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Phase Behavior of the System *n*-Hexane + Ethanol + Carbon Dioxide

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ABSTRACT: Experimental data for the phase behavior of system *n*-hexane (C_6H_{14}) + ethanol (EtOH) + carbon dioxide (CO_2) at temperatures from (308.5 to 328.5) K are presented. Bubble point and cloud point pressures were measured using a variable-volume view cell as functions of temperature, ratio between C_6H_{14}, EtOH, and CO_2. The effect of temperature and CO_2 concentration on bubble point pressure was investigated. In addition, the Peng−Robinson equation of state (PR-EOS) with one binary interaction parameter was used in correlating the experimental data of bubble point at 313.5 K. The results show that the PR-EOS can correlate the experimental data of the bubble point pressure.

INTRODUCTION

Supercritical carbon dioxide ($SCCO_2$) is most commonly used as a supercritical fluid with the advantages of having a low critical temperature ($T_c = 304.15$ K) and pressure ($P_c = 73.8$ bar) and being environmental friendly, nontoxic, noninflammable, and inexpensive.[1] It is widely used in extraction, reaction, and separation to minimize the amount of organic solvents.[2] $SCCO_2$ is often used as an antisolvent to prepare pharmaceutical nanoparticles.[3,4] The $SCCO_2$ antisolvent process (SAS) is induced by the two kinds of fast mass transfer processes: the fast expanding of CO_2 into the organic solvent and the fast dissolution of the organic solvent in the supercritical CO_2. The phase behavior of the system of organic solvents and CO_2 is important for the SAS, because it can significantly influence mass transfer properties.[5]

In recent years, liposomes have found many applications ranging from cosmetics technology and biomedicine to food industry.[6−8] Phosphotidylcholine is one of the most commonly used lipids in the preparation of liposomes.[9] In our previous work,[10] hydrogenated phosphatidycholine was used to prepare the lutein liposome by SAS. It is expected that hydrogenated phosphatidycholine will be a good substance for making proliposomes. In view of C_6H_{14} being less toxic than CH_2Cl_2, and the mixed solvent of C_6H_{14} and EtOH being a good solvent for hydrogenated phosphatidycholine, the mixed solvent of C_6H_{14} and EtOH is favored in making liposomes using hydrogenated phosphatidycholine as a lipid. However, the phase behavior of the ternary system of $SCCO_2 + C_6H_{14}$ + EtOH is scarce, though that of CO_2 + EtOH and $CO_2 + C_6H_{14}$ has been studied by several groups.[11−15] Hence, the study on the phase behavior of the ternary system of $SCCO_2 + C_6H_{14}$ + EtOH is necessary and important to the preparation of liposomes using SAS.

In this work, the experimental data for the ternary system $SCCO_2 + C_6H_{14}$ + EtOH were presented. Bubble point curves were established, depending on the temperatures and compositions of mixtures. The bubble points of the ternary system at 313.5 K were correlated using the PR-EOS with one binary interaction parameter. Several cloud points were also obtained. To our knowledge, this system has not been studied previously.

EXPERIMENTAL SECTION

Materials. CO_2 with the purity of 99.95% was supplied by the store of Shanghai Jiaotong University (Shanghai, China). Analytical grade C_6H_{14} and absolute EtOH were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. (Shanghai, China).

Apparatus and Procedure. The phase behavior of the system of CO_2, C_6H_{14}, and EtOH was investigated through measuring the bubble points and cloud points of the system. Depending on the conditions, either a bubble or a cloud is formed, corresponding to L−V (liquid to vapor) and L−L (fluid to liquid) transitions, respectively. The pressures measured in each case are the pressure at which the first bubble is formed and the pressure at which the magnetic bar is no longer visible.[16]

