Gas−Liquid Critical Properties of Ethylene + Hydrogen and Propylene + Hydrogen Binary Mixtures[†]

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Gas−liquid critical properties of ethylene + hydrogen and propylene + hydrogen are measured in the olefin-enriched region by using a high-pressure view cell with direct visual observation. The critical temperature of the two systems decreases with increasing concentration of hydrogen, whereas the critical pressure increases. The Soave−Redlich−Kwong (PSRK) and group contribution equations of state are used to predict the critical points, and the results agree well with the experimental data.

Introduction

Supercritical fluids (SCFs) have many favorable characteristics for applications in many processes, such as separation, material processing, chemical reactions, and so forth. The processes applying SCFs usually involve two or more components. To use the advantages of SCFs, the mixtures in many processes should be a single phase.[1] Therefore, the locus of critical points is crucial to estimate the phase behavior of the mixtures. The common methods adopted for measuring critical properties of mixtures include the following: visual method,[4,5] flow method,[6] acoustic method,[7] and pulsed heating method.[8] Hicks and Young reviewed the critical properties of binary mixtures.[2] Abdulagatov et al. published a review which summarized the experimental data of critical properties for the binary mixtures containing carbon dioxide.[3] However, there are few reports with regard to the mixtures including hydrogen.

In this work, we build an apparatus to determine the critical properties of ethylene + hydrogen and propylene + hydrogen mixtures via the visual approach for the potential application of olefin industrialization, especially in the supercritical polymerization of ethylene or propylene where hydrogen is added as a chain-transfer agent. Furthermore, the understanding of critical properties of mixtures including hydrogen is important to the rational design of the supercritical hydrogenation process.

Experimental Section

Materials. Both ethylene (mass fraction: ≥ 0.999) and propylene (mass fraction: ≥ 0.9999) are purchased from Foshan Kodi Gas Chemical Industry Co., Ltd. (Foshan, China). Hydrogen (mass fraction: ≥ 0.9999) is supplied by Hangzhou Jingong Special Gas Co., Ltd. (Hangzhou, China).

Apparatus. A schematic diagram of the apparatus for measuring critical points is exhibited in Figure 1. The optical cell with two borosilicate glass windows shown in Figure 2 is similar to that described by Zhang et al.[1]

The maximum inner volume of the optical cell is carefully calibrated by high pure nitrogen when the magnetic stirring bar
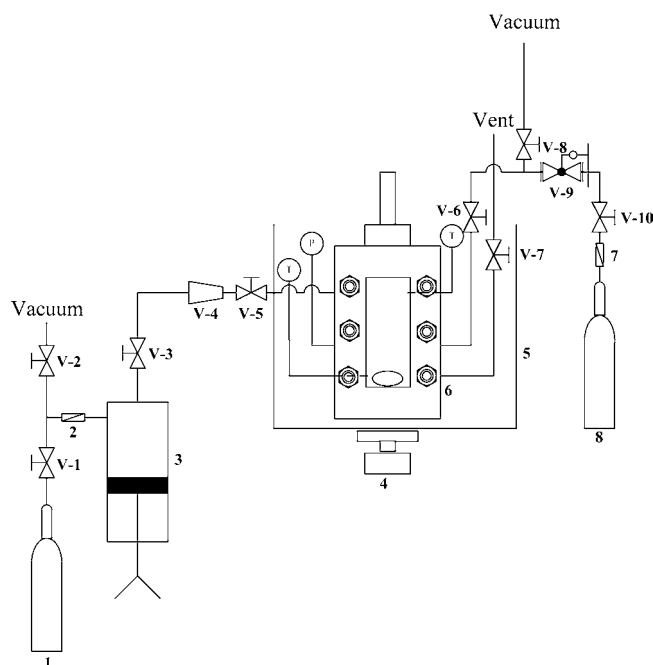

Figure 1. Schematic diagram of the experimental setup: 1, ethylene (propylene) gas cylinder; 2 and 7, filters; 3, high-pressure liquid metering pump; 4, magnetic stirrer; 5, constant temperature oil (water) bath; 6, variable-volume view cell; 8, hydrogen gas cylinder; V-1, V-2, V-3, V-5, V-6, V-7, V-8, and V-10, high pressure needle valve; V-4, check valve; V-9, pressure regulator.

