CONSTANT-VOLUME HEAT CAPACITY OF MIXED SUPERCRITICAL FLUIDS NEAR THE CRITICAL REGION AND INTERMOLECULAR INTERACTION

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Abstract The phase behaviors, constant-volume heat capacity (C_v), and isothermal compressibility (K_T) of ethane + ethanol and ethane + acetone binary mixtures have been measured in supercritical region and subcritical region near the critical point of the mixtures at 309.45 K. The experiments have also been carried at the conditions far from the critical point of the mixtures. It is demonstrated that in supercritical region there exists a maximum in C_v versus pressure curve (C_V^{max}) at fixed composition, which occurs at the pressure where K_T is the largest. In subcritical region, C_v and K_T increase sharply as pressure approaches the critical point (CP) or bubble point (BP), and the C_v at CP or BP can be several times larger than that of the fluids far from the phase separation pressures. The "clustering" between molecules in the mixed fluids in the critical region is the main reason for these phenomena. It is deduced that at fixed composition the degree of "clustering" changes significantly with pressure near the CP or BP, and is the largest at CP and BP. Breaking the clusters in the mixed fluids in the critical region is an endothermic process.

Introduction

It is well known that constant-volume molar heat capacity (C_v) is directly related with the internal energy and intermolecular interaction in a system. The C_v of some pure SCFs has been reported[1,2]. The constant pressure heat capacity (Cp) of some dilute SC mixtures has also been measured[3]. In previous work[4], we determined the C_v of CO_2+ethanol and CO_2+n-pentane binary mixtures at 308.15 K. The results indicated that C_v is very sensitive to pressure near the critical point of the mixtures. CO_2 is a very commonly used SCF.

However, it has quadrupole and is a weak Lewis acid[5] which make the intermolecular interactions in mixtures more complex, and it is difficult to distinguish the contributions of various interactions to C_v and the features of the mixtures. Ethane and CO_2 have similar critical temperatures. However, the interaction between ethane and other compounds is simpler, which is favorable to obtain more detailed information about the intermolecular interaction in the ethane-based mixed fluids. In this work, the phase behavior and critical parameters of ethane+ethanol and ethane+acetone binary mixtures are measured at 309.45 K. The C_v and K_T of the mixed fluids in their critical regions are determined, and the intermolecular interactions are investigated.

Experimental section

Materials Ethane with a purity of >99.9% was supplied by Beijing Analytical Instrument Factory. Acetone and ethanol were A.R. grade produced by Beijing Chemical Reagent Company. The chemicals were used without further purification.

Apparatuses and procedures The calorimeter and the procedures used to determine the heat capacity were similar to that used previously[4]. The apparatus and procedures for determining the critical points and the phase behavior were described earier[6].

Results

Phase behavior In this work we study how the C_v of ethane (1) + ethanol (2) and ethane (1) + acetone (2) binary mixtures changes with pressure and composition near the critical points of the mixtures at 309.45 K. The phase behaviors of the mixed fluids are the basis for selecting suitable conditions. Therefore, we first determined the phase behavior of the mixtures near the critical region. The critical point (CP), bubble point (BP), and dew point (DP) are listed in Table 1.

Table 1. Critical composition, critical pressure, bubble point pressure (BPP), dew point pressure (DPP) of ethane-ethanol and ethane-acetone systems at 309.45K

Ethane (1) + ethanol (2)		Ethane (1) + acetone (2)	
X_2	BPP or DPP /MPa	X_2	BPP / MPa
0.010	5.16	0.010	Single phase*
0.013[C]	5.11[C]	0.015[C]	4.98[C]
0.050	5.01	0.050	4.88

*Single phase in the whole pressure range; [C] Critical composition and critical pressure