The schematic diagram of the experimental apparatus used in this work is shown in Figure 1. A variable-volume vessel with a view window was used to study the phase behavior of the mixture $CO_2 + C_6H_{14}$ + EtOH. The volume can be continuously varied from (3.0 to 30.0) mL by moving the piston in order to change the pressure of the vessel. The vessel is enclosed externally by a two-piece heating jacket. A magnetic stirrer inside the vessel driven by an external magnet is used to mix solution. The heater is connected to a PID controller with a thermocouple and digital indicator installed inside the vessel by which the temperature of it can be measured and controlled to within ± 0.1 K. The system pressure is measured by a pressure transmitter (accuracy of 0.25 % FS) and digital indicator. The amount of CO_2 pumped into the view cell was calculated by its density and volume. At a certain temperature and pressure, the density of CO_2 was known. The volume of CO_2 was obtained by the scale value on the CO_2 metering pump, which is measured to within ± 0.01 mL. The mixed solvent of EtOH and C_6H_{14} was injected into the vessel using HPLC pump. The volume ratio of C_6H_{14}/ EtOH was measured at 20 °C.

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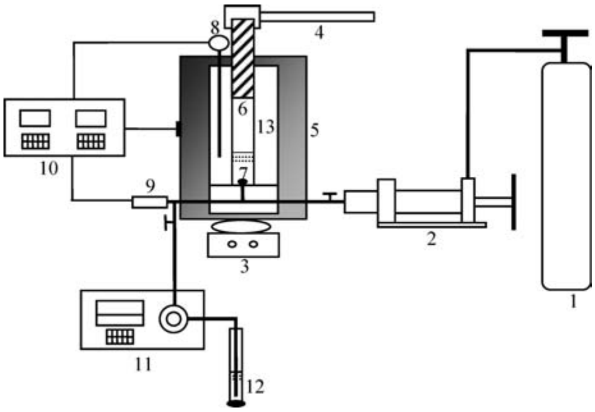

Figure 1. Flowchart of bubble point experiment: (1) CO_2 cylinder; (2) CO_2 metering pump; (3) magnetic stirring apparatus; (4) stainless steel handle; (5) heating jacket; (6) piston; (7) stirring bar; (8) temperature transmitter; (9) pressure transmitter; (10) temperature indicator controller and pressure indicator; (11) HPLC pump; (12) scale flask; (13) variable-volume view vessel.

Briefly, the experimental procedure is as follows. In a typical experiment, a known amount of CO_2 and the mixed solvent of C_6H_{14} + EtOH were injected into the vessel, respectively. Then the mixture of $CO_2 + C_6H_{14}$ + EtOH was well agitated, and the vessel was heated to the desired temperature. The mixture was compressed by moving the piston. Once the state of a single phase was reached, the pressure was slowly decreased at about 0.05 MPa/min until a bubble or a cloud was formed. Every measurement was repeated at least three times for consistent measurements. Reproducibility of the bubble point or cloud point pressure was within ± 0.1 MPa. Thus a pressure–temperature ($P-T$) curve was obtained to indicate the phase behavior for the system of C_6H_{14}, EtOH, and CO_2.

Modeling. The Peng–Robinson equation of state (PR-EOS)[17] is used in this work to correlate the bubble points of the ternary system CO_2–EtOH–C_6H_{14} at 313.5K. The PR-EOS is given by the following equation:

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

$$a(T) = 0.45724\,\frac{R^2 T_c^{\,2}\alpha(T)}{P_c}$$

$$\alpha(T) = \left[1 + (0.37646 + 1.54226\omega - 0.26992\omega^2)\left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2$$

$$b = 0.07780\,\frac{RT_c}{P_c}$$

Equation 1 can be rearranged into following form:

$$Z^3 - Z^2(1-B) + Z(A - 3B^2 - 2B) - AB + B^2 + B^3 = 0 \tag{2}$$

$$A = \frac{aP}{R^2T^2},\quad B = \frac{bP}{RT},\quad Z = \frac{PV}{RT}$$

Table 1. Experimental Data of System of CO_2 (1) in EtOH (2) and C_6H_{14} (3)

