Critical Parameters of Hexane + Carbon Monoxide + Hydrogen and Hexane + Methanol + Carbon Monoxide + Hydrogen Mixtures in the Hexane-Rich Region

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The critical parameters of hexane + carbon monoxide + hydrogen and hexane + methanol + carbon monoxide + hydrogen mixtures have been determined in the *n*-hexane-rich region. The critical temperature and the critical density of the hexane + carbon monoxide + hydrogen system decrease with increasing concentrations of carbon monoxide and hydrogen, whereas the critical pressure increases with the concentrations of the light gases. The critical density of the hexane + methanol + carbon monoxide + hydrogen mixture increases significantly with increasing concentration of methanol, and the critical pressure decreases with increasing methanol concentration.

Introduction

Supercritical fluids (SCFs) have been used in many processes, such as extractions and separations, chemical reactions, particle production, materials processing, and chromatography. The application systems are usually mixtures containing two or more components. To exploit the advantages of SCFs, the mixtures should be homogeneous and should be supercritical mixtures. Critical parameters are key criteria for identifying the supercritical state, and critical parameters of many pure compounds and binary mixtures have been reported.[1−10] However, the data for ternary mixtures or more complex mixtures are scarce.[10−14]

Recently, researchers began to study the critical parameters of reaction systems[15] because the reaction at supercritical conditions has become a very attractive area, and critical parameters are the basic data for conducting reactions at supercritical condition. Reaction mixtures differ from those that are normally studied because their chemical composition changes with time or conversion. Hence, critical parameters change with the conversion. In this work we determined the critical parameters of hexane + carbon monoxide + hydrogen and hexane + methanol + carbon monoxide + hydrogen mixtures in the hexane-rich region. Besides providing some basic critical parameters, the results of this work are of direct importance to the synthesis of methanol from CO and H_2 ($CO + 2H_2 \rightarrow CH_3OH$) in supercritical hexane, which may become a promising reaction system in industry. There are three components in the reaction system before reaction, hexane (solvent), CO, and H_2, and there are four components during the reaction process, hexane, CO, H_2, and CH_3OH. For the quaternary system, the concentrations of the components were selected in such a way that they simulated the compositions of the reaction system at different conversions.

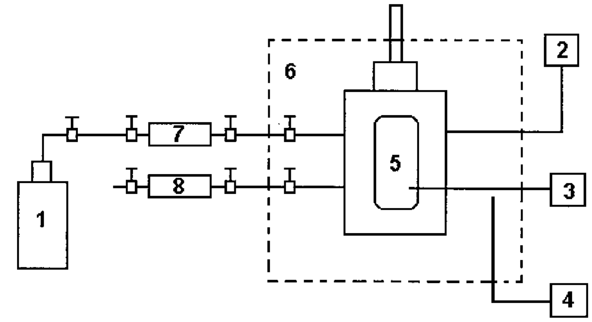

Figure 1. Schematic diagram of the experimental apparatus.

Experimental Section

Materials. Both hydrogen (99.95%) and carbon monoxide (99.9%) were supplied by Beijing Analytical Instrument Factory. *n*-Hexane was purchased from Tianjin First Chemical Reagent Factory, and the purity was >99.8%. Methanol (>99.8%) was purchased from Beijing Chemical Factory.

Apparatus. Different methods have been used to determine the critical points of pure substance or mixtures, such as observation of the appearance and/or disappearance of the meniscus at the vapor−liquid interface,[1] flow methods,[2,3] acoustic methods,[8,12] a pulse heating method,[5] and measurements of the vapor−liquid coexistence.[16]

The observation of the appearance and/or disappearance of the meniscus at the vapor−liquid interface is a reliable method to determine critical points. It is based on the fact that the strong critical opalescence can be observed at the critical point of a pure substance or a mixture.[17] At the same time, the mixture changes from a single phase to two phases as pressure is reduced slightly, and the volume of the liquid phase is equal to that of the vapor phase. Our apparatus was based on this principle. It was similar to that we used previously.[18] The only difference was that the apparatus of this work could be used at a higher temperature. Figure 1 is a schematic diagram of the apparatus. Briefly, it consisted of a high-pressure optical cell, a