Constant volume heat capacity   On the basis of the phase behavior of the two mixtures discussed above, we select some typical conditions for the measurement of the C_v, which can represent the mixed fluids in different phase regions near the critical point of the mixtures. The dependence of C_v of the two systems on pressure is illustrated in Figures 1 and 2, respectively.
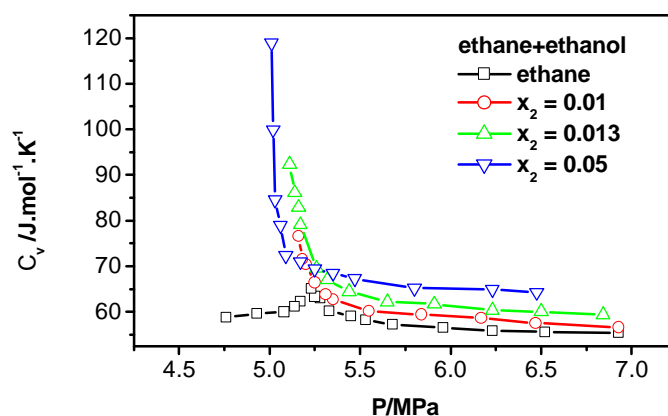

Figure 1. Dependence of C_v of pure ethane and ethane-ethanol mixtures on pressure
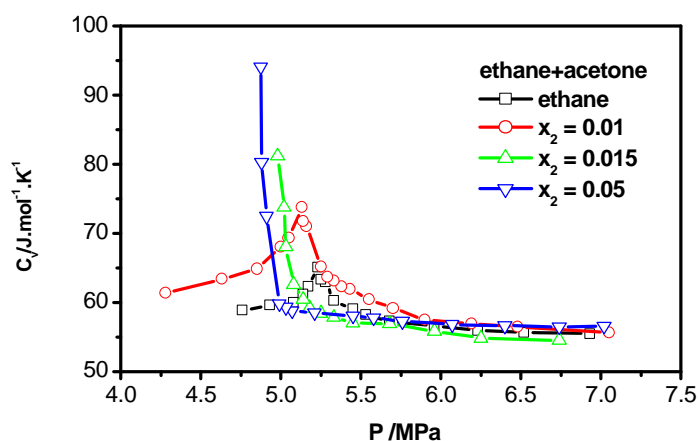

Figure 2. Dependence of C_v of pure ethane and ethane-acetone mixtures on pressure

Isothermal compressibility The isothermal compressibility K_T of a fluid is an important characteristic parameter related with the solution structure. We also calculated K_T of the mixtures at different conditions using the density data determined in this work and the following well-known equation.

$$K_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T \qquad (1)$$

Where ρ is the density of the fluid. The variations of K_T with pressure for the two systems are shown in Figures 3 and 4, respectively.
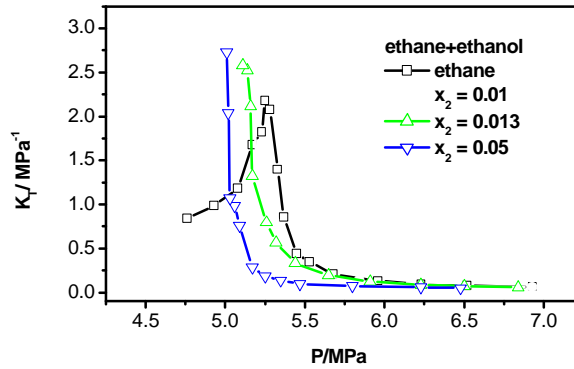

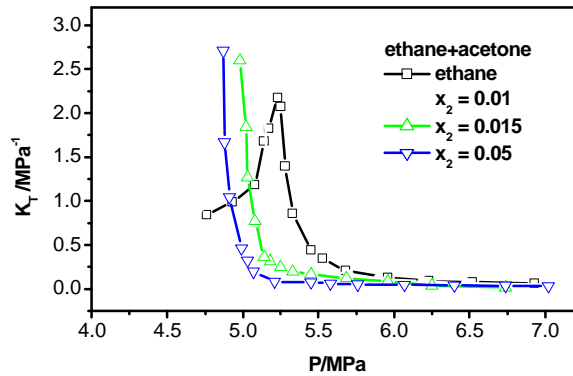Figure 3. Isothermal compressibility of pure ethane and ethane-ethanol mixture

Figure 4. Isothermal compressibility of pure ethane and ethane-acetone mixture

Discussions

C_v of a mixed fluid depends mainly on its composition and intermolecular interaction. At a fixed composition, C_v should depend mainly on the intermolecular interaction. Figures 1 and 2 show that the C_v of pure ethane or the mixtures is nearly independent of pressure in the high pressure region, indicating that the intermolecular interaction is not sensitive to pressure as the fluid is far from the critical region of the mixed fluids. In other words, the properties of the mixed fluids far from the critical points do not vary with pressure

considerably, which is similar to liquids. The dependence of C_v in the critical region on pressure is very complex. We discuss the supercritical region and subcritical region separately.