T	P/MPa at V_2/V_3[b] =1/1			
	w_1[a]			
K	0.6500	0.7000	0.7705	.
308.5	5.0	5.2	5.9	6.4
313.5	5.2	5.6	6.4	7.0
318.5	5.5	6.0	6.9	7.6
323.5	5.8	6.4	7.4	8.2
328.5	6.1	6.8	7.9	8.7

T	P/MPa at V_2/V_3 =1/2			
	w_1			
K	0.6927	0.7498	0.7973	0.8490
308.5	5.9	6.0	6.2	7.0
313.5	6.3	6.4	6.7	7.5
318.5	6.7	6.8	7.3	8.1[c]
323.5	7.1	7.3	7.7	
328.5	7.5	7.9	8.2	

T	P/MPa at V_2/V_3 =1/3			
	w_1			
K	0.6500	0.7000	0.7500	0.8000
308.5	5.3	5.7	6.1	6.4
313.5	5.7	6.1	6.5	6.8
318.5	6.1	6.7	7.1	7.3
323.5	6.5	7.2	7.6	7.9
328.5	6.9	7.7	8.1	8.4[c]

[a] w_1: mass fraction of CO_2. [b] V_2/V_3: volume ratio of EtOH and C_6H_{14}. [c] Cloud points, the rest are bubble points.

For a mixture, the fugacity coefficient, φ, can be calculated

$$\ln \varphi_i = \frac{b_i}{b_m}(Z-1) - \ln(Z-B) - \frac{A}{2\sqrt{2}B}\left[\frac{2\sum_{j=1}^{N} x_i a_{ij}}{a_m} - \frac{b_i}{b_m}\right]\ln\left[\frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B}\right] \tag{3}$$

where a_m and b_m are evaluated using the van der Waals linear mixing rules as follows:

$$a_m = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j a_{ij} \tag{4}$$

$$b_m = \sum_{i=1}^{N} x_i b_i \tag{5}$$

where x_i is the mole fraction of component i in that phase, N is the number of components, and a_{ij} is the cross parameters and determined by the combining rules

$$a_{ij} = (1 - k_{ij})\sqrt{a_i a_j} \tag{6}$$

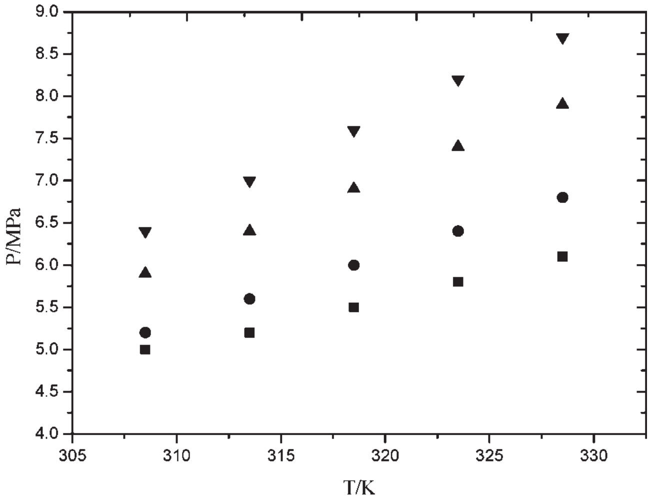

Figure 2. $P-T$ isopleths of bubble points at V_3/V_2 = 1/1. Mass fractions of CO_2 in the mixed solvents: ■, 0.6500; ●, 0.7000; ▲, 0.7705; ▼, 0.8500.