is in place. The volume of cell can be changed in the range of (25.17 to 72.50) cm³ by moving the piston. The cell is immersed in an oil or water bath. The temperature of oil or water is measured by a type K thermocouple (WRNK-191, Beijing Chaoyang Instrument Factory, China) and controlled using a temperature controller (XMTD-7000, Yuyao Temperature Instrument Factory Co., Ltd., China). The water bath can be cooled by a superthermostatic bath when measuring the critical properties of the ethylene + hydrogen system. Two agitators are used to ensure the temperature is uniform in the bath. The cell pressure is monitored with a pressure transducer (HQ1000, Baoji Huaqiang Sensor, China) equipped with a digital pressure indicator (HR-WP-C70, Hongrun Precision Instruments Co.,
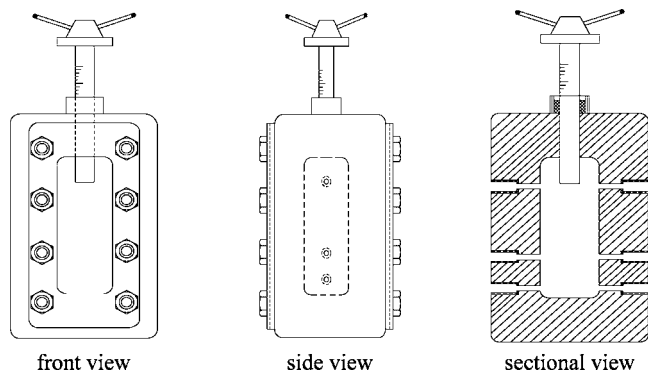
Figure 2. Schematic diagram of the high-pressure variable-volume view cell.

| | front view | side view | sectional view |

Table 1. Critical Temperature and Pressure of Pure Substances

substance	T_c/K		P_c/MPa	
	this work	lit.	this work	lit.
ethylene	282.3	282.34	5.02	5.041
propylene	365.1	364.90	4.63	4.600

Table 2. Critical Properties of Ethylene (1) + Hydrogen (2)

x_2	T_c/K	P_c/MPa
0.0000	282.3	5.02
0.0207	281.7	5.31
0.0358	281.2	5.61
0.0466	280.8	5.78
0.0619	280.4	5.98
0.0769	279.9	6.32
0.0878	279.6	6.51
0.0952	279.4	6.63
0.0998	279.2	6.73
0.1029	279.0	6.87
0.1086	278.9	7.07
0.1213	278.5	7.23
0.1305	278.1	7.56
0.1508	277.5	7.85
0.1737	276.6	8.44

Ltd., China). The error of the pressure gauge is ± 0.02 MPa in the pressure range of (0 to 20) MPa. The temperature in the vapor phase and liquid phase of the view cell is measured by two different Pt resistance thermometers (WZP-Pt1000, Beijing Zhongyihuashi Technology Co., Ltd., China). The uncertainty of the temperature measurement is ± 0.1 K. The pressure of hydrogen charged to the view cell is controlled via a precision pressure regulator (YT-2, Jiangsu Fucheng Chengfeng Valve Plant, China). Ethylene or propylene is loaded by the high-pressure liquid metering pump (JB-3, Jiangsu Haian Oil Scientific Research Apparatus Co., Ltd., China) at an accuracy of 0.01 cm³.

Experimental Procedures. The critical properties for pure substance and binary mixtures are determined by visual observations. Before each measurement, the air in the view cell is evacuated using a vacumm pump. A specified amount of hydrogen is charged into the view cell by controlling the hydrogen pressure with the pressure regulator. The density of hydrogen at the given temperature and pressure is obtained from literature.[9] The mass of hydrogen is determined by the density of hydrogen and the volume of cell. Before being added to the cell, ethylene or propylene existing in the pump is maintained at the desired temperature by a superthermostatic bath. Its pressure is maintained at a specified value to keep it in liquid state. The density of the liquid at the given temperature and pressure is obtained from literature.[9] The mass of ethylene or propylene as well as the composition of mixture in the cell can be changed by controlling the volume of the liquid introduced into the cell. The uncertainty in mole fraction is estimated to be ± 0.0008.

After loading hydrogen and ethylene (or propylene), the temperature of the oil or water bath is increased gradually until the mixture in cell becomes a single phase. There are three different routes to reach the single-phase region. The position of the meniscus changes differently in the corresponding process. If the density of mixture in cell is lower than the critical density, the meniscus falls slowly, and the liquid phase all evaporates eventually. If the density of mixture is greater than the critical density, the meniscus rises, and the liquid occupies the whole inner volume of cell eventually. If the density of mixture is close enough to the critical density, the location of meniscus still stays in the middle of cell and finally disappears in the middle of cell. After the one-phase region is reached, the cell is cooled by decreasing the bath temperature gradually, and the cooling rate is controlled to be less than 0.3 K/min.[10,11] Before the meniscus reappears in the middle of the view cell, the color of fluid can change from colorless to yellow, orange red, and then black. The temperature and pressure readings are noted down at the moment when the complete darkness occurs.[11]

During the measuring process, the density of mixture is adjusted to approximate the critical density by moving the piston. The temperature-increasing and -decreasing processes are repeated at least three times for each measurement, and an average of the readings is offered as the experimental data reported in this work.