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Table 1. Critical Parameters of Hexane + CO + H_2 Mixtures[a]

x_{CO}	x_{H_2}	T_c/K	P_c/bar	ρ_c/g·cm^{-3}	x_{CO}	x_{H_2}	T_c/K	P_c/bar	ρ_c/g·cm^{-3}
0.0102	0	505.8	30.17	0.219	0.0182	0.0182	505.1	31.24	0.193
0.0179	0	505.7	30.96	0.217	0.0252	0.0252	504.7	31.97	0.188
0.0297	0	505.0	31.33	0.207	0.0294	0.0294	504.4	32.86	0.182
0.0402	0	504.6	31.58	0.201	0.0038	0.0075	505.6	30.34	0.213
0.0432	0	504.8	31.67	0.188	0.0072	0.0144	505.5	30.50	0.197
0.0704	0	501.9	33.45	0.179	0.0090	0.0180	504.2	30.69	0.194
0	0.0119	505.2	30.21	0.219	0.0111	0.0222	504.0	30.96	0.191
0	0.0203	504.8	30.47	0.209	0.0142	0.0285	504.1	31.80	0.187
0	0.0307	504.4	31.21	0.196	0.0070	0.0035	506.5	30.38	0.224
0	0.0393	504.4	31.89	0.193	0.0139	0.0069	505.9	30.51	0.217
0.0054	0.0054	506.0	30.11	0.219	0.0202	0.0101	505.5	31.08	0.199
0.0098	0.0098	505.2	30.66	0.201	0.0264	0.0132	504.5	31.53	0.197

[a] Errors of T_c, P_c, and ρ_c are ±0.3 K, ±0.03 MPa, and ±0.005 g·cm^{-3}, respectively.

constant-temperature air bath, a pressure gauge, a temperature controller, and a thermometer, which was inserted into the optical cell to determine the temperature in the cell. The high-pressure view cell was made of stainless steel with two borosilicate windows. The temperature of the air bath was controlled by a PID temperature controller (XS/A-1), and the fluctuation of the air bath temperature was ±0.1 K. The uncertainty of the temperature measurement was ±0.1 K. The pressure gauge was composed of a pressure transducer (FOXBORO/ICT, model 93) and an indicator. The uncertainly of the pressure gauge was ±0.01 MPa in the pressure range of 0−7 MPa.

In a typical experiment, the apparatus was washed thoroughly using different solvents and dried under vacuum. A known mass of hexane or hexane + methanol mixture was charged first using a sample bomb after the air in the system was removed by vacuum pump. The gas mixture of known composition was then charged using a gas sample bomb. The mass of each chemical charged was known by the mass difference of the sample bomb before and after the system had been charged. The composition of the mixture in the system could be calculated from the masses of the chemicals. The air bath was maintained at the desired temperature. After thermal equilibrium had been reached, the piston in the optical cell was moved up and down to change the volume or pressure of the system. The procedures were repeated at other temperatures until critical opalescence was observed. It is estimated that the uncertainties of the critical temperature (T_c), critical pressure (P_c), and critical density (ρ_c) were ±0.3 K, ±0.03 MPa, and ±0.005 g·cm^{-3}, respectively.

Result and Discussion

Pure Hexane. In a previous paper,[18] we confirmed the reliability of the apparatus by determining the critical parameters of CO_2 and compared them with the data reported by other authors.[19] In this work we determined the critical temperature, critical pressure, and critical density of *n*-hexane, and the values are 507.2 K, 3.003 MPa, and 0.231 g·cm^{-3}, respectively, which agree reasonably with the data reported by Kay (507.85 K, 3.034 MPa, and 0.233 g·cm^{-3}).[20]

Hexane + Carbon Monoxide + Hydrogen Ternary Mixture. Table 1 lists the critical parameters of the *n*-hexane + carbon monoxide + hydrogen ternary mixture in the hexane-rich region. The molar ratios of CO/H_2 were 1:0, 2:1, 1:1, 1:2, and 0:1, respectively. The data are also shown in Figures 2−4.

The critical temperature and the critical density decrease with increasing concentrations of the light gases (CO and H_2), whereas the critical pressure increases with the concentrations of the light gases. However, the effect of the ratio of CO/H_2 on the critical pressure of the mixture is very limited at our experimental conditions.