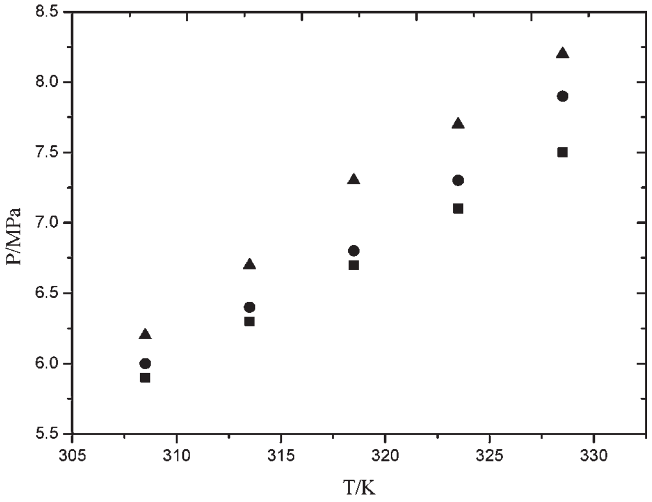

Figure 3. $P-T$ isopleths of bubble points at V_3/V_2 = 2/1. Mass fractions of CO_2 in the mixed solvents: ■, 0.6927; ●, 0.7498; ▲, 0.7973.

The k_{ij} is the binary interaction parameter for an $i-j$ pair. $|1 - \Sigma y_i|$ is minimized to obtain the results of the correlation. y_i is the mole fraction of component i in the liquid phase. The absolute relative deviation percent (ARD) is to indicate the accuracy of the correlation using PR-EOS

$$\text{ARD} = \left|\frac{P_{\text{exp}} - P_{\text{cal}}}{P_{\text{exp}}}\right| \times 100\% \tag{7}$$

where the subscript exp and cal denote the experimental and calculated values, respectively.

■ RESULTS AND DISCUSSION

The phenomenon of L−V and L−L phase transition was observed depending on the CO_2 mass fraction, the volume ratio between C_6H_{14} and EtOH, and the temperatures. The experimental data for the bubble point and cloud point pressures of the systems of C_6H_{14} + EtOH + CO_2 are given in Table 1. Three different volume ratios between C_6H_{14} and EtOH were investigated for temperatures ranging from (308.5 to 328.5) K. The $P-T$ isopleths are shown in Figure 2 to 4 for 1/1, 2/1, and 3/1 volume ratios between C_6H_{14} and EtOH, respectively.

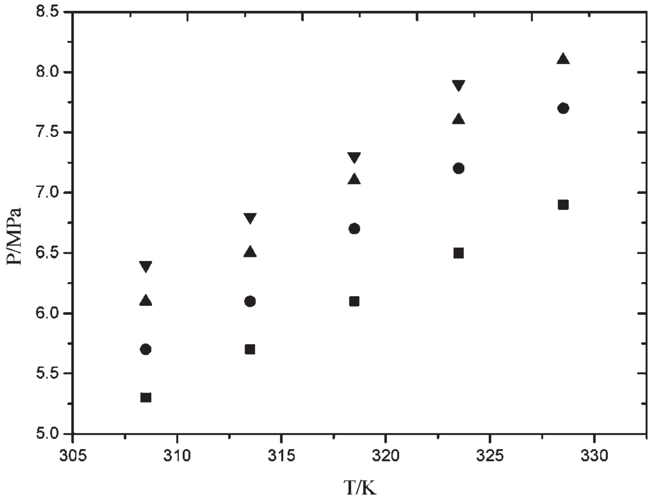

Figure 4. $P-T$ isopleths of bubble points at V_3/V_2 = 3/1. Mass fractions of CO_2 in the mixed solvents: ■, 0.6500; ●, 0.7000; ▲, 0.7500; ▼, 0.8000.

As shown in Table 1, for the system of V_3/V_2 =1/1, no cloud point was determined under our experimental conditions. At 328.5K, and CO_2 mass fraction of 0.80, a cloud point pressure (L−L) of 8.4 MPa was determined at 3/1 volume ratios between C_6H_{14} and EtOH, while a bubble point pressure (L−V) of 8.2 MPa was determined at 2/1 volume ratios between C_6H_{14} and EtOH. In that case, above 8.4 MPa, the system of 3/1 volume ratios between C_6H_{14} and EtOH was still in fluid state, while the system of 2/1 and 1/1 volume ratios between C_6H_{14} and EtOH was in liquid state. It might be because the C_6H_{14} is nonpolar solvent, which is easier to be miscible with CO_2 to reach critical point than EtOH. In addition, when the volume ratio between C_6H_{14} and EtOH was 2/1, at 318.5K, and CO_2 mass fraction of 0.8490, a cloud point pressure of 8.1 MPa can be determined. For the SAS, proper pressures and volume ratios of mixed solvents should be chosen.