Experimental Results

The reliability of the apparatus and the experimental procedure are checked by measuring the critical temperature and pressure of ethylene and propylene. As shown in Table 1, the experimental results agree well with the literature values.[12]

As shown in Table 2 and Figures 3 to 4, the critical temperature of the ethylene + hydrogen system decreases slightly with the increasing concentration of hydrogen. On the other hand, the dependence of critical pressure on hydrogen concentration is more significant. The similar phenomena have been observed by Ke et al.[7] and Gao et al.[5] Heintz and Streett[13] measured the vapor−liquid phase equilibrium of the ethylene + hydrogen mixture at the temperature range of (114.1 to 247.1) K and pressure range of (4.03 to 599.83) MPa and suggested that the phase behavior of this binary system belongs to the type III phase diagram proposed by van Konynenburg and Scott.[14]
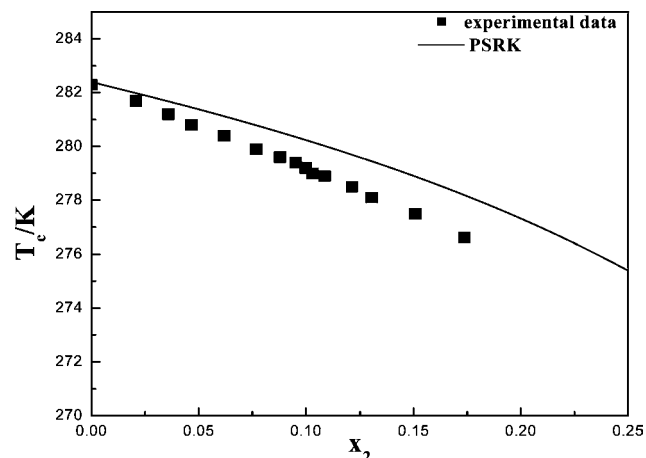

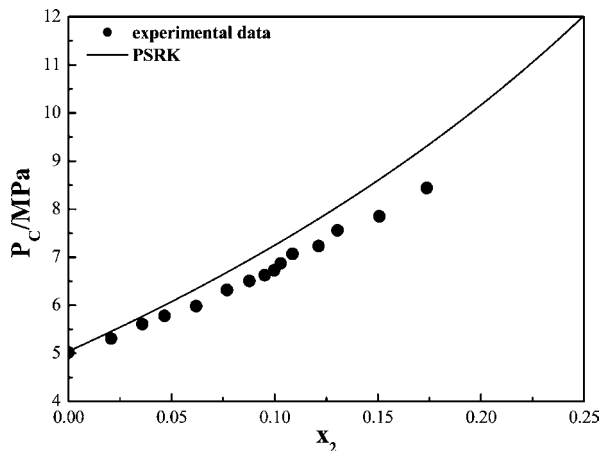**Figure 3.** Critical temperature for ethylene (1) + hydrogen (2).

Figure 4. Critical pressure for ethylene (1) + hydrogen (2).

Table 3. Critical Properties of Propylene (1) + Hydrogen (2)

x_2	T_c/K	P_c/MPa
0.0000	365.1	4.63
0.0288	364.7	4.95
0.0391	364.2	5.16
0.0396	364.2	5.18
0.0494	364.0	5.33
0.0639	363.4	5.61
0.0707	362.8	5.77
0.0880	362.1	6.21
0.0996	361.7	6.35
0.1019	361.7	6.44
0.1052	361.5	6.53
0.1194	361	6.75
0.1306	360.6	7.05
0.1443	360.3	7.29
0.1531	360.1	7.58
0.1650	359.5	7.85
0.1784	359.3	8.12

The critical data for the propylene + hydrogen system are shown in Table 3 and Figures 5 and 6. Similar to the ethylene + hydrogen system, the critical temperature decreases mildly, but the critical pressure increases remarkably with the increase in hydrogen concentration.