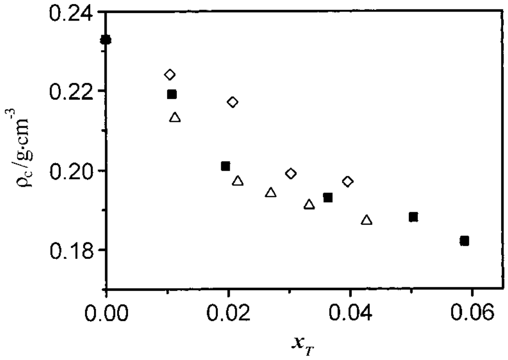

Figure 2. Dependence of the critical density of the ternary mixture on the total mole fraction of CO and H_2 (x_T): ■, CO/H_2 = 1:1; △, CO/H_2 = 1:2; ◇, CO/H_2 = 2:1.

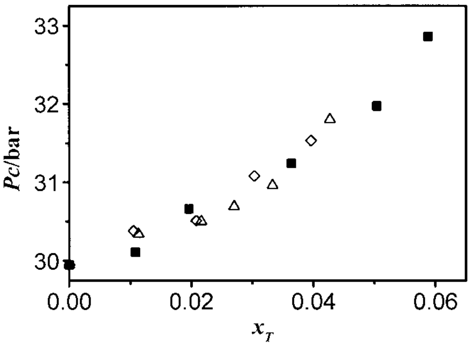

Figure 3. Dependence of the critical pressure of the ternary mixture on the total mole fraction of CO and H_2 (x_T): ■, CO/H_2 = 1:1; △, CO/H_2 = 1:2; ◇, CO/H_2 = 2:1.

Hexane + Methanol + Carbon Monoxide + Hydrogen Quaternary System. The compositions of the mixture were selected to simulate the reaction system for synthesizing methanol using CO and H_2 in hexane at different conversions. The molar ratio H_2/CO is 2:1, and the total original mole fractions (before reaction) of CO and H_2 (x^0_T) are 0.045 and 0.072, respectively. The composition of the reaction system at a fixed x^0_T was calculated on the basis of the conversion of CO(α) for the reaction ($CO + 2H_2 \rightarrow CH_3OH$) in hexane, and the critical parameters at this conversion were determined by preparing the mixture using the pure chemicals. Table 2 gives the critical parameters at different x^0_T and conversions.

The results in Table 2 indicate that the critical temperature is not sensitive to conversion; that is, the critical temperature will not change considerably in the reaction process in the reactant concentration range studied. How-

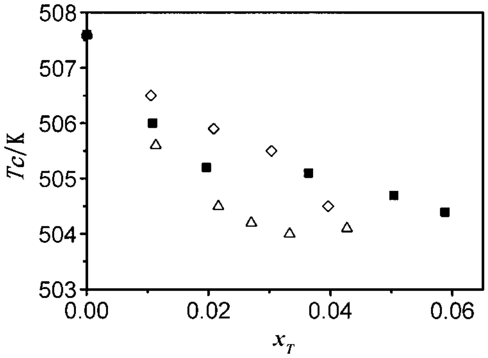

Figure 4. Dependence of the critical temperature of the ternary mixture on the total mole fraction of CO and H_2 (x_T): ■, $CO/H_2 = 1:1$; △, $CO/H_2 = 1:2$; ◇, $CO/H_2 = 2:1$.

Table 2. Critical Parameters of Hexane + CO + H_2 + CH_3OH Mixtures[a]

α	x_{CO}	x_{H_2}	x_{CH_3OH}	T_c/K	P_c/bar	ρ_c/g·cm^{-3}
			$x^0_{H_2+CO} = 0.045$			
0.4	0.0091	0.0182	0.0061	506.2	31.00	0.198
0.6	0.0061	0.0122	0.0092	506.4	30.73	0.206
0.8	0.0031	0.0062	0.0123	506.6	30.47	0.215
1.0	0	0	0.0155	506.2	30.17	0.247
			$x^0_{H_2+CO} = 0.072$			
0.4	0.0147	0.0294	0.0098	504.6	33.03	0.187
0.6	0.0099	0.0198	0.0148	505.3	31.16	0.199
0.8	0.0050	0.0100	0.0200	505.5	30.55	0.209
1.0	0	0	0.0252	505.4	30.09	0.259

[a] Errors of T_c, P_c, and ρ_c are ±0.3 K, ±0.03 MPa, and ±0.005 g·cm^{-3}, respectively. Molar ratio of $H_2/CO = 2:1$; $x^0_{H_2+CO}$ = total original mole fraction of the CO and H_2; α = conversion of CO.

ever, the critical pressure and critical density of the reaction system vary significantly in the reaction process. The critical pressure decreases with increasing conversion, and the critical density increases with the conversion.

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