Supercritical region For pure ethane and ethane (1) + acetone (2) mixture with X_2=0.01, the fluids are in single-phase region in the entire pressure range. The experimental temperature is higher than their critical temperature. For ethane (1) + ethanol (2) mixture with X_2=0.01 the fluid are in single-phase region when the pressure is higher than 5.16 MPa which is the dew point pressure. Therefore, these fluids can be regard as vapor or supercritical fluids. There exists a maximum ($C_V^{\max}$) in each C_v versus pressure curve for pure ethane and the ethane (1) + acetone (2) mixture, as can be known from Figures 1 and 2. For the ethane (1) + ethanol (2) mixture, the C_v is the largest at the dew point. For all the curves, the pressure at which the C_v is largest corresponds to the largest K_T.

Critical and subcritical fluids Figures 1 and 2 show another interesting phenomenon. C_v is very sensitive to pressure as the pressure approaches the critical point (CP) or the bubble point (BP), and the C_v at the CP or BP are largest at fixed composition. The C_v at CP or BP can be several times larger than that in the high pressure range where the C_v is nearly independent of pressure. Compared to the dilute SC solutions, little work has been conducted for studying the properties of subcritical fluids or the mixtures with critical composition. It can be deduced that the degree of "clustering" at CP or BP reaches maximum at fixed composition. The C_v is very sensitive to pressure in the critical region of the mixture, suggesting that the degree of "clustering" in the mixtures is very sensitive to pressure near the critical point.

It can be known by comparing Figures 1 and 2 that the C_v of ethane + ethanol mixture is higher than that of ethane + acetone at the CP and BP. Both ethanol and acetone are polar compounds. The dipole moments of acetone and ethanol are 2.88 D and 1.70 D, respectively. Acetone can not form hydrogen bond itself, while ethanol can form hydrogen bond. It can be expected that ethanol molecules form hydrogen bond themselves in ethane + ethanol system at the conditions studied in this work, while hydrogen bonding does not exists in ethane + acetone mixture. The hydrogen bonding may affect the C_v because some hydrogen bonds are broken as temperature rises, which is favorable to increasing the C_v. Therefore, hydrogen bonding may be the main reason for the phenomenon that the C_v of ethane + ethanol system at CP and BP is larger than that of ethane + acetone.

The results in Figures 1 and 2 also illustrate that in the high pressure region, the C_v of ethane + acetone mixture is nearly independent of the composition, while that of ethane + ethanol mixture increases considerably as the concentration of ethanol is increased. The main reason is that the degree of hydrogen bonding in ethane + ethanol mixture increases with the concentration of ethanol. More hydrogen bonds are broken as temperature rises when more hydrogen-bonded species exist in the system. Therefore, the C_v of ethane + ethanol mixture increases with increasing concentration of ethanol.

The C_v of CO_2 + ethanol mixture determined in our previous work[50] has the similar trend with that of ethane + ethanol system as composition and pressure are changed, i.e., C_V^{max} increased with the concentration of ethanol. We deduced that the clustering of the molecules, hydrogen bonding of ethanol, acid-base interaction between CO_2 and ethanol[51], and the interaction between the quadrupole of CO_2 and the dipole of ethanol might contribute to this phenomenon. It can be deduced from the results of this work that the acid-base interaction, quadrupole-dipole interaction, and hydrogen bonding in CO_2+ethanol mixture are not main factors for the interesting phenomenon because in ethane + acetone mixture, these three kinds of interactions do not exist. Therefore, we can get an important conclusion: the clustering between the molecules in the mixtures results in the interesting phenomena that the C_v is very sensitive to pressure in the critical region and C_V^{max} increases with increasing X_2.

The study on the dramatic change in intermolecular interaction with pressure and composition of mixtures in the critical region is an interesting topic.

References

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