Prediction of Critical Properties. In this work, the method of calculating the gas−liquid critical points of mixture developed by Heidemann and Khalil is selected.[15] Usually, the equation of state is the appropriate thermodynamic model adopted to calculate the gas−liquid critical properties. However, most equations of state can not predict the high-pressure phase
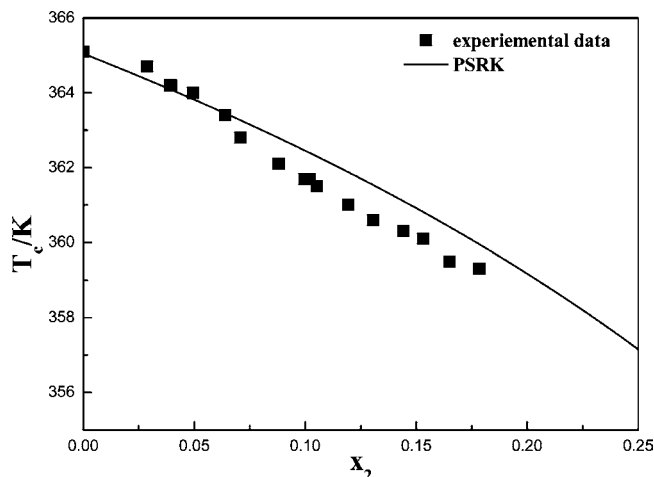

Figure 5. Critical temperature for propylene (1) + hydrogen (2).
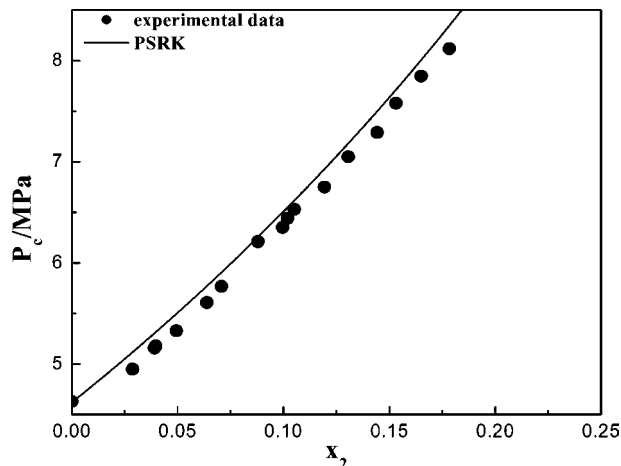

Figure 6. Critical pressure for propylene (1) + hydrogen (2).

Table 4. Average Absolute Deviation (AAD) in the Prediction of Critical Properties with PSRK[a]

system	AADT (%)	AADP (%)
propylene + hydrogen	0.16	2.33
ethylene + hydrogen	0.35	6.41

[a]

$$AADT = \frac{1}{no}\sum_{i=1}^{no}\left|\frac{T_{c,exp} - T_{c,cal}}{T_{c,exp}}\right|_i \cdot 100$$

$$AADP = \frac{1}{no}\sum_{i=1}^{no}\left|\frac{P_{c,exp} - P_{c,cal}}{P_{c,exp}}\right|_i \cdot 100$$

behavior because of the lack of interaction parameters for mixtures. The group contribution PSRK (predictive Soave−Redlich−Kwong) equation of state is developed to predict the vapor−liquid phase equilibrium at a large range of temperatures and pressures.[16] Furthermore, PSRK equation of state is also used to predict critical properties of various systems.[17−19] To check its capacity further, the PSRK equation is adopted. The PSRK model which combines the SRK equation of state with the group contribution model UNIFAC by the PSRK mixing rule can be expressed as follows:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \tag{1}$$

$$\frac{a}{bRT} = \sum x_i \frac{a_i}{b_i RT} + \frac{\frac{G^E}{RT} + \sum x_i \ln \frac{b}{b_i}}{C} \tag{2}$$

$$b = \sum_i x_i b_i \tag{3}$$

The constant C in eq 2 is −0.64663. The parameters of pure substances and the group interaction parameters used in the PRSK model are taken from the literature.[20] The prediction results can be seen from Figures 3 and 6 and Table 4. It is obvious that the agreement between the prediction and the experiments is satisfactory except that the maximum deviation is 6.41 % for the prediction of critical pressure of the ethylene + hydrogen system.

Conclusions

The critical properties of two binary mixtures (ethyene + hydrogen and propylene + hydrogen) are measured by using a high-pressure view cell with visual observation. For both of the

two binary mixtures, the critical temperature decreases slightly, and the critical pressure increase strikingly with increasing hydrogen concentration. The PSRK model is used to predict the critical properties. The agreement between the prediction results and the experimental data is satisfactory.

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