As shown in Figures 2 to 4, bubble points were determined at five different temperatures [(308.5, 313.5, 318.5, 323.5, and 328.5) K] and different mass fractions of CO_2. Each curve corresponds to a specific mass fraction of CO_2. At a constant mass fraction of CO_2, the bubble point increased as the temperature increased, which means it is easier for CO_2 and the mixed solvent to become one phase at lower temperature. At a constant temperature, the bubble point increased as the mass fraction of CO_2 increased, which means it is easier for CO_2 and the mixed solvent to become one phase at lower mass fraction of CO_2. For SAS, proper temperatures and mass fractions of CO_2 should be chosen.

In addition, the bubble point pressures of $CO_2-EtOH-C_6H_{14}$ were correlated using PR-EOS. The binary interaction parameters k_{ij}[18,19] for the systems of CO_2−EtOH, $CO_2-C_6H_{14}$, and EtOH−C_6H_{14} at 313.5 K were chosen to correlate the experimental data shown in Table 2. As the binary interaction parameter k_{ij} is scarce at other temperatures, only that of one temperature, 313.5 K, was used in this paper. Table 3 shows the experimental and calculated results. It can be found that the absolute relative deviation (ARD) is less than 10 %, and 75 % of ARD values are

Table 2. Peng Robinson Equation of State Binary Interaction k_{ij} Parameters at 313.5 K

	CO_2-EtOH	$CO_2-C_6H_{14}$	$EtOH-C_6H_{14}$
k_{ij}	0.1412	0.0954	0.0442

Table 3. Correlated Bubble Point Pressure at 313.5 K and CO_2 Mass Fraction w_1

V_2/V_3	w_1	P_{exp}[a] (MPa)	P_{cal}[b] (MPa)	ARD[c] (%)	Σy_i[d]
1/1	0.6500	5.2	5.30	1.92	0.9896
	0.7000	5.6	5.33	4.82	0.9918
	0.7705	6.4	5.78	9.69	0.9946
	0.8500	7.0	7.25	3.57	1.0011
1/2	0.6927	6.3	6.45	2.38	0.9998
	0.7498	6.4	6.65	3.91	0.9967
	0.7973	6.7	6.95	3.73	0.9937
	0.8490	7.5	7.22	3.73	1.0001
1/3	0.6500	5.7	6.15	7.89	1.0113
	0.7000	6.1	6.50	6.56	1.0003
	0.7500	6.5	6.75	3.85	0.9989
	0.8000	6.8	7.00	2.94	0.9979

[a] $P_{exp.}$: experimental data of bubble point pressure. [b] P_{cal}: correlated data of bubble point pressure. [c] $ARD = |[(P_{exp} - P_{cal})/P_{exp}]| \times 100$ %. [d] Σy_i: sum of component mole fractions in vapor phase.

within 5 %. It is implied that PR-EOS can correlate the bubble points of this system.

CONCLUSIONS

In this work, the bubble points and several cloud points of the system $C_6H_{14} + CO_2 + EtOH$ were determined, depending on five temperatures [(308.5 to 328.5) K], four CO_2 mass fractions (60 to 85 %), and three volume ratios of $EtOH/C_6H_{14}$ (1/1, 1/2, and 1/3). The bubble point pressure increases with increasing temperature at the constant CO_2 mass fraction. In addition, the modeling results indicate that PR-EOS with one interaction parameter can correlate the experimental data for the bubble points. The results of the phase behavior of the system $C_6H_{14} + CO_2 + EtOH$ will be useful for the preparation of proliposomes using SAS in the future.

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