values of the solutes were easily calculated using the density of the pure n-pentane, the densities of the mixtures, and the reported method[3]. **Figure 1** illustrates the PMVs of the solutes at 476.5K. The mole fractions of the solutes are 0.01 for all the solutions.

The critical temperature and pressure of n-pentane are 469.6K and 3.37MPa. The data in **Figure 1** shows clearly that the PMVs of methane and propane, which are smaller than the solvent (n-pentane), are positive near the critical region. However, the PMVs of the large solutes, n-heptane and n-decane, are negative, and the absolute value increases with the molecular size of the solute. In this short paper we will not show the relationship between the density and pressure. However, it should be mentioned that the maxima or the minima in the PMV curve correspond to the largest compressibility of the fluids. This work obtain an very interesting conclusion. That is, the PMVs of methane, propane, n-heptane, and n-decane in n-pentane change from positive to negative as the molecular size of the solutes increases, *i.e.*, the PMV of a solute is positive when its size is smaller than that of the solvent, and becomes negative as its size is larger than that of the solvent.

Figure 1 PMVs of methane, propane, n-heptane and n-decane in n-pentane at 476.5K



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